

Ionic transport in the (AgI:AgCl) mixed-system

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Ionic mobility, conductivity, number of charge carriers and transference number are reported for annealed and rapidly quenched $[x\text{AgI}:(1-x)\text{AgCl}]$ mixed systems, these results are compared with AgI. Of these three materials the quenched mixed-system had the highest Ag^+ ion conductivity. Further, preliminary studies are reported where the high conductivity system (i.e. quenched 0.75 AgI:0.25 AgCl) has been used as host material for the preparation of Ag^+ ion conducting glasses and composites. Detailed thermal/phase diagram studies have also been carried out on the quenched composition. The conductivity enhancement in the quenched system is attributed to the formation of new disordered phases and the introduction of amorphisity, the simple space-charge model applicable to the annealed system failed to explain these results.

1. Introduction

Silver ion conducting solid electrolytes in the glassy/amorphous and composite phases have attracted widespread interest in recent years due to their possible applications in solid state electrochemical devices [1–3]. The majority of these solids have been prepared with AgI as the host compound, where the high conducting α -phase ($> 147^\circ\text{C}$) of AgI has been partially stabilized or preserved at lower temperatures, either by quenching with various glass formers and glass modifiers [4–6] or by dispersing different second phase dispersoids [7–9]. Very few attempts have been made to replace AgI with an alternative host compound. It is suggested here that a quenched-in mixed-system of AgI:AgCl, in the mol wt (%) of 75:25, is an alternate host, exhibiting transport properties superior to AgI, having an indentical $\beta \rightarrow \alpha$ -like transition at ca. 135°C .

Conductivity anomalies in the AgI/AgCl two phase composite system have recently been studied by Lauer and Maier [10]. To prepare the composites, these authors melted the AgI/AgCl composition and left it to anneal at ca. 200°C for 24 h before cooling it to room temperature. They reported that the maximum enhancement in conductivity (σ ca. $3 \times 10^{-5} \text{ S cm}^{-1}$ at 30°C) for the melt and the annealed AgI:AgCl composite occurred at the 75:25% ratio. The conductivity enhancement was attributed to the increased silver ion vacancy conduction in the space-charge region of the AgI/AgCl interface. However, detailed studies on the ionic transport properties (mobility, number of charge carriers etc.) of this mixed-system have not been done. Further, the effect of different thermal treatments of the samples has also not been investigated.

In this paper results of the following experimental investigations on the $x\text{AgI}:(1-x)\text{AgCl}$ mixed-system are reported:

1. the effect of the rate of thermal cooling (slow and rapid quenching) of the melt on the room temperature conductivity values as a function of molar ratio, x ;
2. DTA studies to construct the phase diagram;
3. temperature variation of conductivity;
4. direct measurement of silver ion mobility, μ , as a function of temperature;
5. evaluation of mobile ion concentration, n , [from (3) and (4)] at different temperatures.
6. the use of the best composition of (AgI:AgCl) as host (instead of AgI) in the preparation of Ag^+ ion conducting glass and composite.

2. Experimental procedure

AgI and AgCl [Reidel (India) Ltd] were used as supplied. The homogeneous mixtures of $x\text{AgI}:(1-x)\text{AgCl}$ in the molar proportion x were heated to ca. $600\text{--}700^\circ\text{C}$ to a uniform melt. A portion of the melt was quenched rapidly at ca. $10\text{--}20^\circ\text{C}$ and the other portion was annealed at ca. 200°C for 24 h and then cooled slowly. Samples were ground separately to fine powders, then pressed at ca. 2 ton cm^{-2} to form pellets of dimensions 1.185 cm in diameter and 0.75–2 mm in thickness. Colloidal silver was painted on as electrodes for the electrical conductivity measurements. The bulk resistance was calculated from the complex impedance plots taken at different temperatures with the help of a computer controlled HIOKI Hi Tester LCR meter (model 3520–01) in the frequency range of 40 Hz to 100 kHz. Ionic mobility as a

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Investigation on transport properties of the silver ion conducting composite electrolyte

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We report here a conductivity enhancement ($\sim 10^1$) at room temperature in a new Ag^+ ion conducting composite system. Two silver halides AgI and AgCl, in the mol.wt. (%) ratio 75:25 were taken as first phase host compound for the first time. Inert second phase Al_2O_3 particles of size $< 10 \mu\text{m}$ were dispersed in varying molar proportions in the first phase. The highest enhancement in the conductivity ($\sim 9.2 \times 10^{-4} \text{ S/cm}$) was obtained for the ratio: $0.7[0.75\text{AgI} \cdot 0.25\text{AgCl}] \cdot 0.3\text{Al}_2\text{O}_3$. The plot of electrical conductivity as a function of temperature for the best composition indicated the presence of characteristics $\beta \rightarrow \alpha$ -like transition of AgI or host compound in the composite system with slightly decreased conductivity values from the host in the α -phase. The equations governing $\log \sigma$ versus $1/T$ for the composite system are represented by: $\sigma = 0.016 \exp(-0.074/kT) \rightarrow \beta$ -like phase; $\sigma = 0.041 \exp(-0.024/kT) \rightarrow \alpha$ -like phase give the activation energies as 0.074 eV and 0.024 eV in β and α -like phases, respectively, as compared to the values 0.24 eV and 0.025 eV for the host material. The low activation energy value in the β -region suggest easy ion migration in the composite system. The ionic mobility $\mu \sim (2.37 \pm 1) \times 10^{-2} \text{ cm}^2/\text{Vs}$ was evaluated at room temperature for the best composition using the transient ionic current (TIC) technique, while the value of the transference number t_{ions} is close to unity as obtained by two different techniques, i.e. Wagner's dc polarisation and electrochemical cell potential measurements. For the host material $t_{\text{ion}} \sim 1$ and $\mu \sim (1.5 \pm 1) \times 10^{-2}$.

1. Introduction

Composite electrolytes are dispersed multiphase (mostly two phase) solid mixtures in which two or more materials are combined together in a certain proportion to achieve some desirable material properties, e.g. an enhancement of the ionic conductivity. Conductivity enhancements in two phase composite mixtures was known for about ~ 75 years [1]. However, the activity in the field of composite electrolytes was renewed only after Liang [2] reported a ~ 50 times increase in Li^+ ion conductivity at room temperature simply by dispersing fine particles of inert Al_2O_3 in LiI. Since then, a large number of two phase composite mixtures have been reported to have a conductivity larger than that of the constituent individual phases [3–6]. These electrolytes are prepared by dispersing a second phase compound in the first phase. The first phase, also known as host matrix, is generally a moderate ionic conductor such as

LiI, LiBr, CuCl, AgI, AgCl, AgBr, TlCl, CaF_2 and HgI_2 . Whereas, the second phase is either another ionic solid (such as AgCl or AgBr in AgI) or an inert insulating material (such as Al_2O_3 , SiO_2 , Flyash). The highest conductivity enhancement (~ 2500) has been reported by Shahi and Wagner [3] in AgI– Al_2O_3 composites. In an effort to explain the conduction behaviour in these electrolytes many phenomenological models have been suggested [7–13]. However, in all the models it is assumed that the conductivity anomalies are created in the interfacial region or in the miscibility gap of the two phases. The enhancement in the conductivity also depends upon the radius of the second phase particles, and the volume fraction.

We report in this paper a conductivity enhancement at room temperature in a new Ag^+ ion conducting composite system. Two silver halide compounds AgI and AgCl in the mol% ratio 75:25 was used as the first phase host matrix [13,14]. Since this AgI/AgCl mixed system in the above ratio exhibited a $\beta \rightarrow \alpha$ -like phase transition similar to AgI in a $\log \sigma$

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Estimation of energies of Ag^+ ion formation and migration using transient ionic current (TIC) technique

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Abstract

Transient ionic current (TIC) and impedance spectroscopy techniques were employed to measure the Ag^+ ion mobility (μ) and conductivity (σ) respectively of AgI in both β - and α -phases. Subsequently, the mobile ion concentration (n) was calculated using σ and μ data. σ , μ and n show thermally activated type behaviour in both the regions of the phase transition. From the log μ versus $1/T$ and log n versus $1/T$ Arrhenius plots, the energies of migration and formation of mobile silver ion were estimated as 0.14 and 0.15 eV respectively in the β -phase and 0.05 and 0.006 eV respectively in the α -phase. The extremely low value of energy of formation in the α -phase suggested that a negligibly small number of mobile ions is thermally added to the large n already existing in this phase. On the basis of these experimental studies, it is concluded that the large increase of σ in α -AgI is predominantly due to an abrupt increase of mobile ion concentration. The contribution of ionic mobility to the total conductivity is small.

Keywords: Ionic mobility; Transient ionic current technique; Ionic conductivity – silver; Energy of formation; Energy of migration

1. Introduction

Fast ion conduction in superionic solids depends on various structural and non-structural factors, these include highly disordered lattice, structure “free” volume, mobile ion concentration, mobile ion–mobile ion and/or – neighbouring ion interactions, available equivalent sites, connectivity along the conducting pathways, etc. [1–4]. The structural disorder is generally associated with a well-defined solid state phase transition at a given temperature which is usually accompanied by a significant jump in the conductivity. AgI is well-known for such a behaviour, a conductivity jump of ~ 3 –4 orders of magnitude occurs at $\sim 147^\circ\text{C}$ when AgI makes structural transition to superionic α -phase (cubic) from low conducting β -phase (hexagonal) [5–7]. This unique

superionic property of α -AgI attracted widespread interest to study this material more extensively. Structural and ion transport properties of AgI have been studied using a wide variety of techniques e.g. neutron scattering, EXAFS, Raman scattering, XRD, molecular dynamics, frequency dependent conductivity, thermoelectric power, etc. [1,8–19]. Various attempts were made in the past and are still being tried presently to lock-in or stabilize this high conducting α -phase at lower temperatures (viz. at room temperature) adopting various methods such as replacing either cation or anion or both of AgI by way of solid solution with other salts [1]; introducing amorphosity by rapidly cooling the melt of (AgI + glass modifier + glass former) [20–22]; by dispersion of sub-micron size particles of second phase dispersoid into AgI-host matrix [23–25], etc.

Transport property and battery discharge characteristic studies on $1 - x$ (0.75AgI:0.25AgCl): $x\text{Al}_2\text{O}_3$ composite electrolyte system

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Various experimental studies on a new fast Ag^+ ion-conducting composite electrolyte system: $(1 - x)$ (0.75AgI:0.25AgCl): $x\text{Al}_2\text{O}_3$ are reported. Undried Al_2O_3 particles of size $< 10 \mu\text{m}$ were used. The conventional matrix material AgI has been replaced by a new mixed 0.75AgI:0.25AgCl quenched and/or annealed host compound. Conductivity enhancements ~ 10 from the annealed host and ~ 3 times from the quenched host obtained for the composition 0.7(0.75AgI:0.25AgCl):0.3 Al_2O_3 , can be explained on the basis of the space charge interface mechanism. Direct measurements of ionic mobility μ as a function of temperature together with the conductivity σ were carried out for the best composition. Subsequently, the mobile ion concentration n values were calculated from μ and σ data. The value of heat of ion transport q^* obtained from the plot of thermoelectric power θ versus $1/T$ supports Rice and Roth's free ion theory for superionic conductors. Using the best composition as an electrolyte various solid state batteries were fabricated and studied at room temperature with different cathode preparations and load conditions.

1. Introduction

Heterogeneous composite electrolytes are a new class of high ionically conducting materials which have attracted considerable attention in recent years due to their potential technological applications. These materials are multiphase, mostly two phase, systems where a significant conductivity enhancement is achieved simply by the dispersion of ultrafine (submicron size) particles of inert and insoluble second phase (such as Al_2O_3 , SiO_2 , Fe_2O_3 , fly-ash etc.) into the first phase host matrix (such as AgI, AgBr, AgCl, LiI, CuCl, CaF_2 etc.) [1–9]. Though the conductivity enhancement in the two phase system was known for about 75 years [10], the systematic investigations started only after 1973 when C. C. Liang reported ~ 50 times enhancement of Li^+ ion conduction in the LiI: Al_2O_3 dispersed system [11]. Since then a large number of two phase composite electrolyte systems with Ag^+ , Li^+ , Cu^+ , F^- etc. ion conduction have been reported with conductivity one to three orders of magnitude higher than the constituent phases. Many phenomenological models have been proposed to explain the conductivity enhancement in these electrolyte systems [1–6, 12–16]. The central feature of the majority of these models is the increase in the mobile ion concentration at the interfacial space charge region of the host matrix/dispersoid. Moreover, a well-connectivity

of these interfacial regions creating highly conducting paths would be necessary to facilitate high ionic motion. The volume fraction and the particle size of the second phase dispersoid play crucial roles in the conductivity enhancement. In addition to this, the dispersion of the submicron size particles of the inert second phase may also change the chemistry and microstructure of the host matrix which might control the transport mechanism in these systems. The conductivity enhancements in different composite systems (made of different matrix materials, different compositions, following different preparation routes etc.) cannot be understood by any single mechanism [5]. Hence, the present day goal is to search for a unified model explaining the greatly enhanced carrier concentrations or mobilities in these systems.

In the present paper, we report the preparation of a new fast Ag^+ ion conducting composite electrolyte system: $(1 - x)$ (0.75AgI:0.25AgCl): $x\text{Al}_2\text{O}_3$, where the conventional host matrix AgI is replaced by a new host, a quenched and/or annealed 0.75AgI:0.25AgCl mixed system. The detailed investigations related to the new host material appear elsewhere in the literature [17]. The electrical conductivity σ of the composites were measured as a function of molar concentration x , routes of preparation, temperature etc. whereas the direct measurement of ionic mobility

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[0.75AgI : 0.25AgCl] quenched system: a better choice as host compound in place of AgI to prepare Ag^+ ion conducting superionic glasses and composites

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Abstract

Various transport properties, namely, the electrical conductivity, σ , ionic transference number, t_{ion} , ionic mobility, μ , etc. were measured for the quenched [0.75AgI : 0.25AgCl] system. The mobile ion concentration, n , was calculated using σ and μ data. The results were compared with the values for AgI. The quenched [0.75AgI : 0.25AgCl] system exhibited a $\beta \rightarrow \alpha$ like transition in the $\log \sigma$ versus $1/T$ plot at $\sim 135^\circ\text{C}$ identical to AgI. The present investigations suggest that the quenched [0.75AgI : 0.25AgCl] mixed system is a better choice as a host compound in place of AgI to prepare Ag^+ ion conducting superionic glasses and composites. Using the quenched [0.75AgI : 0.25AgCl] system as host, the following superionic solid systems were prepared and studied: (A) (1) $x[0.75\text{AgI} : 0.25\text{AgCl}] : (1-x)[\text{Ag}_2\text{O} \cdot \text{B}_2\text{O}_3]$, (2) $x[0.75\text{AgI} : 0.25\text{AgCl}] : (1-x)[\text{Ag}_2\text{O} \cdot \text{B}_2\text{O}_3]$, (by the melt-quench method (glass systems)); (B) (1) $(1-x)[0.75\text{AgI} : 0.25\text{AgCl}] : x \text{Al}_2\text{O}_3$ (by dispersing second-phase particles of size ($< 10 \mu\text{m}$) (composite system)). The results of the variation of the room temperature conductivity as a function of the molar weight ratio, x , for the above systems are reported and compared with the results for similar systems using AgI as host.

1. Introduction

There has been widespread technological interest recently in the ion conducting solids because of their possible applications as electrolytes in solid-state electrochemical devices, such as solid-state batteries [1,2]. A large number of fast ion conducting solids, namely with Ag^+ , Cu^+ , Li^+ , Na^+ , K^+ , H^+ , F^- , O^{2-} ion conduction, have been discovered in the

past three decades [3–7]. These solids have high ionic conduction in the range 10^{-1} – 10^{-4} S/cm, with negligible electronic contribution. However, considerable attention has been given in the past decade to developing these solids in amorphous and composite phases [1,2,8,9]. The amorphous phase has definite advantages over the crystalline or polycrystalline counterparts such as isotropic enhanced conduction, absence of grain boundaries and the possibility of moulding into desired shape and size among which a thin film form is possible [10–13].

In the majority of Ag^+ ion conducting glasses or composites, AgI is used as the host compound. The

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Studies on ionic transport properties of a new Ag^+ ion conducting composite electrolyte system $(1-x)[0.75 \text{ AgI}: 0.25 \text{ AgCl}]: x\text{SnO}_2$

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Abstract. A new Ag^+ ion conducting composite electrolyte system $(1-x)[0.75 \text{ AgI}: 0.25 \text{ AgCl}]: x\text{SnO}_2$ using a quenched/annealed $[0.75 \text{ AgI}: 0.25 \text{ AgCl}]$ as host compound in place of conventional host AgI, has been investigated. The effects of various preparation methods and soaking time are reported. The composition $0.8[0.75 \text{ AgI}: 0.25 \text{ AgCl}]: 0.2\text{SnO}_2$ exhibited optimum conductivity ($\sigma = 8.4 \times 10^{-4} \text{ S/cm}$) with conductivity enhancement of $\sim 10^4$ from the annealed host at room temperature. Transport property studies such as electrical conductivity (σ) as a function of temperature using impedance spectroscopy technique, ionic transference number (t_{ion}) using Wagner's d.c. polarization method and ionic mobility (μ) by transient ionic current technique were carried out on the optimum conducting composition. The mobile ion concentration (n) was calculated from ' σ ' and ' μ ' data.

Keywords. Ag^+ ion conductor; composite solid electrolyte; two-phase composite system; ionic conductivity; ionic mobility.

1. Introduction

Composite electrolytes are a new class of fast ion conductors which have attracted widespread interest in the recent years due to their possible technological applications in solid state batteries, electrochromic display devices, fuel cells etc. They are mostly two-phase systems in which conductivity enhancements $\sim 10^4$ – 10^5 have been achieved at room temperature by dispersing ultrafine particles of a chemically inert and insoluble material (termed as second phase or dispersoid) viz. Al_2O_3 , SiO_2 , Fe_2O_3 , SnO_2 , Fly-ash etc into a first phase host material such as AgI, AgBr, AgCl, LiI, CuCl, CaF_2 etc. A large number of two-phase composite electrolyte systems with Ag^+ , Li^+ , Cu^+ , F^- etc ion conduction have been reported and studied so far (Liang 1973; Liang *et al* 1978; Shahi and Wagner 1981; Poulsen 1985; Dudney 1989; Maier 1989, 1992; Wagner 1989; Shukla and Sharma 1992). Several phenomenological models have been suggested to explain the conductivity enhancement in these systems (Bunde *et al* 1985; Blender and Dieterich 1987; Dudney 1989; Maier 1989, 1992; Wagner 1989; Shukla and Sharma 1992; Uvarov *et al* 1992). Majority of these models have many common themes to explain the transport mechanism in these systems e.g. the increase in the mobile ion concentration at the host/dispersoid interfacial space charge region and/or increase in the ionic mobility due to the creation of high conducting paths connecting these regions, are predominantly responsible for the conductivity enhancement. Moreover, the volume fraction and size of the dispersoid particles play very vital roles in controlling the conductivity enhancement in these systems.

We report here the preparation and transport property studies of a new Ag^+ ion conducting composite electrolyte system $(1-x)[0.75 \text{ AgI}: 0.25 \text{ AgCl}]: x\text{SnO}_2$ using

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Detailed investigation of the temperature dependence of ionic transport parameters of a new composite electrolyte system $(1 - x)$ $(0.75\text{AgI}:0.25\text{AgCl}):x\text{SnO}_2$

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Detailed investigations of a new Ag^+ -ion-conducting two-phase composite electrolyte system $(1 - x)$ $(0.75\text{AgI}:0.25\text{AgCl}):x\text{SnO}_2$ are reported, where $0 \leq x \leq 50$ in weight per cent. A "quenched-and-annealed $(0.75\text{AgI}:0.25\text{AgCl})$ mixed system–solid solution" was used as the first phase instead of the commonly used host matrix salt AgI. Micron-sized particles (about $10\text{ }\mu\text{m}$) of SnO_2 were dispersed in the first (matrix) phase. The composition $0.8(0.75\text{AgI}:0.25\text{AgCl}):0.2\text{SnO}_2$ exhibited conductivity enhancements of more than eight times over the annealed host and about three times over the quenched host at room temperature and has been referred to as "optimum composition". The existence of two separate phases has been ascertained by X-ray diffraction and differential thermal analysis techniques. The temperature dependence of the electrical conductivity, σ , ionic mobility, μ , mobile ion concentration, n , ionic transference number, t_{ion} , and ionic drift velocity, v_d , are also reported. The enhancement in the conductivity in this two-phase composite electrolyte has been attributed to the increase in ionic mobility at room temperature.

1. Introduction

Room-temperature enhancements of approximately one to three orders of magnitude have been reported in many heterogeneously doped two-phase Ag^+ -ion-conducting composite electrolyte systems [1–7]. These systems are fabricated simply by controlled dispersion of ultrafine particles of an insulating and chemically inert material, namely, Al_2O_3 or SiO_2 or Fe_2O_3 or fly-ash (referred to as second-phase dispersoids), into the moderately ionic conducting silver halide, namely, AgI or AgBr or AgCl (referred to as the first-phase host matrix). The mechanism of conductivity enhancements in these systems can be understood on the basis of the increased mobile ion concentration at the host–dispersoid interface region and/or increased ionic mobility due to the creation of highly conducting paths interconnecting these regions [8–17]. The volume fraction of the second-phase dispersoid and its particle size are critical factors which decide optimum conductivity in these systems [1–4, 6].

The majority of the fast-silver-ion-conducting composite systems are prepared using AgI as the first-phase host matrix, in general. In a recent investigation, we suggested an alternative compound: "a

quenched-and-annealed $(0.75\text{AgI}:0.25\text{AgCl})$ mixed system", in place of the conventional host AgI [18, 19], exhibiting many transport properties superior to AgI. We have also reported that the new host yields much better composite electrolyte [20, 21] and glass systems [22–24]. In this paper, we report the preparation and transport property studies on a new Ag^+ -ion-conducting two-phase composite system: $(1 - x)$ $(0.75\text{AgI}:0.25\text{AgCl}):x\text{SnO}_2$, where $x = 0.1, 0.15, 0.2, 0.25, 0.3, 0.4$ and 0.5 in weight fraction. The chemically inert and insoluble SnO_2 was used as the second-phase dispersoid. For direct comparison of room-temperature conductivity, the composite systems $(1 - x)\text{AgI}:x\text{SnO}_2$ were also prepared in an identical manner using the conventional host AgI. Various experimental studies carried out on the new composite system are outlined below.

1. Compositional variation in room-temperature conductivity, σ , will enable us to determine the optimum conducting composition.

2. X-ray diffraction (XRD) and differential thermal analysis (DTA) studies on the optimum composition will allow us to identify the existence of two separate phases.

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Studies of Polarization/Self-Depolarization and Electret-type Effect in AgI

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Abstract. A novel d.c. polarization/self-depolarization study and electret-type effect in AgI are reported. AgI pellets of varying thicknesses, placed between two blocking (graphite) electrodes, were subjected to an external d.c. potential. A state of complete polarization was attained within ~10 min, irrespective of the sample thickness. At this state, the potential difference, developed across the sample pellet as a result of polarization/accumulation of mobile Ag^+ ions at the bulk/negative electrode interface, was measured experimentally. The potential difference, obtained immediately after the removal of the external d.c. source, has been referred to as 'instant peak potential (V_p)'. As soon as the external voltage source is switched off, a process of self-depolarization is initiated due to the chemical/self diffusion of polarized mobile Ag^+ ions throughout the bulk. ' V_p ' gives a direct information regarding the extent of mobile ion concentration (n). ' V_p ' measurements were carried out as a function of temperature and ' $\text{Log } V_p$ vs $1/T$ ' variation was compared with the ' $\text{Log } n$ vs $1/T$ ' Arrhenius plot, reported earlier in an entirely independent study. The two variations are almost analogous. This, in turn, supported an earlier assertion that the abrupt conductivity increase in α -AgI, after $\beta \rightarrow \alpha$ -phase transition at ~ 147 °C, is predominantly due to the excessive increase in ' n '. Furthermore, it has also been revealed that the Ag^+ ions play another unique role which led to the existence of 'persistent polarization' states in AgI. These states are identical to the 'electret-type effects', observed in a number of dielectric materials. The polarization state persisted for very long time in 'thermally stimulated polarized' sample. A detailed investigation of the persistence/retention of polarization in the thermally-stimulated-polarized sample is reported.

1. Introduction

Silver iodide is one of the most extensively studied solid systems probably due to the fact that it exhibits a peculiar transition characteristics at ~ 147 °C where it undergoes a structural transition from a low conducting hexagonal β -phase to a very high conducting cubic α -phase [1-3]. The α -phase of AgI has been potentially employed to synthesize a large number of room temperature fast Ag^+ ion conducting systems by arresting this phase either in the solid solutions with other salts [4] or in the glassy network [5-7] or in the dispersed composite electrolyte systems [8-10]. These solid state ionic materials, termed as 'Super Ionic Solids' or 'Solid Electrolytes' or 'Fast

Ion Conductors', exhibit exceptionally high ionic conductivity ($\sim 10^{-1}$ - 10^{-4} S·cm $^{-1}$) at room temperature, comparable to the conductivity of liquid/aqueous electrolytes. α -AgI is often termed as the archetypal of fast ion conductors with conductivity reaching ~ 2.6 S·cm $^{-1}$ in the solid phase close to the melting point ($T_m \sim 552$ °C). Various experimental techniques have been used in the past to study the structural and transport properties as well as the role played by the mobile Ag^+ ions in AgI [4].

The electrical conductivity of ionic/superionic system is mainly governed by two basic transport parameters: the ionic mobility (μ) and the mobile ion concentration (n), as obvious from the well known equation for conductivity

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A study of ionic transport properties on a new Ag^+ -ion-conducting composite electrolyte system: $(1 - x)[0.75\text{AgI} : 0.25\text{AgCl}] : x\text{SiO}_2$

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Abstract. Preparation of a new Ag^+ -ion-conducting two-phase composite electrolyte system $(1 - x)[0.75\text{AgI} : 0.25\text{AgCl}] : x\text{SiO}_2$, $0 \leq x \leq 0.5$ (in molar weight fraction) and studies of its ionic transport properties are reported. Nano-size (≈ 8 nm) particles of insulating and insoluble SiO_2 were used as second-phase dispersoid particles, while a new compound, 'a quenched/annealed $[0.75\text{AgI} : 0.25\text{AgCl}]$ mixed-system/solid solution', recently investigated in the present laboratory, was used as the first-phase host matrix in place of the conventional host salt AgI. Various routes of sample preparation were adopted. The composition $0.9[0.75\text{AgI} : 0.25\text{AgCl}] : 0.1\text{SiO}_2$ exhibited the highest enhancement ($\approx 10^1$) in the room-temperature conductivity from that of the host. We referred to this as the 'optimum conducting composition (OCC)' with room temperature conductivity about $10^{-3} \text{ S cm}^{-1}$. The coexistence of constituent phases was confirmed by x-ray diffraction (XRD) and differential scanning calorimetry (DSC) studies. Various ionic transport parameters, namely the conductivity, mobility, mobile-ion concentration, transference number and drift velocity of the conducting ion, were measured experimentally as functions of the temperature. The results have been explained on the basis of theories proposed for two-phase composite electrolyte systems.

1. Introduction

After the discovery of enhancement by a factor of about 50 of the Li^+ -ion conduction in a two-phase composite electrolyte system, $\text{LiI} : \text{Al}_2\text{O}_3$ by Liang [1], widespread interest was channelled into attempting to prepare newer systems. As a result, a large variety of two-phase composite electrolyte systems, exhibiting enhancements by 1–3 orders of magnitude of the room temperature conductivity, have been discovered during the last two decades. These systems are potential candidates as solid electrolytes in various solid state electrochemical device applications. Two-phase composite electrolyte systems are heterogeneous mixtures of a chemically inert and insoluble compound, namely Al_2O_3 , SiO_2 , Fe_2O_3 or SnO_2 (called the second-phase dispersoid) with a moderately ion-conducting salt such as AgI, AgCl, LiI, CuI or PbF_2 (called the first-phase host matrix) [2–7]. The enhancement of the conductivity in these systems is generally due to the creation of double-layer space-charge regions at the host/dispersoid interfaces and the increase in defect concentration in these regions. In addition to this, highly conducting paths, interconnecting the various space-charge regions, are also created, which

result in an enhancement of the ionic mobility and hence contribute to there being a high ionic conductivity [8–13]. The volume fraction, particle size and chemical nature of the dispersoid as well as the routes adopted during the sample preparation are some other crucial factors which decide the magnitude of conductivity enhancements in these systems [1–13].

The present paper reports a new Ag^+ -ion-conducting two-phase composite electrolyte system. Fast Ag^+ -ion-conducting two-phase composite electrolyte systems reported in the past were prepared using AgI as the first-phase host-matrix salt, in general [2–7]. However, in a recent investigation we suggested a new compound, a quenched/annealed $[0.75\text{AgI} : 0.25\text{AgCl}]$ mixed-system/solid solution, in place of the conventional host AgI [14]. The new host exhibits several transport properties superior to those of AgI and yields better composite electrolytes as well as glass systems [15–19]. In this paper we discuss the details of sample preparation, phase identification/material characterization and transport-property studies on the new Ag^+ -ion-conducting two-phase electrolyte system $(1 - x)[0.75\text{AgI} : 0.25\text{AgCl}] : x\text{SiO}_2$, where $0 \leq x \leq 0.5$ (in molar weight fraction). Ultra-fine

Estimation of ionic drift velocity on some fast Ag^+ ion conducting systems

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Abstract

A novel experimental technique for approximate estimation of drift velocity (v_d) of mobile Ag^+ ions in some superionic systems is reported. Wagner's dc polarisation method, widely used to determine the ionic transference number (t_{ion}), was employed as a tool in these measurements. As v_d is directly proportional to ionic mobility (μ) at a fixed applied dc field, thus, the thermally activated processes involved in the temperature dependence of v_d and μ should exhibit identical behaviour. Energy (E_d) values computed from $\log v_d - 1/T$ plots in the present study are in reasonably good agreement with energy (E_m) values obtained earlier from $\log \mu - 1/T$ plots. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Drift velocity; Ionic transference number; Superionic systems

1. Introduction

Solid state ionic materials, termed as superionic solids, fast ion conductors, solid electrolytes or hyperionic solids, have attracted widespread interest in recent years as they show high technological scopes especially in the fabrication of solid state electrochemical devices such as solid state batteries, fuel cells, electrochromic display devices (ECDs) etc. [1–4]. The high ionic conductivity, comparable to the conductivity of liquid electrolytes, with negligibly small electronic conduction is the characteristic property of these materials. A large number of superionic solids with various mobile ion species viz. Ag^+ , Cu^+ , Li^+ , Na^+ , K^+ , H^+ , F^- , O^{2-} , etc. have been reported and studied in the last three decades. On the basis of microstructure and physical property, these solids have recently been broadly classified into different phases viz. crystalline/polycrystalline, glass/amorphous, composite, polymeric etc. Several models, based on various structural and non-structural factors, have been proposed to understand the mechanism of fast ion transport in these systems. A number of experimental techniques have been employed to explain the macroscopic/microscopic

behaviour of the conducting ions [5]. The direct mass/charge transfer phenomenon in these systems can be understood by studying the temperature dependence of various ionic transport parameters viz. electrical conductivity (σ), ionic mobility (μ), mobile ion concentration (n), ionic transference number (t_{ion}), and ionic drift velocity (v_d).

In the present paper, a novel experimental technique, based on t_{ion} measurements using Wagner's dc polarisation method, is reported for approximate estimation of ionic v_d on following new Ag^+ ion conducting superionic systems:

1. $0.7[0.75\text{AgI}:0.25\text{AgCl}]:0.3[0.833\text{Ag}_2\text{O}:167\text{B}_2\text{O}_3]$ (mixed-glass phase)
2. $0.75[0.75\text{AgI}:0.25\text{AgCl}]:0.25[\text{Ag}_2\text{O}:\text{CrO}_3]$ (mixed-glass phase)
3. $0.7[0.75\text{AgI}:0.25\text{AgCl}]:0.3\text{Al}_2\text{O}_3$ (composite phase)
4. $0.8[0.75\text{AgI}:0.25\text{AgCl}]:0.2\text{SnO}_2$ (composite phase)

These systems were synthesised using a new host compound: a quenched/annealed $[0.75\text{AgI}:0.25\text{AgCl}]$ mixed system-solid solution, investigated by us recently [6], in place of the conventional host AgI . The detailed investigations on the preparation and characterisation of materials and transport properties have appeared elsewhere in the literature [7–11]. However, the actual techniques adopted during σ , μ , n and t_{ion} measure-

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Review

Superionic solids: composite electrolyte phase – an overview

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A general overview on the field of solid state ionics, including materials and transport property, is presented. Superionic systems in the composite electrolyte phase are discussed in great detail. Possible theoretical models suggested to understand the ion-transport mechanism in these systems are reviewed extensively. © 1999 Kluwer Academic Publishers

1. Superionic solids: general aspects

Historically, human endeavours to search for new materials along with their applications in devices, have been the story behind the scientific and technological advancements of mankind. Prior to the 1960s, most of devices were based on electron conducting materials, namely semiconductors. In fact, the discovery of transistors in the 1950s revolutionized the field of semiconductor electronics further and a new branch of science, termed *solid state electronics*, emerged. This branch of science mainly deals with the physics, engineering and technological aspects of electronic materials and has made tremendous strides, since then, especially in the area of integrated electronics. Until the late 1960s, very few devices based on ion-conducting materials, were available. Out of the known devices, the majority of them were liquid–aqueous electrolyte-based devices, namely aqueous batteries. These batteries were reported to suffer from a number of major shortcomings such as: limited temperature range of operation, device failure due to electrode corrosion by electrolytic solution, bulky in size, less rugged, etc. [1–4]. Hence, to eliminate these discrepancies, a need to replace the liquid–aqueous electrolytes with some suitable ion-conducting solids was strongly felt. As an early attempt, the then known ion-conducting solids such as: alkali halides, silver halides, etc., were used, but owing to the fact that these solids were poor conductors (ionic conductivity, σ approximately 10^{-7} – 10^{-12} S cm $^{-1}$), they remained unsatisfactory choices as replacement. However, the search for solids exhibiting high ionic conductivity continued rigorously. Eventually, the situation took a dramatic turn in the year 1967 when two new kinds of solid systems: MAg $_4$ I $_5$ (where M = Rb, K, NH $_4$) [5–7] and Na- β -alumina [8], exhibiting exceptionally high Ag $^+$ and Na $^+$ ion conduction (σ approximately 10^{-1} S cm $^{-1}$) at room and at moderately high temperature, respectively, were discovered. A large

number of fast ion-conducting solids with various mobile ion species, namely H $^+$, Li $^+$, Na $^+$, K $^+$, Ag $^+$, Cu $^+$, F $^-$, O $^{2-}$ etc., have been reported, since then. In fact the year 1967 has been marked as the beginning of a new era in the field of *materials science*, which currently bears the name *solid state ionics*, a terminology parallel to solid state electronics. Solid state ionics mainly deals with the physics, chemistry and technological aspects of high ionic conduction in solids and has become a major thrust area of research worldwide. The solids, exhibiting high ionic conductivity, are termed *superionic solids* or *solid electrolytes* or *fast ion conductors* or *hyperionic solids*. Table I compares room temperature values of some basic transport parameters of electron and ion conducting solids. It can be noted that superionic solids, which can be thought to be ideal electronic insulators, have extremely high ionic conductivity. Fig. 1 shows the temperature variation of electrical conductivity of some normal-ionic and superionic solids along with two aqueous electrolyte systems for direct comparison. One can clearly see that the conductivity values of a number of superionic systems are not only close to those of liquid electrolytes but remain stable over a fairly wide range of temperatures. Superionic solids show immense technological promise, especially in the development of solid state electrochemical devices such as high–low solid state power sources (batteries), sensors, fuel cells, electrochromic display devices, memory devices, supercapacitors, etc. In addition to overcoming several limitations of liquid–aqueous electrolyte based devices, as mentioned above, the major advantages of solid electrolyte based devices are: their utility over a wide range of temperatures, i.e. below 0 °C and above 100 °C, where devices with liquid electrolytes normally cease to work and there is a possibility of miniaturization. In fact, a wide variety of solid state electrochemical devices are already available commercially. The implantable heart-pace-maker

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Polarization/self-depolarization studies on Ag^+ ion conducting quenched [0.75AgI:0.25AgCl] mixed system/solid solution

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Temperature dependent dc polarization/self-depolarization studies, on a Ag^+ ion conducting system : a quenched [0.75AgI:0.25AgCl] mixed-system/solid-solution, are reported. This system has recently been investigated in the present laboratory as a new and better alternate material in place of conventional host salt AgI. Sample pellets of different thicknesses were sandwiched between graphite (blocking) electrodes and polarized under a constant dc potential (~ 0.5 V) for different intervals of time. A potential gradient develops across the sample pellet due to accumulation/polarization of mobile Ag^+ ions at one end. At the state of complete polarization, the potential measured instantly after the removal of the external dc field has been referred to as peak potential V_p . V_p -values directly indicate the availability of number of mobile Ag^+ ions in the system at a particular temperature. V_p -measurements have been carried out as a function of polarization time and temperature in both β and α -like phases of the system. The study revealed that the material attains the state of complete polarization in time $t > 5$ min. irrespective of the sample thickness. It is also observed that $\log V_p$ versus $1/T$ variation, in both β and α -like phases of the material, is almost analogous to $\log n$ versus $1/T$ variation, reported earlier for the present system. This, in turn, has reconfirmed one of our assertion made earlier in regards to superionic conduction of α -like phase of the material which is predominantly due to an abrupt increase in n in this phase.

1 Introduction

'Superionic solids' or 'solid electrolytes' are a new class of solid state ionic materials which exhibit high ionic conductivity comparable to those of liquid/aqueous electrolytes. These solids show tremendous technological promises to develop various kinds of solid state electrochemical devices such as solid state batteries, fuel cells, sensors, electrochromic display devices etc.¹⁻³. Amongst known superionic systems, Ag^+ ion conducting materials exhibit highest room temperature conductivity ($\sim 10^{-1} - 10^{-2}$ S.cm⁻¹) and are available in various phases viz. crystalline/polycrystalline, glassy/amorphous, composite electrolyte etc. These systems are prepared, in general, by stabilizing the characteristic superionic α -phase of AgI at room temperature by way of solid solution with other ionic systems¹ or in a glass former/modifier network⁴ or dispersion of submicron particles of an insulating 'second phase' dispersoids^{5,6}. AgI is well-known for its characteristic structural transition after $\sim 147^\circ\text{C}$ at which it undergoes from a low conducting β -phase to superionic α -phase⁷. Recently, a new compound⁸ : "a quenched/annealed [0.75AgI:0.25AgCl] mixed-system/solid-solution" has been investigated by us, which exhibits exactly identical transport characteristics as AgI including $\beta \rightarrow \alpha$ -like phase

transition at a substantially low temperature i.e. $\sim 135^\circ\text{C}$. Detail investigations on various ionic transport parameters of the new host salt viz. conductivity (σ), ionic mobility (μ), mobile ion concentration (n), ionic transference number (t_{ion}), ionic drift velocity (v_d) etc. revealed that the new host has several ionic transport properties superior to AgI. Hence, the new system can very well be used as an alternate host salt in place of conventional host AgI in the preparation of fast Ag^+ ion conducting systems in various phases, as mentioned above. In fact, number of superionic systems in glassy/composite phases have already been prepared by us using the new host⁹⁻¹³. These systems exhibit superior electrolyte properties as compared to those prepared by conventional host AgI.

The electrical conductivity (σ) measurements, on the new host : "a quenched [0.75AgI:0.25AgCl] mixed-system/solid-solution" were carried out using impedance spectroscopy¹⁴, while ionic mobility (μ) and ionic transference number (t_{ion}) and hence, mobile ion concentration (n) and ionic drift velocity (v_d) were determined by transient ionic current¹⁵ (TIC) and Wagner's dc polarization¹⁶ techniques respectively. TIC and Wagner methods are essentially a dc polarization technique in which

Studies on persistent-polarization/memory-type effect in Ag^+ ion conducting quenched $[\text{0.75AgI:0.25AgCl}]$ mixed-system/solid-solution

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Studies on persistent-polarization/memory-type effect in a Ag^+ ion conducting system : "a quenched $[\text{0.75AgI:0.25AgCl}]$ mixed- system/solid-solution", recently investigated in the present laboratory as a better alternate to conventional host-salt AgI , are reported. A constant dc polarizing field (~ 0.5 V) was applied across the sample, placed in the cell configuration : $\text{C}/[\text{0.75AgI:0.25AgCl}]/\text{C}$. The electronically conducting graphite (C) behaves as a blocking electrode for mobile Ag^+ ions. To study the charge fixation or persistent-polarization/memory-type effect due to thermal stimulation, sample pellet was placed in a furnace at $\sim 200^\circ\text{C}$ (i.e. well above the $\beta \rightarrow \alpha$ -like phase transition temperature of the material) and polarized in two different ways: (1) polarization field was applied for 10 min, then removed; (2) polarization field was kept on and the sample was cooled slowly from 200 – 27°C by switching off the furnace, then the field was removed. The potential gradient developed across the sample pellet due to accumulation/polarization of Ag^+ ions, was measured as a function of temperature during several heating/cooling cycles and over a long span of time ranging from few hours to several hundred hours. All the measurements were carried out instantly to avoid possibility of any discharge. This instant potential has been referred to as peak potential V_p . The study revealed that the polarization states persisted for long time. It was also observed that the effect of persistent polarization is far superior in the sample polarized by method (2). The phenomenon of persistent-polarization in this system indicated "as if the mobile Ag^+ ions retain the memory of their polarization state at a particular temperature". This kind of effect has been observed earlier in AgI also.

1 Introduction

The persistent-polarization/memory-type effect refers to a phenomenon in which the decay time of stored polarization is higher than the characteristic time required in the experiment for polarizing the material by an external dc field. This phenomenon is also termed as electret-type effect, which is commonly observed in number of dielectric materials viz. polymers, divalent impurity doped ionic salts, viz. KCl , KI , AgCl etc.^{1,2} Electrets have several technological applications and are potentially used in dust catchers, microphones, memory devices etc. Electrets have historical background. For the first time in 1732, Gray reported electret-type behaviour, while mentioning the perpetual attractive power in a number of dielectrics viz. waxes, resins and sulphur³. In fact, the word electret was coined by Heaviside in 1892⁴. However, systematic research in this area began in 1919⁵, when a Japanese Physicist Eguchi formed electrets using the same material, reported by Gray. Eguchi adopted thermal methods for electret formation by applying dc electric field to the cooling melt. Adams, for the first time, proposed a phenomenological theory⁶ of electret. A dramatic progress was witnessed in the

field of electret after Randall and Wilkins⁷ introduced thermal depolarization method (TDM) while studying phosphorescence in certain dielectrics. Later, Bucci and coworkers⁸ applied TDM to study dipole-polarization in some dielectric and suggested an alternate name ionic thermal conductivity (ITC). They determined the activation energy and relaxation time with the help of depolarization current obtained during linear heating of the dielectrics. This method was also referred to as thermally stimulated discharge (TSD) of electrets. TSD is a powerful tool for developing better electret materials, because it can quickly reveal the mechanism responsible for the decay of the charges in an electret. It is also useful in optimizing the charging conditions. TSD studies have been performed in wide range of materials viz. inorganic/organic solids, super-cooled organic liquids, liquid crystals, polymers etc.

Ionic/superionic solids are pure ion-conducting systems. Hence, these solids can easily be polarized and depolarized. These materials also obey the Ohm's law well. Due to these physical properties, they are expected to exhibit electret-type/persistent-polarization/memory-type effects. Kumar and Chandra⁹, for the first time,



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Characterization of basic transport properties in a new fast Ag^+ ion conducting composite electrolyte system: $(1-x)[0.75\text{AgI}:0.25\text{AgCl}]:x\text{ZrO}_2$

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Abstract

Studies of some basic ionic transport properties of a new fast Ag^+ ion conducting two-phase composite electrolyte system: $(1-x)[0.75\text{AgI}:0.25\text{AgCl}]:x\text{ZrO}_2$, where $0 \leq x \leq 0.5$ (in molar weight fraction), are reported. A ‘quenched/annealed $[0.75\text{AgI}:0.25\text{AgCl}]$ mixed system/solid solution’ has been used as a first phase host matrix salt as an alternative to the traditional host AgI, while particles ($\leq 5 \mu\text{m}$) of the insulating and inert ZrO_2 were dispersed as second phase dispersoid. In order to find the ‘optimum conducting composition’ (OCC), different compositions of the two phases were mixed homogeneously adopting various routes of preparation. The phase identification studies revealed the coexistence of separate phases. The temperature-dependent transport property studies were carried out on OCC employing various techniques. The mechanism of ion transport has been explained on the basis of models proposed for two two-phase composite electrolyte systems. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Two-phase composite electrolyte; Ionic conductivity; Mobility; Drift velocity

1. Introduction

Two-phase composite electrolytes are special class of solid state ionic materials. They exhibit enhancement in the room temperature conductivity of a moderately ion conducting solid such as LiI, AgI, AgCl, CuI, PbF_2 etc. (termed as first phase host matrix salt) simply by dispersing minute/submicron size particles of an inert and insulating second phase dispersoid compound such as Al_2O_3 , SiO_2 , Fe_2O_3 , ZrO_2 , SnO_2 etc. [1]. These systems have drawn considerable attention due to their unique interfacial

behaviour at the two phase boundary which has led to proposing various phenomenological models to explain conductivity enhancement [1–5]. Liang [6], for the first time, reported ~ 50 times enhancement of Li^+ ion conduction in a two-phase composite electrolyte system: $\text{LiI}-\text{Al}_2\text{O}_3$. A large number of systems has been investigated since then exhibiting one to three orders of magnitude enhancements of Li^+ , Ag^+ , Cu^+ , F^- etc. ion conduction in the different first phase host matrix salts mentioned above. It has generally been observed that a relatively higher conductivity enhancement could be achieved when AgI is used as a first phase host matrix. Shahi and Wagner [7] reported ~ 2500 times (highest to date) enhancement of Ag^+ ion conduc-

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Effects of Ultrasonic Irradiation on Physical Properties of Silica/PEG Hybrids

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ABSTRACT

The effect of ultrasonic radiation is reported for silica-poly(ethylene glycol) system prepared without the solvent using sol-gel processing by varying various parameters such as ultrasonic irradiation time, PEG content and HCl/TEOS molar ratio. The property of sonogel is compared with classic gel which has been prepared with ethanol as a solvent by traditional sol-gel processing. SEM, BET, DTA-TGA, density and Vickers hardness measurements are carried out for analyzing the samples. The gelation time is found strongly dependent on radiation time, PEG content and pH value, and has been discussed on the basis of existing theories. The SiO₂-10 & 20 wt% PEG sonogel exhibited superior optical, physical and gel properties as compared to the classic gel, hence, found suitable for device applications. The ultrasonic radiation increased the density and surface area, and also reduced the pore size which is well supported by the shift in the peak of DTA curve. The DTA thermogram was found similar to that of pure silica gel.

Key words : *Inorganic-organic hybrid, Sol-gel process, Sonogel, Classic gel, Ultrasonic irradiation, SiO₂-PEG*

1. Introduction

The sol-gel process, originally directed towards the synthesis of purely inorganic materials, is increasingly being extended to the preparation of inorganic-organic hybrid materials, called ORMOSIL or ORMOCER, by using tetraethoxysilane(TEOS) as a raw material, through hydrolysis and condensation reactions.¹⁻³⁾ The ORMOSILs have scientific relevance and technological interest because of their application in the field of optics, electronics, mechanics and electrochemistry.⁴⁾ Most of the properties of these materials are related to the synergy between the organic and inorganic parts and to their biphasic nano-structure, providing totally new properties.³⁾ These are essentially porous materials and their structures significantly depend on the preparation conditions, such as pH and water/alkoxide molar ratio, solvent composition, amount of polymer, drying as well as aging. When an organic polymer, e.g. poly(acrylic acid) (PAA), poly(ethylene glycol) (PEG) or poly(ethylene oxide) (PEO), is incorporated into a silica (SiO₂) system, it produces a physical hybrid and/or composite system with better optical transparency and superior properties.^{5,6)} The silica-poly(ethylene glycol) system, an inorganic-organic hybrid system, has wide application as a low-dielectric material, optical material, filter, adsorption material, electrochromic material, high energy density material, etc.⁷⁾

Ultrasound has recently been used for hydrolyzing TEOS,

getting more homogeneity and reducing the gelation time.¹⁰⁾ Sonogels, which are prepared in the presence of acid catalyst without solvent, exhibit peculiar ultra-structural properties due to the nature of the preparation method. Thus, unlike the classic gels prepared by the traditional sol-gel method, alkoxide and water reacts in the vapor phase inside the numerous bubbles produced by cavitation provoking the formation of many microgel particles which aggregate later.⁸⁻¹¹⁾ The cavitation is effective to accelerate the hydrolysis of alkoxides making it possible to obtain a homogeneous liquid, which quickly gels, without using a solvent of the alkoxide-water mixture.¹²⁻¹⁵⁾

We report in this paper, an effect of ultrasonic irradiation on preparation of silica-poly(ethylene glycol) system. TEOS and PEG were chosen as the inorganic and organic precursors, respectively. The sonogels were prepared without the solvent by varying the processing variables, e.g. ultrasonic radiation time, amount of PEG and HCl/TEOS molar ratio. For direct comparison, classic gels were also prepared by traditional sol-gel process using the ethanol as a solvent under identical condition. SEM, BET, DTA-TGA, density and Vickers hardness measurements were carried out to understand the effect of ultrasonic irradiation on gelation, structure and properties of SiO₂-PEG sonogel system.

2. Experimental

2.1. Gel Preparation

Tetraethoxysilane (Si(OC₂H₅)₄, TEOS, 98%, Aldrich), a source of silica, and poly(ethylene glycol) (-H(-CH₂CH₂O)_n

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Transport property and mixed former effect studies on a new fast Ag^+ ion conducting glass system: $0.7[0.75\text{AgI} : 0.25\text{AgCl}] : 0.3[\text{Ag}_2\text{O} : \{x\text{B}_2\text{O}_3 : (1 - x)\text{MoO}_3\}]$

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Abstract

Mixed former effect (MFE) and transport property studies on a new fast Ag^+ ion conducting silver boro-molybdate glass system— $0.7[0.75\text{AgI} : 0.25\text{AgCl}] : 0.3[\text{Ag}_2\text{O} : \{x\text{B}_2\text{O}_3 : (1 - x)\text{MoO}_3\}]$ —are reported. A ‘quenched $[0.75\text{AgI} : 0.25\text{AgCl}]$ mixed system/solid solution’ has been used as the host salt in place of the traditional AgI host. The glass former compositions were varied from $x = 0$ to $x = 0.9$ in molar weight fraction, while the Ag^+ ion salt concentration was kept constant. The composition $0.7[0.75\text{AgI} : 0.25\text{AgCl}] : 0.3[\text{Ag}_2\text{O} : \{0.7\text{B}_2\text{O}_3 : 0.3\text{MoO}_3\}]$ exhibited highest conductivity ($\sigma_{27^\circ\text{C}} = 6 \times 10^{-3} \text{ S cm}^{-1}$) at room temperature, and has been referred to as the optimum conducting composition (OCC). The conductivity enhancement in OCC, approximately 6 times from the pure molybdate glass system, has been found to be due to an increase in the Ag^+ ion mobility. This has been attributed purely as a consequence of MFE. Temperature dependence on some important ion transport parameters such as conductivity (σ), mobility (μ), mobile ion concentration (n), ionic transference number (t_{ion}) and drift velocity (v_d) were done for the OCC samples only, and energies involved in the different thermally activated processes were evaluated from the respective Arrhenius-type plots. The ion transport mechanism has been discussed in the light of models suggested for superionic glasses.

1. Introduction

Silver ion conducting systems in glassy/amorphous phase attracted widespread academic as well as technological interests recently due to the reason that they exhibited several advantageous material properties over their crystalline/polycrystalline counterparts, including very high isotropic conduction ($\sigma \sim 10^{-2} - 10^{-3} \text{ S cm}^{-1}$) at room

temperature. These systems are prepared, in general, by rapidly cooling the molten homogeneous mixture of common silver salts: AgI as host and Ag_2O as glass modifier (GM), with any one of the glass formers (GFs) such as B_2O_3 , CrO_3 , MoO_3 , P_2O_5 , SiO_2 , etc. Traditionally, AgI is chosen as the host salt due to the reason that it possesses a characteristic superionic α -phase (above $\sim 147^\circ\text{C}$), and with a view to stabilize or lock-in this phase at room temperature in the GM–GF network [1–4]. Attempts have also been made to optimize the

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Preparation and Characterization of Hybrid Silica-Poly(ethylene glycol) Sonogel

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An inorganic-organic hybrid system, silica-poly(ethylene glycol) sonogel is reported. This system was prepared *via* sol-gel method by varying various processing variables, *e.g.* ultrasonic radiation time, gelling temperature, PEG content and its molecular weight. Various experimental techniques were employed to analyze the morphological, mechanical and optical properties of the system. The results were discussed in the light of existing theories. The sonogel system exhibited the common features of inorganic-organic hybrids. SiO₂-10 wt% PEG sonogel exhibited the morphological, mechanical and optical properties superior to those reported earlier for the classic gels and found suitable for device applications.

Keywords : Sol-Gel, Sonogel, Ultrasonic irradiation, SiO₂-PEG hybrid, Inorganic-organic hybrid.

Introduction

The inorganic-organic hybrids are a new class of materials which favorably combine the properties of the organic materials to those of the inorganic ones, hence, offer a variety of advantageous properties, such as mechanical, optical, electrical and thermal fulfill the criteria for industrial applications.¹⁻⁵ Such a hybrid system is synthesized *via* sol-gel processing by controlled hydrolysis and subsequent condensation of an organic precursor *e.g.* alkoxysilane in the presence of water, a solvent and a catalyst followed by aging and drying. This process strongly depends on the nature of alkoxy group & the solvent, the concentration of each species in the solvent, the water to alkoxysilane molar ratio, the temperature and the pH value of sol.^{1,2} An alkoxysilane derivative is usually used to provide an inorganic (SiO₂) back-bone, generally three-dimensional, onto which organic groups are attached through covalent bands. Tetraethoxysilane (TEOS) is the most common precursor which offers high porosity and large surface area to the system.⁵ Acid/base catalyzed SiO₂-PEG hybrid system has recently been studied by various workers due to the following significant features.⁶⁻¹³ (i) PEG exhibits certain liquid-like properties such as it acts as an immobile solvent for many metallic salts which are found suitable for developing fast ion conductors,¹⁴ (ii) The presence of silica network allows the transparent materials to be obtained with mechanical property superior to pure PEG system,¹⁴ and (iii) It exhibits low dielectric constant.¹¹

The samples, prepared by traditional method, exhibit, in general, shrinkage/cracks as well as the longer gelation time.¹⁻³ Zarzycki *et al.* and Donatti *et al.* showed separately that the sonocatalysis method can be utilized to avoid the use of solvent and to improve the gelation time, the density, degree of syneresis, elastic and viscoelastic parameters.¹⁵⁻¹⁸

The ultrasonic energy produces an atomization effect, emulsifying the water-alkoxysilane mixture and provoking a release of alcohol, which, in turn, accelerates the homogenization process. More precisely, on the propagation of ultrasonic wave through the solution, a microcavity is formed in the low pressure phase at a nucleus by a gas bubble. This microcavity expands quasi-isothermally and becomes filled with the vapors of the reactants resulting a high pressure phase. Consequently, due to the high pressure, the microcavity collapses adiabatically and produces high temperature which accelerates the hydrolysis-condensation reaction. Donatti *et al.* showed that the hydrolysis rate is directly proportional to the applied radiation time.^{17,18} The SiO₂-PEG hybrid sonogel system has also been reported, in past, in which the effect of drying control chemical additives (DCCA) *e.g.* PEG on SiO₂ was studied with various dose of ultrasonic irradiation.¹⁹ No other studies are found reported in the literatures for the SiO₂-PEG sonogel system.

In the present paper, a detailed investigation of the hybrid SiO₂-PEG sonogel system is reported. This system was synthesized by controlling the processing variables, such as ultrasonic irradiation time, aging temperature, PEG content and its molecular weight. Another hybrid system with 10 wt% of poly(dimethoxysilane) (PDMS) was also prepared under the same conditions for direct comparison. The microstructural, mechanical and optical studies on the bulk samples were carried out using BET, SEM, density & Vicker's hardness measurements and polarizing microscopy. Some novel results are obtained.

Experimental Section

Preparation. Organic precursors: tetraethoxysilane (Si(OC₂H₅)₄, TEOS, Aldrich, 98%) as a source of silica, poly(ethylene glycol) (-H(-CH₂CH₂O)_nOH-, PEG, Aldrich, Average molecular weight = 400 g/mole, 4600 g/mole) and poly(dimethylsiloxane) ((CH₃)₂SiOH-((CH₃)₂SiO₂)_x(CH₃)₂-SiOH, PDMS, U.C.T., Average molecular weight = 450 g/

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Ion Transport and Solid State Battery Studies on a New Silver Molybdate Superionic Glass System: $x[0.75\text{AgI}: 0.25\text{AgCl}]: (1-x)[\text{Ag}_2\text{O}: \text{MoO}_3]$

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Abstract. Preparation, material characterization, ion transport and battery discharge characteristic studies are reported for a new silver molybdate glass system: $x[0.75\text{AgI}: 0.25\text{AgCl}]: (1-x)[\text{Ag}_2\text{O}: \text{MoO}_3]$, where $0 < x < 1$ in molar weight fraction. The traditional host AgI has been replaced by an alternate compound: “a quenched $[0.75\text{AgI}: 0.25\text{AgCl}]$ mixed system/solid solution”. Electrical conductivity (σ), ionic mobility (μ) and mobile ion concentration (n) measurements were carried out as a function of ‘x’. The composition: $0.8[0.75\text{AgI}: 0.25\text{AgCl}]: 0.2[\text{Ag}_2\text{O}: \text{MoO}_3]$ exhibited the highest conductivity ($\sim 6 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$) at room temperature and has been referred to as ‘optimum conducting composition (OCC)’. The compositional variation of ‘ μ ’ and ‘ n ’ revealed that the enhancement in the room temperature conductivity of OCC is predominantly due to the increase in mobile ion concentration. The XRD and DSC analysis on OCC indicated the formation of glassy phase with partial presence of unreacted polycrystalline phase of the host salt. The temperature dependence of various ionic transport parameters viz. ‘ σ ’, ‘ μ ’, ‘ n ’ and ionic transference number (t_{ion}) were carried out on the OCC and the results have been discussed on the basis of theoretical models suggested for superionic glasses. In addition to this, solid state batteries were fabricated using OCC as electrolyte and discharge characteristics were studied under varying load conditions.

1. Introduction

In view to develop solid state electrochemical devices viz. batteries, sensors, fuel cells, supercapacitors, electrochromic display devices etc., silver ion conducting superionic glasses attracted widespread attention in the recent years. These glasses exhibit several distinct advantages over their crystalline/polycrystalline counterparts [1-5]. They show isotropic ionic conductivity as high as $\sim 10^{-2} - 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ at room temperature. Traditionally, Ag^+ ion conducting superionic glasses have been prepared by melt-quenching technique. AgI and Ag_2O have been used in common as host salt and glass modifier respectively, while $\text{B}_2\text{O}_3/\text{CrO}_3/\text{P}_2\text{O}_5/$

MoO_3 etc. as glass former. Attempts have also been made to improve the conductivity and stability of the system by mixing two or more glass formers. This has been referred as ‘mixed former effect (MFE)’ [6,7]. The present paper reports the preparation of a new silver molybdate glass system: $x[0.75\text{AgI}: 0.25\text{AgCl}]: (1-x)[\text{Ag}_2\text{O}: \text{MoO}_3]$, where $0 < x < 1$ in molar wt. fraction, in which an alternate host compound: “a quenched $[0.75\text{AgI}: 0.25\text{AgCl}]$ mixed system/solid solution” has been used in place of the traditional host AgI. The new host, investigated in the present laboratory, exhibits transport characteristics identical to AgI [8,9]. However, it has been observed that the new host yielded

Transport properties of a new Li^+ ion-conducting ormolyte: $(\text{SiO}_2\text{-PEG})\text{-LiCF}_3\text{SO}_3$

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The transport properties of a new fast Li^+ ion-conducting sol-gel-derived ormolyte, $(\text{SiO}_2\text{-10 wt\% PEG})\text{-[Li/O] LiCF}_3\text{SO}_3$, with $[\text{Li/O}] = 0\text{--}0.1$ (mol/mol), is reported. The composition with $[\text{Li/O}] = 0.04$ exhibited the highest conductivity ($\sigma_{25\text{ }^\circ\text{C}} = 1 \times 10^{-4} \text{ S cm}^{-1}$), with an enhancement of 10^3 over the host matrix ($\text{SiO}_2\text{-10 wt\% PEG xerogel}$), and has been found to be the 'optimum conducting composition'. Direct determination of Li^+ ion mobility (μ) and mobile ion concentration (n) revealed that the enhancement was due to the increase in both μ and n . Studies of the variation of σ , μ , and n versus temperature indicated that the system shows Arrhenius-type behavior. The activation energy and energies of migration and formation were evaluated from their respective Arrhenius plots. Measurement of the ion transference number (t_{ion}) confirmed that the ions are the sole charge carriers in the system. These results are discussed in the light of existing theories.

1 Introduction

Li^+ ion-conducting polymer composite electrolytes have attracted widespread interest in recent years due to their potential industrial applications, namely, in solid-state rechargeable batteries, fuel cells, sensors, electrochromic display devices, and super capacitors. These solid electrolytes offer a variety of advantageous properties, *viz.*, high ionic conductivity ($\sigma \approx 10^{-3} \text{ S cm}^{-1}$), light weight, transparency, flexibility, thin film formation, a wide electrochemical voltage window (0–4 V), *etc.*, although with poor mechanical properties. Inorganic fillers (also called dispersoids), such as SiO_2 or Al_2O_3 , have been added during sample preparation to improve the mechanical properties, but with limited success (for reviews on the subject, see ref. 1–3). Ravaine *et al.* successfully eliminated this problem using the sol-gel method and reported room temperature ionic conductivity ($\sigma \approx 7 \times 10^{-5} \text{ S cm}^{-1}$) with an enhancement of more than four orders of magnitude by incorporating a lithium salt, LiNO_3 or LiClO_4 , into the $\text{SiO}_2\text{-poly(ethylene glycol) (PEG) xerogel}$.⁴ The sol-gel method combines the properties of organic (*e.g.* PEG, PEO, PPG) and inorganic (SiO_2) materials, which results in materials with superior properties, such as high room temperature conductivity, homogeneity, mechanical and thermal stability, optical transparency, ease of molding into a desired shape, *etc.*, due to its low temperature processing and high compositional flexibility *via* control of the processing variables.¹ Since then, a number of solid electrolytes have been investigated and exhibit ionic conductivities of $10^{-6}\text{--}10^{-4} \text{ S cm}^{-1}$.^{5–16} These solid electrolytes are now widely known as ormolytes (an abbreviation of *organically modified electrolytes*) and their properties strongly depend on the connectivity of the inorganic-organic phases and the mobility of both the structural network and the active species.^{6–14}

This paper reports the transport properties of a new Li^+ ion-conducting sol-gel-derived ormolyte, $(\text{SiO}_2\text{-10 wt\% PEG})\text{-[Li/O] LiCF}_3\text{SO}_3$. The $\text{SiO}_2\text{-10 wt\% PEG xerogel}$ has recently been investigated in this laboratory^{17,18} and exhibits superior physical, mechanical, optical, and thermal properties, confirming its potential as a host matrix for incorporating lithium salts. Furthermore, LiCF_3SO_3 (lithium trifluoromethanesulfonate) is also quite thermally and electrochemically stable, as well as

being weakly coordinated, and therefore does not tend to form ion pairs.¹⁰ The aim of the present work is to: (1) identify the 'optimum conducting composition' of the ormolyte for device applications from a study of $\sigma_{25\text{ }^\circ\text{C}}$ versus $[\text{Li/O}]$ ratio, (2) explore the reasons for the conductivity enhancement by direct determination of the ionic mobility (μ) and, hence, the mobile ion concentration (n), as a function of the $[\text{Li/O}]$ ratio, (3) determine the phase and thermal stability *via* X-ray diffraction (XRD) studies and thermal differential analysis-thermal gravimetric analysis (DTA-TGA), respectively, (4) explain the ion transport mechanism by evaluating the temperature dependence of σ , μ , and n , and finally, (5) identify the nature of charge carriers by ionic transference number (t_{ion}) measurement. These results are then discussed in the light of existing theories.

2 Experimental

Highly pure Aldrich chemicals ($\geq 99\%$) were used in preparing the ormolyte $(\text{SiO}_2\text{-10 wt\% PEG})\text{-[Li/O] LiCF}_3\text{SO}_3$. A mixture of tetraethoxysilane (TEOS), PEG (MW: 400 g mol^{-1}), and LiCF_3SO_3 with composition $\{1 \text{ mol TEOS:10 wt\% PEG with respect to TEOS:[Li/O] mole ratio with respect to PEG etheral oxygens}\}$ was stirred at room temperature for 15 min, then mixed with a solution of composition $0.01 \text{ HCl:4 H}_2\text{O:3.8 ethanol}$ (all mol/mol with respect to TEOS; the total volume of solution was $\sim 25 \text{ ml}$). Subsequently, the hydrolysis-condensation reactions was performed under reflux at $75 \pm 3\text{ }^\circ\text{C}$ for 1 h, resulting in a clear solution. The sol was left to cool for a few minutes at room temperature, then poured into a polypropylene-based container and covered with paraffin film with small holes in it in order to control the evaporation rate. Gelation occurred after about 48 h. The wet gel was further aged at $50\text{ }^\circ\text{C}$ for a week and then dried at $90\text{ }^\circ\text{C}$ for a further week. The finished products were quite transparent bulk samples, with diameters of around 2 cm and thicknesses of 2–3 mm. The sample preparation was carried out in a Labconco glove box filled with dry N_2 gas ($\text{RH} < 15\%$).

Before performing the experimental studies, the samples were kept at *ca.* $90\text{ }^\circ\text{C}$ for 12 h in a vacuum oven to eliminate moisture effects. A Rigaku D/Max 2500/K X-ray diffractometer

Transport property of novel sono-catalysed LiCF_3SO_3 doped SiO_2 –PEG ormolyte

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Abstract

Transport property of a novel sono-catalysed LiCF_3SO_3 doped SiO_2 –10 wt% PEG ormolyte is reported. The ormolyte was synthesized by sol–gel method by varying the LiCF_3SO_3 concentration $[\text{Li}/\text{O}]$ from 0 to 0.1 in mole. The composition with $[\text{Li}/\text{O}] = 0.05$ exhibited the highest conductivity ($\sigma_{25^\circ\text{C}} = 2.4 \times 10^{-4} \text{ S cm}^{-1}$) with an enhancement of 10^3 from that of the host matrix: SiO_2 –10 wt% PEG sono gel and has been referred to as ‘optimum conducting composition (OCC)’. The direct determination of Li^+ ion mobility (μ)/mobile ion concentration (n) indicated that the enhancement was due to the increase in μ and n both. The temperature dependence of σ , μ and n were carried out for the OCC samples in order to evaluate the respective energies involved in different thermally activated processes and to understand the ion transport mechanism. The ion transference number (t_{ion}) measurement inferred the ions as the sole charge carriers of the system. The results have been discussed in the light of existing theories.

1. Introduction

The Li^+ ion conducting ORMOLYTEs where the ormolytes stood for an abbreviation of *organically modified electrolytes* and a class of inorganic–organic composites, attract widespread academic and technological interests recently due to the reasons that they exhibit several advantageous material properties over their organic (e.g. PEG, PEO, PPG) and inorganic (SiO_2) counterparts, such as high room temperature conductivity (10^{-6} – $10^{-4} \text{ S cm}^{-1}$), a wide range of electrochemical voltage window (0–4 V), mechanical and thermal stability, optical transparency, desired shape formation; hence, find possible industrial applications in solid state rechargeable batteries, fuel cells, sensors, electrochromic display devices and super-capacitors, etc [1–16]. A lithium salt viz LiCF_3SO_3 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ etc is doped into the inorganic–organic hybrid by sol–gel method, which offers a variety of advantages, e.g. high homogeneity, low temperature processing and high flexibility over composition and material’s property via controlling the processing variables [1]. Ravaine

et al [4] were the first who used this method for synthesizing SiO_2 –PEG– LiNO_3 / LiClO_4 ormolyte systems exhibiting room temperature ionic conductivity $\sim 7 \times 10^{-5} \text{ S cm}^{-1}$ with an enhancement of more than four orders of magnitude. It was also noted that the properties of these materials strongly depend on the connectivity of the inorganic–organic phases and the mobility of both the structural network and the active species [6–14]. For example, the ormolytes having weak physical bonds between SiO_2 and polymer, prepared by sono-catalysed sol–gel method, result in a better conductivity than those having covalent bonds [6–9].

This paper reports the transport property of a new Li^+ ion conducting ormolyte: (SiO_2 –10 wt% PEG)– $[\text{Li}/\text{O}] \text{ LiCF}_3\text{SO}_3$ synthesized by the sono-catalysed-sol–gel method. The use of the lithium trifluoro-methane-sulfonate (LiCF_3SO_3) in the preparation of ormolytes is known to be advantageous because: (1) it is thermally and electrochemically very stable, (2) it is weakly coordinated and therefore does not tend to form ion-pairs and (3) as it has internal vibrational modes which are easily detected both in infrared and Raman spectra, it is a recognized excellent ion probe which allows to investigate

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Influence of pH and Dye Concentration on the Physical Properties and Microstructure of New Coumarin 4 Doped SiO₂-PDMS ORMOSIL

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Physical properties and microstructure of new coumarin 4 doped SiO₂-PDMS ORMOSILs, synthesized by one-step (*OS*, acid-catalysis) and two-step (*TS*, acid-base catalysis) routes of sol-gel method with varying pH (0.6 to 7) and dye content (5×10^{-4} to 5×10^{-2} mole), are reported. BET, UV-visible spectroscopy and SEM were used for characterizations. The increase in acid or base concentration increased the size of pores and aggregated silica particles. The samples with pH ≤ 2.5 were transparent and attributed to the small size of pores (~ 20 Å) and silica particles. The samples with pH > 2.5 were translucent or opaque due to non-uniform pore system formed by voids and large aggregated silica particles. The surface area was found a key factor controlling the interactions between the gel matrix and the dye. The *OS* samples with the highest dye concentration exhibited the minimal values of pore size, surface area and silica particle size, resulting in the *concentration-quenching* phenomenon.

Key Words : Physical properties, Microstructure, Organic dye, ORMOSIL

Introduction

The organic dye doped ORMOSILs (organically modified silicates) attract widespread interests in recent years due to their wide application as gain media in laser materials, non-linear optical materials, photochemical hole burning, luminescence solar concentrator, chemical sensor, pH sensor, etc.¹⁻³ The organic dyes show the high fluorescent quantum yields, large cross-sections for absorption-emission, low threshold power for laser action, attractive gain characteristics and tunability in the visible region.¹⁻³ The sol-gel derived ORMOSIL network contains a significant amount of organic functionalities, which offers great flexibility with respect to the chemical compatibility of the gel with the organic dye. Further, due to the low processing temperature, excellent homogeneity at molecular level, large flexibility in the control of sol-gel processing variables and high compositional purity, the sol-gel derived organic dye doped ORMOSIL showed several advantageous properties over the organic dye as a solute in a fluid media, *e.g.* elimination of translational freedom by avoiding inter-molecular interaction, immunization of optical properties from high concentration interferences, reduction in rotational relaxation of the excited state of laser dyes, elimination of inherent problems with physical pumping, ease of use and replacement, and fabrication of samples in the desired form and shape.¹ Amongst the several investigated organic dye doped ORMOSILs,⁴⁻¹² the chemical bonded SiO₂-PDMS ORMOSIL is noted as a useful host-matrix for doping a dye. A detailed investigation on the SiO₂-PDMS ORMOSIL has already been carried out in the present laboratory because the tetraethoxysilane (TEOS,

an inorganic precursor for SiO₂) shows a controllable hydrolysis reaction rate and PDMS (poly(dimethylsiloxane)) possesses specific properties like transparency, hydrophobicity, good chemical and thermal stability and similarity of its backbone structure (-Si-O-) to that of TEOS.^{13,14} Recently, we doped coumarin 4 organic dye into the SiO₂-PDMS ORMOSIL using one-step (acid catalysis) and two-step (acid-base catalysis) routes of sol-gel processing with varying acid (HCl), base (NH₄OH) and dye concentrations to synthesize *OS* and *TS* samples, respectively.¹⁵ Coumarin 4 was chosen as a organic dye because of its high fluorescence efficiency, chemical- and photo-stability.⁷⁻⁹ It also exhibits specific molecular species associated with protonation-deprotonation reactions.⁷⁻⁹ It was observed that the increase in the acid or base concentration increased the photo-luminescence peak intensity, which was attributed to an increase in the interaction between the gel matrix and the dye molecules.¹⁵ *Concentration-quenching* phenomenon was also noted with increasing dye concentration due to the deactivation process by the intermolecular energy transfer originating from the collision and aggregation of dye molecules.¹⁵

The present paper, in series, reports the effects of pH and dye concentration on the physical properties and microstructure of new coumarin 4 dye doped SiO₂-PDMS xerogels: *OS* and *TS*. BET and scanning electron microscopy (SEM) were used to characterize the physical properties and microstructure, respectively. The transparency of the samples was monitored by UV-visible spectroscopy.

Experimental Section

Figure 1 shows the schematic flow chart for synthesizing *OS* and *TS* samples by acid catalysis (one-step) and acid-base catalysis (two-step) routes of sol-gel processing, respec-

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Effects of pH and Dye Concentration on the Optical and Structural Properties of Coumarin-4 Dye-Doped SiO₂-PDMS Xerogels

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Abstract. Optical and structural properties of coumarin-4 dye-doped SiO₂-PDMS xerogels synthesized by acid catalyzed (one-step) and acid-base catalyzed (two-step) sol-gel routes with varying pH (0.6 to 7) and dye content (5×10^{-4} to 5×10^{-2} mole) are reported. Spectroscopic methods such as photo-luminescence, FT-IR and FT-Raman were used for characterizations. The acid catalyzed xerogels prepared with pH < 2.5 exhibited two fluorescence peaks, I at ~390 nm and II at ~480 nm. The acid-base catalyzed xerogels synthesized with pH < 2.5 also exhibited two peaks, I at ~400 nm and II at ~475 nm. Peak II was not observed for the samples with pH ≥ 2.5. This phenomenon was attributed to the existence of pH dependent different forms of coumarin-4 molecule. The *concentration-quenching* phenomenon was observed for the acid catalyzed xerogels prepared with different dye concentration. The FT-IR spectra indicated the existence of hydrogen bonds between the carbonyl groups of dye molecules and the silanol groups of gel matrix. The hydrogen bonding was the highest for the samples with the extremity pH, 0.6 and 7, resulting in the highest dye/gel matrix interactions, hence, the highest fluorescence peaks. The Raman studies indicated that the samples prepared with pH < 2.5 possessed relatively more number of 3-membered siloxane rings than 4-membered siloxane rings. The ring statistics was reversed for the samples with pH > 2.5. The number of silanol groups was higher for the samples with pH > 2.5.

Keywords: sol-gel, ormosil, SiO₂-PDMS, coumarin, optical material, vibrational spectroscopy

1. Introduction

The organic dyes, which have wide application as gain media in laser materials, non-linear optical materials, optical memories, etc., are one of the most attractive materials due to their high fluorescent quantum yields, large cross-sections for absorption-emission, low threshold power for laser action, attractive gain characteristics and tunability in the visible region [1]. These dyes are incorporated into the ORMOSILs (*organically modified silicates*) by the sol-gel method for getting the advantages over the fluid media, viz., elimination of translational freedom by avoiding inter-

molecular interaction, immunization of optical properties from high concentration interferences, reduction of rotational relaxation of the excited state of laser dyes, elimination of inherent problems with physical pumping, and fabrication of samples in the desired shape [1–3]. The ORMOSILs provide desired optical, thermal, physical and structural properties by controlling the sol-gel processing variables such as pH, the concentration of each species in the solvent, etc. Anvir et al. [2] was the first who doped an organic rhodamine 6G dye into a silica matrix using sol-gel method and studied its optical properties. Since then, a number of organic dyes of various families such as rhodamine [3, 4], coumarin [5–9], fluorescein [10], pyromethane [11], UV [12], thionin [13], etc. have been utilized to synthesize

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Transport Properties and Battery Discharge Characteristics of the Ag^+ Ion Conducting Composite Electrolyte System $(1-x)[0.75\text{AgI}: 0.25\text{AgCl}]: x\text{Fe}_2\text{O}_3$

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Abstract. Ion transport and battery discharge characteristic studies are reported for a new Ag^+ ion conducting two-phase composite electrolyte system $(1-x)[0.75\text{AgI}: 0.25\text{AgCl}]: x\text{Fe}_2\text{O}_3$, where $0 \leq x \leq 0.5$ in molar weight fraction. An alternative single-phase host-matrix 'annealed $[0.75\text{AgI}: 0.25\text{AgCl}]$ mixed system/ solid solution' has been used in place of the traditional host, AgI. Submicron size particles ($< 1 \mu\text{m}$) of Fe_2O_3 has been used as second phase dispersoid. The composition $0.8[0.75\text{AgI}: 0.25\text{AgCl}]: 0.2\text{Fe}_2\text{O}_3$, exhibiting the highest room temperature conductivity has been referred to as the optimum conducting composition (OCC). The reason for an enhancement of an order of magnitude in the conductivity from that of the pure host has been identified through direct determination of ionic mobility (μ) and mobile ion concentration (n) using transient ionic current (TIC) technique. The XRD study confirmed the coexistence of the constituent phases. The ionic transference number is found to be very close to unity. This reveals the fact that the silver ions are the sole charge carriers in the system. The results are discussed in the light of space-charge models proposed for the two-phase composite electrolyte systems. Solid state batteries, fabricated using OCC as electrolyte, Ag-metal as anode and mixtures of iodine & graphite, viz. $(\text{C}+\text{I}_2)$, $(\text{C}+\text{KI}_3)$, $(\text{C}+(\text{CH}_3)_4\text{NI}_3)$, $(\text{C}+(\text{C}_2\text{H}_5)_4\text{NI}_3)$, etc. as cathodes, were discharged under different load conditions. The battery with $(\text{C}+\text{I}_2)$ cathode performed satisfactorily specially under low current drain states.

1. Introduction

Silver ion conducting two-phase composite electrolyte systems have attracted worldwide attention due to their potential uses in solid state electrochemical devices such as solid state batteries, fuel cells, sensors, supercapacitors, etc. A conductivity enhancement of 1-3 orders of magnitude with room temperature conductivity value $\sigma_{\text{rt}} \sim 10^{-3} \text{ Scm}^{-1}$ can be achieved in the Ag^+ ion conducting two-phase composite systems simply by dispersing submicron size particles of an inert and insoluble solid system such as Al_2O_3 , SiO_2 , ZrO_2 , Fe_2O_3 , etc., known as second-phase dispersoid, into a moderately ion-conducting first-phase host-matrix salts like AgI, AgCl, AgBr etc. [1-3]. It has generally been observed that composite systems prepared with AgI host exhibit superior electrolyte properties [1-3]. However, in the present laboratory, an alternate host-matrix salt 'a quenched/annealed $[0.75\text{AgI}: 0.25\text{AgCl}]$ mixed system/solid

solution has been discovered, which can appropriately replace the traditional host AgI [4]. The new host also yielded several glass/ composite electrolyte systems exhibiting superior electrolyte properties than those prepared by AgI [4-12].

The present paper reports synthesis of another new Ag^+ ion conducting two-phase composite electrolyte system: $(1-x)[0.75\text{AgI}: 0.25\text{AgCl}]: x\text{Fe}_2\text{O}_3$ by dispersing submicron particles (size $< 1 \mu\text{m}$) of second-phase dispersoid Fe_2O_3 into the first-phase host: $[0.75\text{AgI}: 0.25\text{AgCl}]$. The x is varied in molar weight fraction from 0 to 0.5. The compositional dependence of conductivity studies were performed using impedance spectroscopy (IS) for identifying optimum conducting composition (OCC). For direct comparison of room temperature conductivity, composite systems: $(1-x)\text{AgI}: x\text{Fe}_2\text{O}_3$ using traditional host, AgI, were also prepared in identical manner. The temperature

Electrical Properties of a New Ag^+ Ion Conducting Glassy System: $x[0.75\text{AgI}:0.25\text{AgCl}] : (1-x)[\text{Ag}_2\text{O} : \text{P}_2\text{O}_5]$

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Abstract. A new fast Ag^+ ion conducting glassy system: $x[0.75\text{AgI}:0.25\text{AgCl}] : (1-x)[\text{Ag}_2\text{O} : \text{P}_2\text{O}_5]$, where $0.1 \leq x \leq 1$ in molar weight fraction, has been synthesized by melt-quench technique using a high-speed twin roller-quencher. An alternate host salt: 'quenched $[0.75\text{AgI} : 0.25\text{AgCl}]$ mixed system/ solid solution', has been used in place of the traditional host AgI . The compositional dependence conductivity studies on the glassy systems: $x[0.75\text{AgI}:0.25\text{AgCl}] : (1-x)[\text{Ag}_2\text{O} : \text{P}_2\text{O}_5]$ as well as $x\text{AgI} : (1-x)[\text{Ag}_2\text{O} : \text{P}_2\text{O}_5]$ prepared identically, indicated that the composition at $x = 0.75$ exhibited the highest room temperature conductivity. The composition: $0.75[0.75\text{AgI} : 0.25\text{AgCl}] : 0.25[\text{Ag}_2\text{O} : \text{P}_2\text{O}_5]$ has been referred to as optimum conducting composition (OCC). The study also revealed that the new/ alternate host yielded better electrolyte system. The activation energy (E_a), involved in the thermally activated conductivity process has been computed from 'log $\sigma - 1/T$ ' Arrhenius plot.

1. Introduction

Fast ion conducting glassy/amorphous systems were interesting solid state ionic materials as regard to develop various electrochemical devices such as mini/micro batteries, fuel cells, supercapacitors etc. Amongst the known superionic glasses, Ag^+ ion conducting systems attracted special attention as they exhibit relatively very high ionic conductivity at room temperature as well as several advantageous material properties over other glass electrolytes [1-5]. Majority of the fast Ag^+ ion conducting glasses, reported in the past, is AgI based systems. They are prepared in general by melt-quenching the mixture of AgI as host salt with glass modifier Ag_2O and glass former such as B_2O_3 , MoO_3 , CrO_3 , P_2O_5 etc. in appropriate molar compositions. The conductivity/ stability of this system gets improved further if two or more glass formers are used. This has been referred to as mixed former effect [MFE] [6-7].

In the present paper we report a preliminary studies on the conductivity measurement in a newly synthesized silver ion conducting phosphate glass system: $x [0.75\text{AgI} :$

$0.25\text{AgCl}] : (1-x)[\text{Ag}_2\text{O} : \text{P}_2\text{O}_5]$, where $0 < x < 1$ in molar wt. fraction, in which a "quenched $[0.75\text{AgI}:0.25 \text{AgCl}]$ mixed system/ solid solution" has been used as an alternate host in place of the traditional host salt AgI [8]. A number of glass/composite electrolytes have been discovered in the present laboratory using this alternate host which exhibits superior electrolyte properties than those prepared by the traditional host [9-12]. To identify the optimum conducting composition (OCC) the compositional dependence of conductivity (σ) has been carried out using impedance spectroscopic technique. The activation energy E_a has been computed from log $\sigma - 1/T$ Arrhenius plot for OCC sample only.

2. Experimental Details

Silver phosphate glass systems $x : [0.75 \text{AgI} : 0.25 \text{AgCl}] : (1-x) [\text{Ag}_2\text{O}:\text{P}_2\text{O}_5]$, were prepared by rapidly cooling the homogeneous molten mixtures of commercially available chemicals: AgI (purity $>98\%$), AgCl ($>99\%$), Ag_2O ($>98\%$) & P_2O_5 (99%) supplied by Reidel India Ltd. The

Electrical and electrochemical properties of a new silver tungstate glass system: $x[0.75\text{AgI}: 0.25\text{AgCl}]: (1-x)[\text{Ag}_2\text{O}: \text{WO}_3]$

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Abstract

Investigations on electrical and electrochemical properties of a new silver tungstate glass system: $x[0.75\text{AgI}: 0.25\text{AgCl}]: (1-x)[\text{Ag}_2\text{O}: \text{WO}_3]$, where $0.1 \leq x \leq 1$ in molar weight fraction, are reported. A “quenched $[0.75\text{AgI}: 0.25\text{AgCl}]$ mixed system/solid solution” was used as a host salt in place of the traditional host AgI for synthesizing the glass system. Compositional variation of room temperature conductivity of the glass systems prepared identically using both the new and traditional hosts exhibited σ -maxima at $x=0.7$. The composition: $0.7[0.75\text{AgI}: 0.25\text{AgCl}]: 0.3[\text{Ag}_2\text{O}: \text{WO}_3]$ shows the highest room temperature conductivity ($\sigma_{27^\circ\text{C}}=4.0 \times 10^{-3} \text{ S cm}^{-1}$) and has been referred to as optimum conducting composition (OCC). Formation of glass in the OCC was confirmed by X-ray diffraction (XRD) and differential thermal analysis (DTA). A direct determination of ionic mobility (μ), was done by transient ionic current (TIC) technique, subsequently, mobile ion concentration (n) was evaluated using σ and μ data. An increase in μ has been ascribed as the reason for the enhancement in the room temperature conductivity as compared to pure host. Temperature dependence of ionic parameters, namely, σ , μ , n , ionic transference number (t_{ion}) and ionic drift velocity (v_d) was carried out on the OCC sample only and the mechanism of ion transport has been discussed in the light of models suggested for superionic glasses. The electrochemical study on solid state batteries, fabricated using OCC as electrolyte with Ag-metal as anode and $\text{C}+\text{I}_2$ as cathode, exhibited a satisfactory performance during low current drain.

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Keywords: Solid State Ionics materials; Superionic glass; WO_3 ; Ionic mobility; Mobile ion concentration; Solid state battery

1. Introduction

Silver ion conducting superionic solids in glassy/amorphous phase are interesting materials specially to develop solid-state electrochemical devices such as batteries, fuel cells, sensors, supercapacitors, electrochromic display devices, etc. [1–5]. These materials have recently attracted widespread attention mainly due to their high isotropic ionic conductivity ($\sigma_{25^\circ\text{C}} \sim 10^{-2}–10^{-3} \text{ S cm}^{-1}$) as well as ease of material handling and synthesization. In the majority of the known fast Ag^+ ion conducting glasses, AgI has traditionally been used as a host salt with a view to stabilize superionic α -phase of AgI at room temperature in a glass-matrix consisting of a glass modifier (GM): Ag_2O and a glass former (GF), e.g. B_2O_3 , CrO_3 , MoO_3 , WO_3 , V_2O_5 , etc.

[1–11]. In order to achieve further enhancement in the room temperature conductivity and increased stability of the glassy phase, attempts have also been made to mix two or more glass formers, referred to as mixed former effect (MFE) [12,13]. However, in a recent investigation Agrawal et al. [14,15] suggested an alternate host: a *quenched $[0.75\text{AgI}: 0.25\text{AgCl}]$ mixed system/solid solution* which exhibits transport characteristics identical to AgI with $\beta \rightarrow \alpha$ like phase transition at a lower temperature ($\sim 135^\circ\text{C}$). They also discovered that the alternate host yields fast Ag^+ ion conducting glass systems exhibiting superior electrolyte properties as compared to those prepared with the traditional host AgI [16–20].

The present paper reports another Ag^+ ion conducting glass system in this series prepared with the new host; a silver tungstate glass system: $x[0.75\text{AgI}: 0.25\text{AgCl}]: (1-x)[\text{Ag}_2\text{O}: \text{WO}_3]$, where $0.1 \leq x \leq 1$ in molar weight fraction. Silver tungstate glass systems of similar compositions were also synthesised in the identical manner using traditional host AgI to enable a direct comparison of the

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Vibrational spectroscopic studies of sol–gel derived physical and chemical bonded ORMOSILs

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Abstract

Fourier transform infrared (FT-IR) and FT-Raman Spectroscopy have been utilized to characterize the structure of physical and chemical bonded ORMOSILs (organically modified silicates) and to compare with the physical properties, reported earlier. The classic and sono ORMOSILs were synthesized by sol–gel method via traditional- and sono-catalysis routes, respectively. The physical and chemical bonding is established by Poly(ethylene glycol) (PEG) and Poly(dimethoxysilane) (PDMS), respectively. Existence of band at $\sim 560\text{ cm}^{-1}$ (FT-IR) and $\sim 490\text{ cm}^{-1}$ (FT-Raman) for the sono and classic gels with 5–10 wt% of PEG indicates the presence of structural defect due to the four-membered siloxane rings. Application of long molecular PEG chain and PDMS increases this defect. Modification in the intensity and peak position of siloxane (Si–O–Si) bands is found correlative with the physical properties. The xerogels with 5–10 wt% of PEG possess a large number of residual surface silanol groups than the xerogels with long molecular PEG chains and PDMS and is found related with the $\nu(\text{OH})$ band at $\sim 3470\text{ cm}^{-1}$. These results are attributed to the way of hydrolysis–condensation reactions and discussed with the help of Percolation and DLVO models.

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1. Introduction

The sol–gel derived ORMOSILs (an acronym for organically modified silicates and a class of inorganic–organic hybrids) exhibit superior mechanical, optical, electrical and thermal properties over their organic and inorganic counterparts due to the definite advantageous properties of sol–gel processing, e.g. molecular level homogeneity, purity, large flexibility in processing and low processing temperature. Hence, these hybrids find tremendous scopes in various industrial applica-

tions [1,2]. The physical bonded silica–poly(ethylene glycol) [SiO_2 –PEG] hybrid system, synthesized by traditional route of sol–gel method, has been studied by various research groups due to its excellent optical properties [3–11]. The sono-catalysis processing was also adopted to synthesize SiO_2 –PEG gel without solvent [12]. The sono-catalysis processing offers faster hydrolysis reaction resulting in improved density, degree of syneresis, elastic, and viscoelastic parameters of the xerogels [13]. The physical, mechanical and optical properties of the sono gels were found superior to those of classic gels [11,12]. It was also noted that the replacement of PEG by poly(dimethoxysilane) (PDMS) resulted in less dense chemical bonded sono gel [12].

The present paper reports the vibrational spectroscopic studies of SiO_2 –PEG and SiO_2 –PDMS ORMOSILs.

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Structural study of a sol–gel derived novel solid oxide fuel cell perovskite: $(\text{La}_{1-x}\text{Sr}_x)(\text{Cr}_{0.85}\text{Fe}_{0.05}\text{Co}_{0.05}\text{Ni}_{0.05})\text{O}_{3-\delta}$

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Abstract

The effect of composition on the structure of the new solid oxide fuel cell (SOFC) perovskite $(\text{La}_{1-x}\text{Sr}_x)(\text{Cr}_{0.85}\text{Fe}_{0.05}\text{Co}_{0.05}\text{Ni}_{0.05})\text{O}_{3-\delta}$ is studied using x-ray diffractometry, pycnometry, and Fourier-transform infrared and Raman spectroscopy. Samples were synthesized using the Pechini method via doping the La site with Sr^{2+} , to a composition with $x = 0\text{--}0.4$ mole fraction, and at the Cr site with 0.05 mol of Co^{2+} , Fe^{2+} and Ni^{2+} , and the structural results were compared with those for orthorhombic LaCrO_3 . The samples were orthorhombic perovskite of the $Pnma$ space group. A second phase, monoclinic SrCrO_4 , was also observed, whose content increased linearly with increasing x . A large decrease in the lattice and hence volume was observed for the sample with $x = 0.1$, which was accompanied by a sharp decrease in the Cr–O bond length, tilt angle and crystallite size. The structural parameters were almost invariant for $x = 0.1\text{--}0.4$, probably due to an increase in content of the high valence cations of smaller ionic radii, as suggested by an increase in the intensity of the defect band ($\sim 515\text{ cm}^{-1}$, IR). The octahedral CrO_6 stretching, bending and tilting modes were found shifted accordingly. A mechanism employing a partial-charge model was proposed to explain the results.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Owing to excellent oxidation, sulfidation and carburization resistances; stability in terms of dimension, microstructure, chemistry and phase; high electronic and thermal conductivity; and comparable coefficient of thermal expansion (CTE) to the adjacent components, Sr^{2+} doped

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Physical and Dielectric Properties of Aluminoborosilicate-Based Dielectrics Containing Different Divalent Oxides

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ABSTRACT

The variations of physical and dielectric properties of low temperature dielectrics based on typical aluminoborosilicate glasses modified with several divalent oxides were investigated. The divalent oxides studied here included CaO, MgO, BaO, SrO and ZnO. All samples containing either 35 wt% or 45 wt% alumina filler were prepared at the same processing condition and then fired at 850°C for 30 min. The resultant characteristics of fired samples depended on the choice of the divalent ion and the content of the alumina filler. Except for the ZnO modification, all other samples containing 35 wt% filler demonstrated promising densification as they exhibited reasonably high densities of 3.07-3.31 g/cm³ and high shrinkages of 14.0-16.4%. Particularly, the sample containing ZnO was distinguished with large variations compared to the base sample, which can be highlighted with earlier densification and crystallization at unexpectedly low temperatures. The negative effects of the ZnO modification on densification and dielectric properties were thought to be associated with earlier crystallization potentially by influencing effective densification via viscous flow. As an optimum composition, the sample containing only CaO showed the most promising characteristics such as $k \sim 8.05$ and $\tan \delta \sim 0.0018$ when 35 wt% alumina filler was used.

Key words : Dielectric, LTCC, Aluminoborosilicate, Crystallization

1. Introduction

Low temperature co-fired ceramics (LTCC) have been actively investigated primarily focusing on the field of ceramic electronic packages requiring high density integration.¹⁻³⁾ The proper design of the LTCC materials is essential in producing successful ceramic-based packages utilizing inexpensive co-fireable Ag-based conductors. Several requirements for the LTCC materials, such as low temperature processing below 850°C and low dielectric constant, make the glass as an evitable choice in producing the LTCC materials. The low k LTCC usually consists of low temperature softening glass and ceramic filler. The ceramic filler is required mainly for providing dimensional stability and physical strength. Among a lot of known low temperature softening glasses, calcium aluminoborosilicate-based glasses have been known as one of the most promising in terms of resultant physical, thermal and dielectric properties.⁴⁻¹²⁾ However, there is no systematic report on the effects of detailed compositional changes of glass on the final LTCC performance although many competitive commercial LTCC materials are based on the calcium aluminoborosilicate glasses.

This work intends to provide an example of the effects of

divalent substitutions, such as Mg, Ba, Sr and Zn, in a typical calcium aluminoborosilicate glass on the physical and dielectric properties of the LTCC samples containing alumina (Al₂O₃) filler. Densification and crystallization behavior resulted from the different divalent oxides will be correlated to the observed performance of the samples.

2. Experimental

Calcium aluminoborosilicate glasses modified with various divalent oxides such as MgO, BaO, SrO and ZnO were prepared by melting corresponding raw materials in a platinum crucible at 1500°C for 2 h and by subsequent quenching into a water bath. The base glass composition contains 25 mol% CaO, as designated with the "CaO" glass. Only 10 mol% of 25 mol% CaO was substituted with each divalent oxide, i.e., MgO, BaO, SrO or ZnO, while the relative ratios among all other glass constituents such as Al, Si and B were kept in all glasses. For example, the "MgO" glass means that it contains 15 mol% CaO and 10 mol% MgO.

The quenched glass was ball-milled with stabilized zirconia balls for ~20 h to make frit. A fixed filler materials of Al₂O₃ (99.9%, ALM43, Sumitomo) was chosen to produce the final dielectrics. The glass frit and alumina filler were admixed at two fixed weight ratios of 65/35 and 55/45 by ball-milling in ethanol for 18 h. The mixture was dried on a hot plate and mixed with a 1.5 wt% PVA (poly vinyl alcohol)

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Improvement of Temperature Coefficient of Frequency in Ba-deficient $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ Microwave Dielectrics

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Ba-deficient non-stoichiometric compositions of $\text{Ba}_{5-x}\text{Nb}_4\text{O}_{15-x}$ ($x=0$ to 0.5) have been investigated for the purpose of improving microwave dielectric properties. While there was no significant variation in dielectric constant, variations in $Q \times f$ and TCF (temperature coefficient of frequency) values with the degree of Ba deficiency were prominent. Near zero TCF value was obtained for the composition of $\text{Ba}_{4.77}\text{Nb}_4\text{O}_{14.77}$. The apparent formation of a second BaNb_2O_6 phase for the Ba-deficient compositions was believed as responsible for the improved TCF. It was interesting to note that the second phase was present more preferably inside of the sample.

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Key-words: Microwave dielectrics, $\text{Ba}_5\text{Nb}_4\text{O}_{15}$, BaNb_2O_6 , TCF

1. Introduction

There have been extensive studies in developing new low temperature co-fired ceramic (LTCC) materials, particularly having relatively high dielectric constants >20 for various electronic passive components and module packages.^{1)–4)} Due to the restriction of firing temperature below 900°C, an appropriate content of glass was regarded as an essential choice in producing successful LTCC compositions.^{5)–7)} At the same time, there have been continuing efforts in developing glass-free LTCC compositions in order to overcome shortcomings, such as high dielectric loss and low dielectric constant, which primarily come from the common silicate glasses.

The BaO–Nb₂O₅ system has been known as one of the promising candidates in providing sufficient densification around 900°C without using glass as a sintering aid.^{8),9)} $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ was reported as possessing high $k \sim 40$ –44, $Q \times f \sim 53,000$ GHz and $\text{TCF} \sim +50$ –78 ppm/°C at 16 GHz when fired at 1425°C.^{9),10)} Addition of small contents of low melting oxides such as B₂O₃, CuO, V₂O₅ and Bi₂O₃ reduces the sintering temperature from 1425°C to $\sim 900^\circ\text{C}$. $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ is known to be sensitive to the choice of additive oxides in sustaining the desirable microwave dielectric properties.^{11),12)}

The present work intends to demonstrate the beneficial effects of Ba-deficient $\text{Ba}_{5-x}\text{Nb}_4\text{O}_{15-x}$ compositions for the purpose of enhancing TCF while other microwave dielectric properties are kept within the practical ranges, $k > 40$ and $Q \times f > 15,000$ at GHz frequencies. Phase development and its dependence on dielectric properties were discussed with supporting experimental evidences.

2. Experimental procedure

The samples with nominal compositions of $\text{Ba}_{5-x}\text{Nb}_4\text{O}_{15-x}$ with different x values from 0 to 0.5 were prepared by the typical solid state reaction utilizing high-purity BaCO₃ (99.9% purity, Aldrich, Milwaukee, WI) and Nb₂O₅ (99.9% purity, Aldrich, Milwaukee, WI). The raw materials were admixed by ball milling in ethanol for 15 h, dried at 120°C in an oven and calcined at 1100°C for 2 h in ambient atmosphere. The calcined powder was mixed with fixed additives of 0.1 mass% Cu₂O and 0.5 mass% B₂O₃ by ball milling. The mixture was dried on a hot plate while stirring with a magnetic bar and then

pressed uniaxially at ~ 80 MPa. An 1.5 mass% polyvinyl alcohol (PVA) solution was used as a binder to make pellets. Sintering was performed by firing pressed pellets at 900°C for 2 h with a fixed heating rate of 5°C/min.

The crystalline phases were determined using an X-ray diffractometer (XRD; Rigaku B/Max-2500/PC, Tokyo, Japan) with CuK α radiation. Microstructures of the sintered samples were examined by scanning electron microscopy (SEM; Model S-4200, Hitachi, Nissei Sangyo, Japan). Bulk density was measured by using the Archimedes principle. The microwave dielectric properties of the sintered samples were measured using a network analyzer (Agilent 8720ES, Palo Alto, CA). The dielectric characteristics such as dielectric constant, k and quality factor, Q were determined by the Hakki-Coleman dielectric resonator method in the S₂₁ transmission mode.¹³⁾

3. Results and discussion

Figure 1 shows the XRD patterns obtained for the $\text{Ba}_{5-x}\text{Nb}_4\text{O}_{15-x}$ samples ($x=0$ to 0.5), sintered at 900°C for 2 h. The pellet samples were grinded into fine powder for the XRD measurement. As expected, only $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ phase was observed for the stoichiometric $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ ($x=0$) whereas all Ba-deficient samples showed the presence of a second phase, i.e., BaNb_2O_6 . The increase in relative peak intensity of the second phase with increasing x suggests that the percentage of BaNb_2O_6 in the sample becomes more apparent with further Ba-deficiency. The peaks of the hexagonal $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ phase tended to shift to higher angles for the Ba-deficient samples. The values of lattice constant calculated were $a=5.815$, $b=5.815$, and $c=11.79 \times 10^{-10}$ m for the stoichiometric sample while they changed into $a=5.788$, $b=5.788$, and $c=11.81 \times 10^{-10}$ m for the $x=0.1$ sample. The lattice constants were found to vary meaninglessly for the nonstoichiometric samples regardless of x value.

Figure 2(a) shows the intensity changes of BaNb_2O_6 phase relative to $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ as a function of Ba-deficiency as expressed by the equation of $I_{\text{BaNb}_2\text{O}_6(220)} / [I_{\text{BaNb}_2\text{O}_6(220)} + I_{\text{BaNb}_2\text{O}_6(220)}]$. $I_{\text{BaNb}_2\text{O}_6(220)}$ is the intensity of the strongest $\text{BaNb}_2\text{O}_6(220)$ peak and $I_{\text{Ba}_5\text{Nb}_4\text{O}_{15}(103)}$ is the intensity of the strongest $\text{Ba}_5\text{Nb}_4\text{O}_{15}(103)$ peak. The intensity ratio gives an idea on the approximate molar content of BaNb_2O_6 phase existing at each composition. For example, a ratio value of 0.124 for composition corresponding to $x=0.5$ indicates that

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Effects of anion and synthesis route on the structure of $(\text{La}_{0.9}\text{Sr}_{0.1})(\text{Cr}_{0.85}\text{Fe}_{0.05}\text{Co}_{0.05}\text{Ni}_{0.05})\text{O}_{3-\delta}$ perovskite and removal of impurity phases

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Abstract

A novel approach to synthesize a single-phase orthorhombic perovskite, $(\text{La}_{0.9}\text{Sr}_{0.1})(\text{Cr}_{0.85}\text{Fe}_{0.05}\text{Co}_{0.05}\text{Ni}_{0.05})\text{O}_{3-\delta}$, is reported. Samples are synthesized using two groups of precursors, metal nitrates and metal acetates by various routes of sol–gel method. The effects of the anion and synthesis route on the perovskite structure and removal of impurity phase are investigated using X-ray diffractometry and Fourier-transform infrared spectroscopy. Impurity phases, SrCrO_4 and CoCr_2O_4 are observed only for the samples prepared using metal nitrates and ascribed due to the pH dependence of citric acid and the cation–anion bonding character, which also affect the reactivity of the mixed solvents. Variation in cell volume with route is corroborative with route-dependent high frequency stretching modes. A mechanism using a partial-charge model is proposed to explain the results.

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Keywords: SOFC; Pechini; Perovskite; Anion; Doped LaCrO_3 ; XRD; Infrared spectroscopy

1. Introduction

An orthorhombic lanthanum chromite (LaCrO_3) of Pnma space group is one of the best inter-connecting perovskite materials for solid oxide fuel cells (SOFC) applications. It offers excellent oxidation, sulfidation, and carburization resistances; stability in terms of dimension, microstructure, chemistry and phase at oxidizing and reducing atmospheres; high thermal conductivity; high mechanical strength; and a comparable coefficient of thermal expansion (CTE) to the adjacent components. However, it exhibits poor air sinterability due to volatility of chromium oxide from the surface and low electronic conductivity ($\sim 1 \text{ S cm}^{-1}$) at SOFC operational temperature $\sim 1000^\circ\text{C}$. For an excellent review on the subject, go through the references, [1–4]. In efforts to achieve high air sinterability and electrical conductivity with highly surface reactive, ultra-fine powders, several LaCrO_3 perovskites doped with cations into La- and/or Cr-sites have been synthesized by various

methods—these include solid state reaction [5–8], combustion [9–11], polymeric gel [12,13], Pechini [14,15], and drip-pyrolysis [16–18]. Substitution of La^{3+} by 0.1–0.2 mole of Sr^{2+} is found to be the most suitable approach in terms of a combined effect of sintering, electrical, thermal and mechanical properties in oxidizing and reducing atmospheres [2–4,6]. Doping of a cationic species, *e.g.* Fe^{2+} , Co^{2+} , and Ni^{2+} with a concentration of 0.05–0.2 mole in the Cr-site largely improved the conductivity and bulk density of $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$ ($x=0\text{--}0.15$ mole) [2–4,8,11,14,15]. It was observed that Co^{2+} - and Ni^{2+} -doping slightly increased and decreased the CTE of $\text{La}_{0.85}\text{Sr}_{0.15}\text{CrO}_3$, respectively [8]. Doping of two or more cations, namely, Co^{2+} , Fe^{2+} , and Ni^{2+} also improved the electrical conductivity and sinterability by maintaining the CTE comparable to that of YSZ [3,4,8,14,16]. Pure LaCrO_3 exhibits orthorhombic symmetry at room temperature and transforms to rhombohedral symmetry at $\sim 255^\circ\text{C}$ [2,5]. However, doping of a metal cation in La- and/or Cr-sites of LaCrO_3 arrests either of orthorhombic and rhombohedral structures, or both at room temperature depending on the dopant, doping concentration, preparative method, and sintering temperature [2,5–18]. Impurity phases, namely SrCrO_4 , La_2O_3 , La_2CrO_6 , etc., also exist along with the perovskite phase [6,9,10,13–18]. Peck et al. [18] noted that solubility range of

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FAST TRACK COMMUNICATION

Mechanical, electrical and micro-structural properties of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ perovskite-based ceramic foams

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Abstract

Mechanical, electrical and micro-structural properties of new electronic conducting ceramic foams are reported. Ceramic foams are prepared using the slurry of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF) by the polymeric sponge method, which is followed by spray coating for increasing the number of coatings–sinterings on polyurethane foams of 30, 45 and 60 ppi (pores per linear inch). An increase in the number of coatings–sinterings and ppi improved the compressive strength, density and electrical conductivity by decreasing the porosity to $\sim 76\%$, as also observed by the SEM study. The three-times coated–sintered ceramic foams (60 ppi) exhibited optimum values of compressive strength of ~ 1.79 MPa and relative density of ~ 0.24 at 25°C and electrical conductivity of $\sim 22\text{ S cm}^{-1}$ at 600°C with an activation energy of $\sim 0.22\text{ eV}$ indicating its suitability as a solid oxide fuel cell current collector. The experimental results are discussed in terms of the Gibson and Ashby theoretical model.

1. Introduction

Solid oxide fuel cells (SOFCs), operational at $\sim 1000^\circ\text{C}$, are the most efficient way of generating electricity due to internal reforming of hydrocarbon fuels, high quality by-product heat for co-generation, low level of pollutants and electrical power of multi-megawatt. The performance of an SOFC depends on the oxygen reduction reaction, 2e^- (cathode) + $1/2\text{O}_2$ (air) \rightarrow O^{2-} (electrolyte) at the triple phase boundary. This reaction is significantly affected by cathode geometric parameters such as the location and size of pores for gas flow and the presence or the absence of a current-collector layer. Thus, in addition to promoting electron transport, the

current collector actually serves as a gas distributor allowing uniform distribution of gas to the functional layer of the active cathode [1, 2]. Currently, a platinum mesh is applied as a cathode current collector due to its excellent oxidation, sulfidation and carburization resistances, stability in terms of dimension, microstructure, chemistry and phase, high electrical and thermal conductivity, high catalytic activity and a comparable coefficient of thermal expansion (CTE) to the adjacent components [1]. In general, mesh electrodes are preferred to pastes because of reduced performance reported for pastes as well as diffusion of the metal into grain boundaries and compound formation due to paste [3]. It is also highly expensive and exhibits inhomogeneous current densities due to an insufficient area for contact [4]. Hence, for manufacturing cost-effective SOFCs, it was suggested to replace the platinum mesh by a $\text{La}_{0.84}\text{Sr}_{0.16}\text{Mn}_{0.98}\text{Co}_{0.02}\text{O}_3$

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Effects of solvent and chelating agent on synthesis of solid oxide fuel cell perovskite, $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_{3-\delta}$

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Abstract

Effects of solvent and chelating agent on synthesis of $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_{3-\delta}$ perovskite are reported. Samples are synthesized using a solvent (ethylene glycol or 2-methoxyethanol) and a chelating agent (acetylacetone, citric acid or ethylene diamine tetraacetic acid) by polymeric-gel method, and characterized by X-ray diffractometry and Fourier-transform infrared spectroscopy. Citric acid to metal cations molar ratio (R_c) is varied for ethylene glycol–citric acid system. Samples are mainly orthorhombic perovskite. SrCrO_4 is appeared as a secondary phase and found to be the lowest for ethylene glycol–citric acid combination with R_c equal to 7. Crystallographic parameters of perovskite phase are determined and compared with those of LaCrO_3 . A mechanism employing a partial-charge model, chelating effect and solvent-cage effect is proposed to explain the results. Effect of sintering temperature on phase, relative density and morphology of samples prepared using ethylene glycol and citric acid ($R_c = 7$) is also reported.

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Keywords: A. Ceramics; B. Sol–gel chemistry; C. Infrared spectroscopy; C. X-ray diffraction; D. Crystal structure

1. Introduction

$\text{La}_{1-x}\text{Sr}_x\text{CrO}_{3-\delta}$ ($x = 0.1$ – 0.25 mol) is extensively used as a solid oxide fuel cell (SOFC) inter-connecting perovskite material. It offers excellent oxidation, sulfidation, and carburization resistances; stability in terms of dimension, microstructure, chemistry and phase at oxidizing and reducing atmospheres; high thermal conductivity; sufficiently high electrical conductivity ($\sigma_{1000\text{ }^\circ\text{C}} \sim 14$ – 25 S cm^{-1}); high mechanical strength; and a comparable coefficient of thermal expansion (CTE) to the adjacent components [1–4]. The $\text{La}_{1-x}\text{Sr}_x\text{CrO}_{3-\delta}$ arrests the structure: orthorhombic or rhombohedral or both, at room temperature, strongly depending on x and synthesis route [5–14]. It is synthesized by solid-state reaction method [5–7] and wet-chemical methods such as combustion [8,9], polymeric-gel [10–12], and drip-pyrolysis [13,14]. The wet-chemical methods lead to higher inter-dispersion of metal ions and higher reactivity of the amorphous precursor, assuring enhanced purity of the final product together with better control of the powder morphology. In the polymeric-gel method, the salts are mixed with a hydrocarboxylic acid, e.g. acetylacetone, citric acid, etc. for metal complexation and/or a polymer, namely ethylene glycol serving as a solvent as well as esterification agent. It provides a stable metal complex in the solution and preserves atomic scale homogeneity by hindering the ions mobility and segregation [15]. A high level of homogeneity of metal complex is achieved in the

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Characterization of perovskite-type cathode, $\text{La}_{0.75}\text{Sr}_{0.25}\text{Mn}_{0.95-x}\text{Co}_x\text{Ni}_{0.05}\text{O}_{3+\delta}$ ($0.1 \leq x \leq 0.3$), for intermediate-temperature solid oxide fuel cells

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Phase evolution, structure, thermal property, morphology, electrical property and reactivity of a perovskite-type cathode system, $\text{La}_{0.75}\text{Sr}_{0.25}\text{Mn}_{0.95-x}\text{Co}_x\text{Ni}_{0.05}\text{O}_{3+\delta}$ ($0.1 \leq x \leq 0.3$), are reported. The samples are synthesized using metal acetates by the Pechini method. A perovskite-type phase is formed after calcination at $\sim 700^\circ\text{C}$ and a rhombohedral symmetry of $R-3c$ space group is stabilized at $\sim 1100^\circ\text{C}$. An increase in x decreases the unit cell volume linearly, accompanying with a linear decrease in bond lengths and tilt angle. The differential thermal analysis suggests the phase stabilization for a temperature range, $50\text{--}1100^\circ\text{C}$. The thermo-gravimetric, thermal expansion, and electrical and ionic conductivities studies suggest presence of a Jahn–Teller transition at $\sim 260\text{--}290^\circ\text{C}$. The samples with $x = 0.1$ mol exhibit electrical conductivity of $\sim 55\text{ S cm}^{-1}$ at $\sim 600^\circ\text{C}$, activation energy of $\sim 0.13\text{ eV}$, coefficient of thermal expansion of $\sim 12 \times 10^{-6}^\circ\text{C}^{-1}$, crystallite size of $\sim 45\text{ nm}$, Brunauer–Emmett–Teller (BET) surface area of $1.26\text{ m}^2\text{ g}^{-1}$ and average particle size of $\sim 0.9\text{ }\mu\text{m}$. A fairly high ionic conductivity, $5\text{--}9 \times 10^{-2}\text{ S cm}^{-1}$ makes the sample with $x = 0.1$ mole suitable for intermediate-temperature solid oxide fuel cell cathode applications. The experimental results are discussed with the help of the defect models proposed for $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3+\delta}$.

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1. Introduction

Intermediate-temperature solid oxide fuel cells (IT-SOFCs) operating at $600\text{--}800^\circ\text{C}$, are the most efficient way of generating electricity due to internal reforming of hydrocarbon fuels, high quality by-product heat for co-generation, low level of pollutants, high energy conversion efficiency and electrical power of multi-mega Watt. The low temperature operation reduces not only the challenges regarding the materials' compatibility but also the manufacturing cost by using relatively inexpensive metal components for inter-connector, current collector, heat exchanger and structure components. A reduction in unit cell thickness to micro-level also enhances thermal shock resistance and reduces thermal mass, consequently reducing the start up and turn off time of the device [1–3]. It requires a new highly catalytic active cathode in place of the traditionally applied cathode, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3+\delta}$ (LSM, $x = 0.2\text{--}0.3$ mol), which exhibits a low oxygen self-diffusion coefficient (D^*) $\sim 10^{-14}\text{ cm}^2\text{ s}^{-1}$ at 900°C . A number of cathodes, derived from the highly catalytic active Sr^{2+} doped $\text{LaM}'\text{O}_{3-\delta}$ ($M' = \text{Co, Fe or Ni}$), has already been investigated in the past [2]. Some of the cathodes are, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF) [4], $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.9}\text{Ni}_{0.1}\text{O}_3$ (LSCN) [5], $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$

(LSFN) [5], $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.98}\text{Fe}_{0.98}\text{Cu}_{0.02}\text{O}_3$ (LSFCu) [6], $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.6}\text{Ga}_{0.4}\text{O}_3$ (LSCG) [7] and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ (BSCF) [8]. The LSCF exhibited several superior properties, namely high electrical conductivity (σ) $\sim 330\text{ S cm}^{-1}$ at 600°C , high $D^* \sim 10^{-7}\text{ cm}^2\text{ s}^{-1}$ at 800°C , theoretical density (ρ_{th}) $\sim 6.36\text{ g cm}^{-3}$, relative density (ρ) $\sim 89\%$, rhombohedral structure and no reaction with electrolytes [2,4,9]. However, the coefficient of thermal expansion (α) $\sim 15.3 \times 10^{-6}^\circ\text{C}^{-1}$ of LSCF was higher than those of IT-SOFC electrolytes, e.g. scandia-stabilized zirconia (ScSZ), $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (CGO) and $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$ (LSGM) [2]. An attempt was also made to increase the catalytic activity of LSM (Sr^{2+} content = 0.16, 0.4 or 0.5 mol) by doping Fe^{2+} , Co^{2+} or Ni^{2+} (≤ 0.4 mol) in the Mn-site [9–13]. The doping decreased the electrical conductivity of LSM; however, the coefficient of thermal expansion was increased for Co^{2+} -doping, and left invariant for Fe^{2+} - and Ni^{2+} -doping. The doping also largely reduced the interfacial polarization resistance between the doped LSM and an electrolyte, and consequently enhanced the power density [12,13]. Carter et al. [9] noticed that a co-doping of Co^{2+} (0.12 mol) and Ni^{2+} (0.4 mol) is very effective in increasing the catalytic activity of $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$, as the D^* of LSM was enhanced approximately 6 orders of magnitude at 900°C due to formation of additional oxygen vacancies.

In the present paper, an effect of co-doping of Co^{2+} and Ni^{2+} in Mn-site of a commonly used composition of the LSM, $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_{3+\delta}$ is reported for IT-SOFC application via studying the phase evolution, structure, oxygen stoichiometry, thermal expansion,

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Improved electrochemical properties of $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$ cathode for lithium ion batteries with controlled sintering conditions

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Abstract Improved electrochemical properties of $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$ cathode material are reported. Samples were synthesized by the co-precipitation method with various sintering conditions, namely temperature, time and atmosphere. $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$ sintered at 850 °C for 14 h in air exhibited the lowest unit cell volume accompanied with relatively higher values of c/a and I_{103}/I_{104} reflection peaks ratios. This also exhibited superior electrochemical properties, such as high charge–discharge capacity, high Coulombic efficiency, and low irreversible capacity loss. This can be attributed to improved hexagonal ordering, crystallinity and morphology. The electrochemical cell parameters were better than the reported ones, probably due to controlled sintering conditions.

Keywords Lithium nickel cobalt oxide ·
Lithium batteries · Structural properties ·
Electrochemical properties · Sintering conditions

1 Introduction

Lithium-ion batteries are an attractive power source for a wide variety of applications, namely laptops, cellular phones, digital cameras, and electric or hybrid vehicles [1–5]. Lithium cobalt oxide (LiCoO_2) is commercially

applied as a cathode active material in lithium-ion batteries due to its easy preparation, good reversibility and high theoretical specific capacity. However, it has some disadvantages, such as a low effective specific capacity, and high toxicity and cost. It also has safety problems, especially when the lithium content (x) is lower than 0.5 in Li_xCoO_2 or charge voltage exceeds 4.3 V [1–6]. Lithium nickel oxide (LiNiO_2) has also been proposed as a cathode active material because of its layered structure similar to LiCoO_2 , high discharge capacity, low cost and the fact that it is environmentally benign. However, synthesis of stoichiometric LiNiO_2 on a large scale with an ideal layered structure by the conventional solid state reaction method is difficult. It exhibits poor thermal stability in its highly oxidized state ($\text{Ni}^{3+}/\text{Ni}^{4+}$) [3–9]. It also exhibits poor cycling performance due to its structural instability upon cycling [3–6].

Partial doping of Co with 0.2–0.3 mole fraction in Ni-site has been considered as a convenient way to overcome the drawbacks of LiNiO_2 as cobalt stabilizes the layered structure in a two dimensional fashion. This improves the reversibility of the intercalation and the deintercalation [3–6, 10–12]. An enhancement in hexagonal ordering of layers improves the electrochemical properties [3–6]. The ordering of Li-sites also improves the electrochemical properties [3, 6, 11]. The electrochemical properties of the electrode material are also sensitive to the microstructure, which strongly depends on the synthesis conditions [4–6, 12–19]. For example, sintering temperature and time are reported to largely affect the structure of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ and hence the electrochemical properties [15–19].

To the best of our knowledge, no similar study, i.e., effects of sintering temperature, time and atmosphere on structure, microstructure and electrochemical properties,

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Dependence of Processing Parameters on Structural Properties and Microstructures of Pulsed Laser Deposited LiMn_2O_4 Thin Films

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LiMn_2O_4 thin films grown on a Pt/Ti/SiO₂/Si(100) substrate by pulsed laser deposition were studied with focusing on the effects of growth parameters on crystallographic and structural characteristics. The growth parameters, namely oxygen pressure, target–substrate distance, laser energy density, pulse frequency and substrate temperature were established in a sequential manner to obtain smooth, dense and single-phase LiMn_2O_4 films. The smooth, dense LiMn_2O_4 single-phase thin films were found to show the improved cycle performance of cathode of thin film battery. © 2009 The Japan Society of Applied Physics

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1. Introduction

The development of a micro-device, namely ubiquitous sensor network, micro-electromechanical system, interstitial antenna and micro air vehicle (MAV) requires micron sized electronic components having a high volumetric efficiency with compact chip configurations and cost effectiveness. It also needs an inbuilt all-solid-state thin film battery of thickness less than 10 μm as a power source.^{1,2)} The cubic lithium manganate (LiMn_2O_4) spinel has been considered as one of the most prospective cathode materials for thin film batteries.^{2–5)} It reversibly intercalates lithium ions, without altering the MnO_2 framework resulting in fast charging and high discharge capacity. It also exhibits wide cell potential limit, non-toxicity, cost-effectiveness and environmental benignity. The pulsed laser deposition (PLD) technique, which has been proved to produce films of excellent quality with respect to the compositional homogeneity of the source material, has also been used to obtain LiMn_2O_4 in thin film form.^{5–13)} However, no complete optimization of the processing conditions has been performed for obtaining smooth, dense and single-phase LiMn_2O_4 films. The phase purity and morphology of cathode largely affect the electrochemical property of a lithium battery.^{14–16)} The sub-micron size of grains with smooth surface greatly facilitates the lithium diffusion process during the electrochemical intercalation/de-intercalation process.^{6,15,16)} In view of these, it is important to study effects of deposition parameters on the phase, surface morphology and electrochemical property.

In the present paper, effects of numerous deposition parameters, such as oxygen pressure, target–substrate distance, laser energy density, pulse frequency and substrate temperature on the phase and surface morphology of LiMn_2O_4 thin films were investigated using the X-ray diffractometry (XRD) and scanning electron microscopy (SEM).

2. Experimental Methods

The LiMn_2O_4 target was prepared by the conventional solid state reaction method. Commercially-available Aldrich chemicals, Li_2CO_3 (99%) and MnO_2 (99%) in a stoichio-

metric proportion were ball-milled in an anhydrous ethanol medium for 20 h. After drying at 393 K for 24 h, the powder was ground and then calcined at 973 K for 5 h. The calcined powder was ground again and then thoroughly mixed with a few drops of 0.05 wt % solution of poly(vinyl alcohol) (PVA). The mixture was uniaxially pressed at 490 MPa to form a pellet and then sintered at 1473 K for 2 h. The density of target measured by the Archimedes method was $\sim 3500 \text{ kg/m}^3$, $\sim 82\%$ of the theoretical density (4281 kg/m^3).¹⁷⁾

The LiMn_2O_4 film was deposited for 45 min on a Pt/Ti/SiO₂/Si(100) substrate by the PLD method using a KrF excimer laser (wave length, $\lambda = 248 \text{ nm}$ and pulse width, $\tau = 25 \text{ ns}$). The standard conditions used for deposition are as follows: (i) laser power density 4.6 J/cm^2 , (ii) pulse frequency 10 Hz, (iii) target–substrate distance 4 cm, (iv) working (oxygen) pressure 26.7 Pa, and (v) substrate temperature 723 K. For process optimization, the experimental parameters varied from the standard conditions. The base pressure of the chamber for PLD was lower than 10^{-3} Pa . An X-ray diffractometer (Rigaku RINT 2000) was used to record a diffractogram in a range of $10\text{--}65^\circ$ with a step of 0.1° and a scan speed of 1° min^{-1} . An SEM (FEI XL-30 FEG) was used for morphological study of the films. Electrochemical measurements were carried out, using a lab-made half cell unit. Electrolyte was a 1 M solution of LiPF_6 based on a 1 : 1 vol % mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). The counterelectrode was a lithium metal foil. The charge/discharge was performed at a current density of 330 mA/g between 3.0 and 4.5 V.

3. Results and Discussion

Figure 1 shows XRD pattern of the LiMn_2O_4 target sintered at 1473 K for 2 h. The XRD pattern is similar to those reported earlier and exhibits a cubic spinel structure of $Fd3m$ symmetry.^{3–17)} In this structure, the Li occupies the 8a tetrahedral sites, the Mn occupies the octahedral (16d) sites and the oxygen forms a face centered cubic array with 32e sites, while the other octahedral site (16c) is vacant.³⁾ Therefore, the intense reflection peaks are indexed according to the literature.^{4,17)} As the target material has no additional peaks due to impurities, it has been utilized to deposit on Pt/Ti/SiO₂/Si(100) substrate by the PLD method via varying various growth parameters such as oxygen pressure, target–

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Thermal, Micro-Structural, and Electrical Properties of a $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{0.85}\text{Fe}_{0.05}\text{Co}_{0.05}\text{Ni}_{0.05}\text{O}_{3+\delta}$ ($x = 0\text{--}0.4$ Mole) Cathode System

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The oxygen stoichiometry, thermal expansion, morphology, and electrical conductivity of a co-doped perovskite-type cathode system, $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{0.85}\text{Fe}_{0.05}\text{Co}_{0.05}\text{Ni}_{0.05}\text{O}_{3+\delta}$ ($x = 0\text{--}0.4$ mole), are studied for intermediate-temperature solid oxide fuel cell applications. Sr^{2+} -doping led to a decrease in the unit cell volume, oxygen stoichiometry, particle size, and activation energy, and an increase in the coefficient of thermal expansion and electrical conductivity. The sample with $x = 0.3$ mole exhibited four to five fold weight loss with respect to $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_{3+\delta}$ at an intermediate temperature range and suggested the availability of a large number of oxygen vacancies due to a co-doping effect. This sample also showed sufficiently high electrical conductivity ($\sim 76 \text{ S cm}^{-1}$) at 650°C , a low activation energy ($\sim 0.15 \text{ eV}$), and a coefficient of thermal expansion ($\sim 12.1 \times 10^{-6} ^\circ\text{C}^{-1}$) comparable to those of the adjacent components and submicron sized particles. The experimental results are explained using defect models.

Keywords: SOFC, cathode, oxygen stoichiometry, thermal expansion, electrical conductivity

1. INTRODUCTION

Intermediate-temperature solid oxide fuel cells (IT-SOFCs), operational at 600°C to 800°C , have attracted widespread interest in recent years due to several advantageous properties. They offer low production cost, internal reforming of hydrocarbon fuels, high quality by-product heat for co-generation, a low level of pollutants, high energy conversion efficiency, and electrical power of multi-mega Watts. The $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3+\delta}$ ($x = 0.2\text{--}0.3$ mole; abbreviated as LSM) perovskite is utilized, in general, as a cathode material in high temperature SOFCs due to its high electrical conductivity, as well as high mechanical and chemical stability in an oxidizing atmosphere along with a comparable coefficient of thermal expansion to the adjacent components [1–3]. However, it exhibits poor oxygen reduction activity, 2e^- (cathode) + $1/2\text{O}_2$ (air) $\rightarrow \text{O}^{2-}$ (electrolyte), at the triple phase boundary (TPB) in the intermediate temperature region, demonstrated by low values of the oxygen ion transport parameters (oxygen tracer diffusion coefficient of $1.3 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ and ionic conductivity of $5.9 \times 10^{-7} \text{ S cm}^{-1}$) at 900°C [1,4]. In response, the Mn-site of the LSM has been partially doped with Fe^{2+} [5–8], Co^{2+} [7–12], Ni^{2+} [7,13,14], Cu^{2+} [15] and Sc^{3+} [16] in order to

improve the oxygen vacancy concentration and/ or oxygen ion mobility. As a result, the interfacial polarization resistance [7,16], oxygen stoichiometry [5,11,15,17], and activation enthalpy [5,9] were decreased while the oxygen ion transport parameters [1,5,9] of the LSM were enhanced, consequently improving the power density of the SOFCs [7,16]. Doping of Fe^{2+} or Co^{2+} with a concentration of 0.2 mole led to improvement (nearly one to two orders of magnitude) in the oxygen ion transport parameters of the LSM at 700°C to 800°C due to an increase in the oxygen vacancy concentration and/ or oxygen ion mobility [1,5,9]. The co-doping improved the oxygen ion transport parameters by nearly four orders of magnitude due to a manifold increase in the oxygen vacancy concentration and/ or the oxygen ion mobility [1,9,18]. Recently, Gupta *et al.* thoroughly studied the structure of a new perovskite-type co-doped system, $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{0.85}\text{Fe}_{0.05}\text{Co}_{0.05}\text{Ni}_{0.05}\text{O}_{3+\delta}$ ($x = 0\text{--}0.4$ mole; abbreviated as LSMFCN), and compared their findings with results for LSM. Mn-site co-doping with a small fraction (0.05 mole each) of Fe^{2+} , Co^{2+} , and Ni^{2+} was assumed to largely improve the oxygen vacancy concentration and/ or the oxygen ion mobility of the LSM without significantly affecting the structure, the coefficient of thermal expansion, or the micro-structure of the LSM. The LSMFCN exhibited a decrease in the unit cell volume, average bond lengths, tilt angle, and crystallite size with increasing x , similar to those of the LSM [19].

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Effect of strontium ion doping on structural, thermal, morphological and electrical properties of a co-doped lanthanum manganite system

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ABSTRACT

An effect of strontium ion doping on the structural, thermal, morphological and electrical properties of a co-doped lanthanum manganite system, $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{0.85}\text{Fe}_{0.05}\text{Co}_{0.05}\text{Ni}_{0.05}\text{O}_{3+\delta}$ ($x = 0\text{--}0.4$ mole) is investigated for the solid oxide fuel cell cathode application. The submicron and rhombohedral structured sample, synthesized by the Pechini method, exhibited a decrease in the unit cell volume with increasing x . The thermogravimetry study portrayed nearly fivefold weight loss for a sample with $x = 0.3$ mole relative to the $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_{3+\delta}$ and suggested an improvement in the concentration of the oxygen vacancy for ion migration due to the co-doping effect. It also showed sufficiently high electrical conductivity ($\sim 76 \text{ S cm}^{-1}$) at 650°C along with a low activation energy ($\sim 0.15 \text{ eV}$), a comparable coefficient of thermal expansion ($\sim 12.1 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) and a chemical compatibility with the solid electrolytes. The results were explained using the defect models.

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1. Introduction

The problems of energy crises and global warming demand to develop environmentally benign and cost-effective power sources, e.g., intermediate-temperature solid oxide fuel cells (IT-SOFCs) operating at a temperature of $600\text{--}800^\circ\text{C}$. The IT-SOFC offers a low level of pollutants, a low production cost, internal reforming of hydrocarbon fuels, high energy conversion efficiency, high quality by-product heat for co-generation and electrical power of multi-mega Watt. It requires improving the catalytic activity for the reaction 2e^- (cathode) + $(1/2)\text{O}_2$ (air) $\rightarrow \text{O}^{2-}$ (electrolyte) at the interfacial triple phase boundary (TPB) of the conventional perovskite-type cathode material, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3+\delta}$ ($x = 0.2\text{--}0.3$ mole; abbreviated as LSM) [1,2]. The LSM exhibits high electrical conductivity, high mechanical and chemical stability in oxidizing atmosphere, and a comparable coefficient of thermal expansion to the adjacent components; however, with a poor catalytic activity at the intermediate-temperature region [1–3]. It was shown that a partial substitution of Mn^{3+} by a di- or tri-valent ion improves the catalytic activity of the LSM as demonstrated by the oxygen stoichiometry, interfacial polarization resistance, and oxygen ion transport property studies [4–8]. The co-doping with Co^{2+} and Ni^{2+} was noted to be more effective to improve the catalytic activity of the LSM as indicated by nearly four to five orders of the

magnitude enhancement in the oxygen ion transport parameters at the intermediate-temperature range [8,9].

In this paper, an effect of strontium ion doping on the structural, thermal, morphological and electrical properties of a new co-doped lanthanum manganite system, $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{0.85}\text{Fe}_{0.05}\text{Co}_{0.05}\text{Ni}_{0.05}\text{O}_{3+\delta}$ (hereafter referred to as LSMFCN) is reported. The Mn-sites are partially co-doped with a small fraction (0.05 mole each) of Fe^{2+} , Co^{2+} and Ni^{2+} for attaining a large number of oxygen vacancies without significantly affecting the structural, thermal and electrical properties of the LSM [4–12]. The strontium ion content (x) is varied from 0 to 0.4 mole for equalizing the unit cell volume of the LSMFCN with those of the LSM [13,14]. The reactivity study is carried out for the LSMFCN ($x = 0.3$ mole) as the $\text{La}_{0.8}\text{Sr}_{0.2}\text{BO}_{3-\delta}$ ($\text{B} = \text{Co}$ and Ni) portrays a severe reaction with the YSZ [1,2]. The results are explained in the light of the defect models.

2. Experimental

The Pechini method [15] was applied to prepare the LSMFCN. Strontium acetate hydrate (97%), lanthanum (III) acetate hydrate (99.9%), manganese (II) acetate tetrahydrate (99%), iron (II) acetate (95%), cobalt (II) acetate tetrahydrate (99%) and nickel (II) acetate tetrahydrate (99%), all from the Aldrich or Fluka Chemicals (USA), were dissolved in distilled water under stirring in an order to obtain a clear 0.3 M solution (50 ml). Ethylene glycol (99%, Aldrich; an esterification agent) and then citric acid (99.5%, Aldrich; a chelating agent), both with mass equals to the total mass of cations available, were added dropwise under stirring. The continuous stirring of solution at $\sim 80^\circ\text{C}$ led to polymeric resin, which was then dried at $\sim 150^\circ\text{C}$ for 8 h to remove the solvent. The residue was pre-calcined at $\sim 450^\circ\text{C}$ for 30 min to burn out organic components. It was then calcined at $\sim 900^\circ\text{C}$ for 2 h and subsequently at $\sim 1100^\circ\text{C}$ for another 2 h to produce ceramic oxide in powder form.

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Poly(ethylene oxide) : succinonitrile—a polymeric matrix for fast-ion conducting redox-couple solid electrolytes

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Abstract

A blend of poly(ethylene oxide), PEO, and succinonitrile, SN, was investigated for the first time for applying it as a polymeric matrix of low-cost and thermally stable fast-ion conducting redox-couple solid polymer electrolytes. The PEO–SN blend in equal weight fraction showed room temperature ionic conductivity of $1 \times 10^{-8} \text{ S cm}^{-1}$ with nearly two orders of magnitude higher than that of PEO due to reduced crystallinity. The blend resulted in a solid electrolyte with improved ionic conductivity of $\sim 7 \times 10^{-4} \text{ S cm}^{-1}$ at 25°C . The blend and its electrolyte showed thermal stability up to 100°C , which is essential for outdoor application of dye-sensitized solar cells.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Dye-sensitized solar cells have received much attention in recent years as a promising alternative to expensive silicon-based solar cells due to their simple cell structure and low manufacturing cost [1]. Liquid electrolyte-based solar cells, currently achieving the highest energy conversion efficiency (η) of $\sim 11\%$ under irradiation of 100 mW cm^{-2} [2, 3], have several disadvantages. Some of the problems are lack of stability due to leakage/evaporation of organic solvent especially at elevated temperatures ($\sim 80^\circ\text{C}$), need of a hermetic sealing and scale-up of the manufacturing process [4, 5].

In order to replace liquid electrolytes, quasi-solid-state polymer electrolytes, solid polymer electrolytes and molecular crystal-based electrolytes were investigated. Fast-ion conducting quasi-solid-state polymer electrolytes were synthesized by incorporating a large amount of organic liquid solvent/liquid plasticizer/ionic liquids into a polymer matrix, e.g. PEO [4, 5]. Nano-sized clay was also used as an active gelator to achieve high ionic conductivity in the range 10^{-4} – $10^{-3} \text{ S cm}^{-1}$ at room temperature with η of 5–10% [6, 7]. However, these electrolytes possess shortcomings similar to those of the liquid electrolytes. The use of an

ionic liquid also makes the electrolyte relatively expensive. PEO-based solid polymer electrolytes were thermally stable; however, they showed poor ionic conductivity, 2×10^{-6} – $6 \times 10^{-5} \text{ S cm}^{-1}$ at 25°C resulting in η of 0.8–2% [4, 5, 8, 9]. Dispersion of nanoparticles of TiO_2 helped to decrease the PEO crystallinity, resulting in an improved efficiency of 4.2% at 66 mW cm^{-2} [10]. Redox-couple electrolytes prepared using a molecular crystal (succinonitrile), an ionic liquid and iodine showed relatively fast ionic conductivity, 10^{-4} – $10^{-3} \text{ S cm}^{-1}$ at 25°C with iodine ion diffusivity of $\sim 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, and hence η of 5–6.7% [11, 12]. However, low melting temperature (T_m , $\sim 40^\circ\text{C}$) and high-temperature instability limit their use for indoor applications only. Recently, Li^+ -ion conducting polymer electrolyte systems, (PEO–LiX):SN, have shown $\sigma_{25^\circ\text{C}}$ of 10^{-4} – $10^{-3} \text{ S cm}^{-1}$ and relatively better battery characteristics [13, 14].

In this paper, a PEO–SN blend is thoroughly studied for the first time in order to use it as a polymeric matrix for preparing low-cost and thermally stable fast-ion conducting redox-couple solid polymer electrolytes. PEO offers dissociation/complexation of the salt because it has a dielectric constant (ϵ) of 4–8 [15]. It also provides segmental motion of polymeric chain for ion transport [4, 15]. Succinonitrile possesses a high value of dielectric constant (~ 55) and a low value of T_m

Research Article

Highly Conductive Redox-Couple Solid Polymer Electrolyte System: Blend-KI-I₂ for Dye-Sensitized Solar Cells

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Ionic conductivity of a redox-couple solid polymer electrolyte system, (1 - x) blend: $x[0.9\text{KI}:0.1\text{I}_2]$ with $x = 0-0.15$ in weight fraction, is reported. A blend of poly(ethylene oxide) (abbreviated as PEO) and succinonitrile in equal weight fraction was used as a polymeric matrix instead of the PEO and succinonitrile because of its low-cost, electrical conductivity superior to the PEO, and thermal stability better than the succinonitrile. The electrolyte with $x = 0.15$ showed ionic conductivity of $7 \times 10^{-4} \text{ S cm}^{-1}$ and iodine ion diffusivity of nearly $4 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ at 25°C. The conductivity and diffusivity values were nearly two orders of magnitude higher than those of the PEO-KI-I₂ due to the improved PEO crystallinity. It also exhibited dye-sensitized solar cell efficiency of 2.2% at 100 mW cm⁻², which is twice of the cell prepared using the PEO-KI-I₂ only.

1. Introduction

Following the invention of low-cost dye-sensitized solar cells (DSSCs), redox-couple solid polymer electrolytes have attracted considerable attention in recent years [1, 2]. These electrolytes eliminate the shortcomings of the liquid/gel electrolytes, such as leakage/evaporation of organic solvent especially at elevated temperatures, electrode corrosion, a need of hermetic sealing, and scale up of the manufacturing process. The PEO-MI-I₂ (M = Li, Na, or K) electrolyte-based DSSCs exhibited energy conversion efficiency (η) of 0.01–2% under the irradiation of 100 mW cm⁻² [2–6]. It was attributed to low ionic conductivity ($\sigma_{25^\circ\text{C}} \sim 10^{-6}$ – $10^{-5} \text{ S cm}^{-1}$) of electrolytes and poor interfacial contacts between the electrolyte, TiO₂, and dye at nanopores. The blending of PEO with a low molecular weight ether-based polymer improved the ionic conductivity, interfacial contacts, and, thus, the cell performance [3, 6, 7]. Dispersion of inorganic nanofiller into the electrolyte enhanced conductivity via providing the highly conductive space-charge regions and improved cell efficiency via penetration into the TiO₂ nanopores [6, 8].

Recently, DSSCs with succinonitrile-ionic liquid-based electrolytes have showed relatively high efficiency, 5–6.7%

at 25°C due to high ionic conductivity (10^{-4} – $10^{-3} \text{ S cm}^{-1}$), and iodine ion diffusivity ($\sim 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) of electrolytes along with better interfacial contacts [9, 10]. The succinonitrile (abbreviated as SN) acts as a solvent because of its low melting temperature (T_m , $\sim 54^\circ\text{C}$) and high dielectric constant (~ 55). It also provides vacancies for ion transport in its plastic crystal phase between -35°C and 54°C . However, low T_m -value ($\sim 40^\circ\text{C}$) and high-temperature instability of the electrolytes limited the use of the DSSCs for the indoor application only.

In a recent investigation, we showed that a blend of PEO and succinonitrile in equal weight fraction can also be utilized as a polymeric matrix [11]. The blend exhibited $\sigma_{25^\circ\text{C}}$ two orders of magnitude higher than that of the PEO and thermal stability better than the succinonitrile. The PEO offers dissociation/complexation of salt and segmental motion of polymeric chains. The succinonitrile is relatively cheap and provides vacancies for ion conduction. It also acts as organic filler that provides highly conductive free volume for ion transport [11–13]. In the present paper, PEO-SN blend is used as a matrix to synthesize a new low-cost and thermally stable fast ion conducting solid polymer electrolyte system, (1 - x)[PEO-SN] : $x[0.9\text{KI}:0.1\text{I}_2]$, where $0 \leq x \leq 15$



Effect of succinonitrile on electrical, structural, optical, and thermal properties of [poly(ethylene oxide)-succinonitrile]/LiI–I₂ redox-couple solid polymer electrolyte

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ABSTRACT

Effect of succinonitrile on electrical, structural, optical, and thermal properties of [poly(ethylene oxide)-succinonitrile]/LiI–I₂ redox-couple solid polymer electrolyte is reported for the first time. For the poly(ethylene oxide)-succinonitrile blend-based electrolyte electrical conductivity was noted as high as $\sim 3 \times 10^{-4} \text{ S cm}^{-1}$ at 25 °C, which is an order of magnitude higher than that of pure poly(ethylene oxide)-based electrolyte. It also exhibited relatively better pseudo-activation energy ($\sim 0.08 \text{ eV}$). X-ray diffractometry, polarized optical microscopy, and differential scanning calorimetry studies revealed that succinonitrile is helpful in reducing the poly(ethylene oxide) crystallinity due to its plasticizing property. FT-IR study showed significant modification of the poly(ethylene oxide) chain conformation due to the succinonitrile.

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1. Introduction

The energy crises, nuclear power hazards and worldwide pollution problem drive to develop low-cost and efficient renewable energy sources, e.g., dye-sensitized solar cells (DSSCs). Currently, redox-couple liquid electrolyte based-DSSCs exhibit the cell conversion efficiency (η) as high as $\sim 11\%$ [1–3]. The liquid electrolytes possess electrical conductivity (σ) of $10^{-2} \sim 10^{-3} \text{ S cm}^{-1}$ and iodine ion diffusivity of $10^{-5} \sim 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at 25 °C [3]. They also show good interfacial contact between the electrolyte and dye-sensitized TiO₂ nanoparticles at the nano-pores. However, a use of liquid electrolyte reduces long-term stability of DSSCs at the ambient conditions. DSSCs also need hermetic sealing. It also faces scale-up problem of manufacturing. These problems suggest replacement of the liquid electrolytes. The gel electrolytes, ionic liquid electrolytes or quasi-state solid electrolytes are able to provide similar ionic conductivity and iodine ion diffusivity values; however, they possess similar problems. Hence, in order to develop robust, economic, and efficient DSSCs, it is necessary to use a redox-couple solid polymer electrolyte with high electrical conductivity and iodine ion diffusivity. For excellent reviews, see Refs. [3–6].

In general, a redox-couple solid polymer electrolyte comprises of a polymer matrix and a mixture of alkali iodide and elemental iodine [3–6]. Poly(ethylene oxide) commonly abbreviated as PEO is one of the oldest and the most fascinating polymer matrices [3–14]. It offers dissociation/complexation of salt and segmental motion of polymeric chains for the ion transport. Further, it is cheap, eco- and bio-benign, and thermally stable up to 200 °C. Pure PEO-based redox-couple electrolytes resulted in conversion efficiency of 0.01–2% under illumination of 100 mW cm^{-2} [3–11]. It was attributed to poor electrical conductivity in a range of $10^{-6} \sim 10^{-5} \text{ S cm}^{-1}$ of electrolytes due to high PEO crystallinity. In addition, the scanning electron microscopy and atomic force microscopy revealed poor interfacial contact between the electrolyte and dye-sensitized TiO₂ at the nano-pores due to large coil size of the polymer chain [8–11].

In the past, strategies such as blending [8–13], copolymerization [5], and dispersion [9,10,13,14] were employed to improve the electrical conductivity and interfacial contact, and thus the cell performance. The blending of PEO with low molecular weight ether-based polymer such as poly(propylene glycol) [8], poly(ethylene glycol) dimethyl ether [9], poly(ether urethane) [10], and poly(ethylene glycol) (abbreviated as PEG) [11,12], poly(vinylidene fluoride) [13], and ionic liquid [11,12] resulted in free-volume across PEO chains and a reduction of PEO crystallinity as well as easy penetration into the TiO₂ nano-pores due to its low coil size. Copolymerization worked in a similar fashion and improved the cell efficiency [5]. Dispersion of inorganic nano-filler

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Improved performance of silicon-nanoparticle film-coated dye-sensitized solar cells

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Silicon (Si) nanoparticles with average size of 13 nm and orange–red luminescence under UV absorption were synthesized using electrochemical etching of silicon wafers. A film of Si nanoparticles with thickness of 0.75 μm to 2.6 μm was coated on the glass (TiO_2 side) of a dye-sensitized solar cell (DSSC). The cell exhibited nearly 9% enhancement in power

conversion efficiency (η) at film thickness of $\sim 2.4 \mu\text{m}$ under solar irradiation of 100 mW/cm^2 (AM 1.5) with improved fill factor and short-circuit current density. This study revealed for the first time that the Si-nanoparticle film converting UV into visible light and helping in homogeneous irradiation, can be utilized for improving the efficiency of the DSSCs.

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1 Introduction Renewable energy sources, e.g., solar cells, are promising for the solution of energy crises, nuclear power hazards, global warming and pollution problems [1]. Si-based solar cells exhibit η as high as 25% (crystalline), 20.4% (multicrystalline), 19.1 (thin film transfer), 10.1% (amorphous), and 10.5% (thin film sub module), and 27.6% (crystalline with solar concentrators) [2]. Nanocoax design was proposed to improve the mean free paths of electrons in the amorphous Si-based solar cells and thus the efficiency [3]. Stupca et al. [4] coated an ultrathin film of luminescent Si nanoparticles on the top of the polycrystalline silicon solar cell. They observed expansion of the spectral region via ultraviolet (UV) conversion into visible region, which resulted in power performance improvement of 60% in the UV–blue range and nearly 10% in the visible region for the red particles with size of nearly 2.85 nm. They also noted that the larger particles respond more strongly in the visible region. This finding motivated us to use the luminescent property of Si nanoparticles for improving η of DSSCs. Silicon is eco- and bio-benign, abundant, and the backbone of electronics and solar cell industry [1]. Whereas, phosphors, e.g. II–IV semiconductors possessing photoluminescence quantum effi-

ciency greater than 90%, exhibit toxicity due to the group-II element and a relatively high synthesis cost [5].

DSSC is considered as one of the most attractive third generation power sources [6]. A DSSC offers simple cell fabrication and low manufacturing cost, and recently achieved power efficiency of 12.3% at the laboratory scale [7]. Uchida et al. [8] recently showed that a mixture of Si nanoparticles and N719 dye can also be utilized as a sensitizer to improve the short-circuit current density and, hence, the cell efficiency. They observed an improvement in the incident photon-to-current conversion efficiency (IPCE). However, they noticed a nearly 9% decrease of the fill factor and degradation of Si nanoparticles in electrolyte solution.

In the present communication, we fabricated Si-nanoparticle film-coated DSSCs for the first time and studied the effect of film thickness on the cell performance parameters, such as short-circuit current density, open-circuit voltage, fill factor, and power efficiency for optimization. The Si-nanoparticle film was utilized in order to convert UV into visible light and thus to increase the spectral region. The film was also expected to play a crucial role in the homogeneous distribution of light flux on the cell [4].

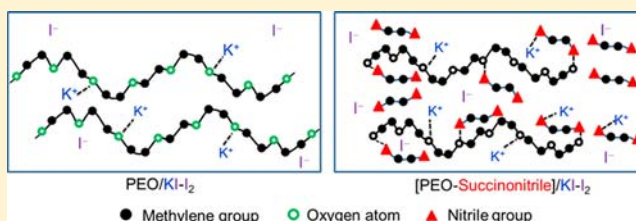
Plasticizing Effect of K^+ Ions and Succinonitrile on Electrical Conductivity of [Poly(ethylene oxide)–Succinonitrile]/KI– I_2 Redox-Couple Solid Polymer Electrolyte

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ABSTRACT: The plasticizing effect of the K^+ ions and succinonitrile on the electrical conductivity of a new redox-couple solid polymer electrolyte system, $(1 - x)[0.5\text{poly}(\text{ethylene oxide}):0.5\text{succinonitrile}]:x[0.9\text{KI}:0.1\text{I}_2]$ with $x = 0$ – 0.2 in weight fraction, is reported. An increase of x resulted in an increase of the electrical conductivity ($\sigma_{25^\circ\text{C}}$) of the electrolyte. The electrolyte with $x = 0.15$ exhibited the highest $\sigma_{25^\circ\text{C}}$ value, $\sim 7 \times 10^{-4} \text{ S cm}^{-1}$, and is referred to as the optimum conducting composition (OCC). In addition to an increase of the mobile ion concentration with increasing x , X-ray diffractometry, Fourier-transform infrared spectroscopy, polarized optical microscopy, UV–vis spectroscopy, and differential scanning calorimetry studies revealed a decrease of poly(ethylene oxide) crystallinity/an increase of ionic mobility, indicating the plasticizing effect of the K^+ ions. Plasticizing and molecular diffusing properties of the succinonitrile further helped to improve the electrical conductivity of the electrolyte.



INTRODUCTION

Following the problems of global warming, energy crises, and nuclear hazards, the area of low-cost dye-sensitized solar cells (DSSCs) has been investigated worldwide as an alternative to expensive silicon-based solar cells.¹ At present, a liquid electrolyte-based DSSC exhibits an energy conversion efficiency (η) as high as 11.9% under solar irradiation of 100 mW cm^{-2} .² Use of liquid electrolyte may create problems, such as leakage/evaporation of organic solvent at ambient conditions, electrode corrosion, a need for hermetic sealing, and scale up of the manufacturing process. This shows a requirement for solid polymer electrolytes in order to develop robust, economical, and efficient DSSCs operating at 60 – 80°C .^{3–5}

High molecular weight poly(ethylene oxide), acronym PEO, is one of the most utilized polymeric matrices of solid polymer electrolytes.^{6–8} It offers properties such as self-standing film forming, thermal stability up to 200°C , eco- and biobeneign, relatively low material cost, dissociation/complexation of salt, and segmental motion of polymeric chains for ion transport through ethereal oxygen. PEO/MI– I_2 (M = alkali ion) redox-couple solid electrolytes exhibited $\sigma_{25^\circ\text{C}}$ in a range of 10^{-6} – $10^{-5} \text{ S cm}^{-1}$ due to high PEO crystallinity.^{3–5,9–15} Moreover, scanning electron microscopy and atomic force microscopy revealed poor interfacial contact between the electrolyte and dye-sensitized TiO_2 at nanopores due to a large coil size of PEO resulting in η of 0.01 – 1.8% under solar irradiation of 100 mW cm^{-2} .^{9,12,13,15} Kang et al.¹⁶ observed a limiting value, e.g., $\sigma_{25^\circ\text{C}} \geq 10^{-4} \text{ S cm}^{-1}$ and PEO molecular weight $\leq 2000 \text{ g mol}^{-1}$ (coil size $\approx 2.82 \text{ nm}$) for the DSSC application.

Use of ether-based plasticizer, e.g., poly(propylene glycol),⁹ poly(ethylene glycol),^{14,17} poly(ether urethane),¹⁵ and poly-

(ethylene glycol) dimethyl ether,¹⁶ largely improved the electrical conductivity of the PEO/MI– I_2 electrolytes via decreasing the PEO crystallinity. It also resulted in significantly improved interfacial contact at nanopores and thus cell efficiency. Several other methodologies, such as blending with poly(vinylidene fluoride),^{18,19} plasticization using ionic liquid,^{11–14} copolymerization,⁴ dispersion of an inorganic nanofiller,²⁰ and mixing of cations of different ionic radii,²¹ worked in a similar fashion and improved cell efficiency. Vittadello et al.²² showed that alkali iodide can be replaced by an alkaline earth metal iodide (e.g., MgI_2), where species like Mg^{2+} , $[\text{MgI}]^+$, and MgI_2 participate in the conduction process.

Succinonitrile, a plastic crystal between -35°C (crystal to plastic crystal phase transition temperature, T_{pc}) and 54°C (melting temperature, T_{m}), has had immense widespread interest in recent years.^{23–29} It exhibits various interesting features, such as low molecular weight, low T_{m} value, waxy nature, economically cheap, high molecular diffusivity via trans–gauche isomerization (involving rotation about the central C–C bond) of the molecules and molecular jumps from one diagonal position of the cubic structure to another, high dielectric constant (~ 55 at 25°C), and plasticizing property. These features yielded electrolytes with high ionic conductivity (10^{-4} – $10^{-3} \text{ S cm}^{-1}$) and high iodine ion diffusivity ($\sim 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) at 25°C .^{28,29} However, the low T_{m} value ($\sim 40^\circ\text{C}$) and high-temperature instability of the electrolyte limits its utility for robust DSSCs.

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Improved cell efficiency of [poly(ethylene oxide)-succinonitrile]/LiI-I₂ solid polymer electrolyte-based dye-sensitized solar cell

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The effect of succinonitrile on cell efficiency, interfacial resistance, and dye regeneration time of [0.5 poly(ethylene oxide):0.5 succinonitrile] blend/LiI-I₂ solid polymer electrolyte is reported for the first time. The addition of succinonitrile increased the electrical conductivity of poly(ethylene oxide)/LiI-I₂ by more than an order in magnitude to $\sim 3 \times 10^{-4} \text{ S cm}^{-1}$

due to the plasticizing and molecular diffusing properties of succinonitrile. This resulted in an enhancement of the cell efficiency from 0.5% to 2%. The electrochemical impedance spectroscopy revealed a large decrease of interfacial resistances. The transient absorption spectroscopy showed an improvement of the dye regeneration time from 15 to 5 μs .

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1 Introduction The renewable energy sources especially the low-cost and simple cell structured dye-sensitized solar cells (DSSCs) have been considered one of the best alternatives to the conventional power sources [1]. The highest power conversion efficiency (η) $\sim 11\%$ at a solar irradiance of 100 mW cm^{-2} , was reported for the liquid electrolyte-based DSSCs [2]. The liquid electrolytes offer high electrical conductivity ($\sigma_{25^\circ\text{C}}$) of 10^{-2} to $10^{-3} \text{ S cm}^{-1}$, excellent interfacial contact between dye-sensitized TiO₂ and the electrolyte at the TiO₂ nanopores, and the fast dye regeneration time of nearly $1 \mu\text{s}$ [1]. However, liquid electrolyte-based devices are prone to leakage/evaporation of the organic solvent under ambient conditions and electrode corrosion. These devices also require hermetic sealing and show scaling up problem of the manufacturing process. DSSCs based on the highly conductive electrolytes in the form of gel (quasisolid) or ionic liquid exhibit problems similar to those observed for the liquid electrolyte-based ones [1, 3]. These issues demonstrate the need for a highly conductive solid polymer electrolyte to develop robust, economical, and efficient DSSCs operating at $60\text{--}85^\circ\text{C}$.

The solid polymer electrolytes having a form of polymer matrix/MI-I₂ (M, alkali ion) exhibited $\eta \sim 0.1\text{--}4\%$ at a solar irradiation of 100 mW cm^{-2} [3]. The poly(ethylene oxide)

abbreviated as PEO has been widely used as a matrix [3]. The PEO offers self-standing film formation, thermal stability up to 200°C , eco- and biofriendliness, low material cost, the dissociation/complexation of salt, and ion transport through ethereal oxygen. However, PEO/MI-I₂ electrolytes showed poor $\sigma_{25^\circ\text{C}}$ and η values, and very high values of interfacial resistances due to high PEO crystallinity [3]. The PEO crystallinity was reduced via (i) blending with a low molecular polymer, e.g., poly(propylene glycol), poly(ethylene glycol), poly(ethylene glycol) dimethyl ether, and poly(ether urethane), (ii) copolymerization with epichlorohydrin, and (iii) plasticization with an ionic liquid, poly(vinylidene fluoride)], or an inorganic nanofiller.

Recently, Gupta et al. [4] studied a $(1-x)\text{PEO}:x$ succinonitrile blend system, where $x = 0\text{--}0.75$ in weight fraction. They noted that the blend with $x = 0.5$ results in low PEO crystallinity, high electrical conductivity, and improved thermal property relative to the succinonitrile. The succinonitrile, hereafter denoted as SCN is a low molecular weight, low melting temperature, waxy, and high dielectric constant plastic crystal [5]. It offers high molecular diffusivity and plasticizing properties [5–7]. An addition of MI-I₂ salt mixture into the $[0.5\text{PEO}:0.5\text{SCN}]$ blend resulted in superior electrolyte properties, e.g., $\sigma_{25^\circ\text{C}}$ of

A comparative study of Ru(II) cyclometallated complexes *versus* thiocyanated heteroleptic complexes: thermodynamic force for efficient dye regeneration in dye-sensitized solar cells and how low could it be?[†]

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Four novel Ru(II) bipyridyl complexes **MH12–15** were synthesized and characterized for dye-sensitized solar cells (DSSCs). Their photovoltaic performance including incident photon-to-current conversion efficiency (IPCE), total solar-to-power conversion efficiency ($\eta\%$) and ground and excited state oxidation potentials and photoelectrochemical properties were evaluated on mesoporous nanocrystalline TiO₂ and compared with the benchmark **N719**-dye under the same experimental conditions. **MH12–15** showed stronger MLCT with significantly higher molar extinction coefficient for the lower energy absorption bands at 553 nm (27 500 M⁻¹ cm⁻¹), 554 nm (34 605 M⁻¹ cm⁻¹), 577 nm (23 300 M⁻¹ cm⁻¹), and 582 nm (39 000 M⁻¹ cm⁻¹), respectively, than that of **N719** (14 200 M⁻¹ cm⁻¹). The introduction of a cyclometallated ligand in dyes **MH14** and **15** improved the optical properties and red-shifts of 24 nm and 28 nm, respectively, compared to the non-cyclometallated analogs **MH12** and **13**. The red shift in the UV-Vis spectra of **MH14** and **15** can be attributed to the destabilization of the HOMO t_{2g} of Ru(II). However, the destabilization of the HOMO furnished an upward shift of the ground state oxidation potentials (GSOPs) of **MH14** and **15** at -5.44 eV and -5.36 eV against *vacuum*, respectively, which resulted in a driving force of only 0.22 and 0.16 eV for regeneration of dyes **MH14** and **15**, respectively. In the case of NCS analogs, **MH12** and **13**, the GSOPs, however, were -5.56 and -5.51 eV, respectively, which produced a driving force of more than 0.25 eV for dye regeneration. The nanosecond transient absorbance measurements showed that the time needed for the oxidized forms of **MH12–MH15** to regenerate the neutral dye is 6 μ s, 4 μ s, 13 μ s and 18 μ s, respectively, compared to **N719** (2.3 μ s). These kinetic data confirmed that the weak thermodynamic force, small negative free energy ($-\Delta G$), for regeneration of **MH14** and **15** neutral dyes makes the dye regeneration process kinetically sluggish, which contributed significantly to the loss of both photocurrent and photovoltage. This study clearly elucidated that although cyclometallation may produce significantly better light harvesting, the driving force of less than 0.25 eV is not sufficiently enough for effective dye regeneration.

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1. Introduction

The use of photovoltaic devices has increased in popularity as an alternative method to generate electricity from the sunlight. These devices function by converting solar photons into useful

electrons through photoelectrochemical processes and ultimately produce photocurrent. Currently, the majority of photovoltaic cells are based on silicon because of their suitable physical and chemical properties. However, the main issue with these cells is the expensive processing cost to produce the pure silicon needed for optimum solar cell efficiency. Due to the high cost of production, silicon cells are limited in their ability to compete with fossil fuels and the emerging new PV technologies. Dye-sensitized solar cells (DSSCs) are considered as potential alternatives to traditional silicon solar cells because of their cost-effective solar-to-power conversion efficiency.^{1,2} So far the best performances in terms of solar-to-power conversion efficiency are shown by Ru(II) polypyridyl sensitizers^{3,4} attributed to their strong metal-to-ligand charge

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More stable and more efficient alternatives of Z-907: carbazole-based amphiphilic Ru(II) sensitizers for dye-sensitized solar cells†

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Here we report two novel amphiphilic Ru(II) heteroleptic bipyridyl complexes, HD-14 and HD-15, compared to previously reported NCSU-10. We have combined the strong electron donor characteristics of carbazole and the hydrophobic nature of different long alkyl chains, C7, C18 and C2 (NCSU-10), tethered to *N*-carbazole to study their influence on photocurrent, photovoltage and long term stability for dye-sensitized solar cells. Photon harvesting efficiency and electron donating characteristics of carbazole-based ancillary ligands were found to be unaffected by different alkyl chain lengths. However, a slight drop in the V_{oc} of HD-14 and HD-15 was observed compared to that of NCSU-10. It was found by nanosecond flash photolysis transient absorption (TA) measurements that the faster the dye regeneration the higher the photocurrent density response, and the dye regeneration time was found to be 2.6, 3.6, and 3.7 μ s for HD-14, HD-15, and N719 dyes, respectively. The difference in the amplitude of the transient absorption (TA) signal of the oxidized dye as measured by femtosecond TA studies is in excellent agreement with the photocurrent generated, which was in the following order HD-14 > HD-15 > N719. Under 1000 h light soaking conditions, HD-15 maintained up to 98% (only 2% loss) of the initial power conversion efficiency compared to 8% loss for HD-14 and 22% loss in the power conversion efficiency for NCSU-10. HD-15 was strikingly stable to light soaking conditions when employed in the presence of an ionic liquid electrolyte, which paves the way for widespread applications of dye-sensitized solar cells with long term stability. The total power conversion efficiency (η) was 9.27% for HD-14 and 9.17% for HD-15 compared to 8.92% for N719.

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1. Introduction

It is unfortunate that to date, most of the current energy demands are met by fossil fuels. To realize the dream of a low carbon society, and ensure the widespread application of renewable energy sources such as solar energy, photovoltaic devices should be highly efficient, cheap and stable for a long time. Solar energy has been recognized as one of the cleanest, most reliable and abundantly available renewable energy sources on the planet Earth.¹ Compared to silicon-based single layer p-n junction photovoltaic devices, dye-sensitized solar cells (DSCs) are promising candidates for

an alternative form of solar cells owing to their unique features of being flexible and efficient under year around conditions.^{2–5} Since the breakthrough report by O'Regan and Grätzel,⁶ immense research has been carried out to better understand, and improve the fundamental science of this technology. As a result, DSCs with efficiency as high as 13% (η)⁷ were achieved by a Zn-porphyrin complex. Additionally, perovskite-sensitized solid state dye solar cells have reached a record high efficiency of 15.9%,⁸ and efficiencies of 17.9% (ref. 9) and 19.3% (ref. 10) were reported recently. However, perovskite solar cells contain Pb and are far behind in long term stability compared to DSCs.¹⁰

Owing to the unique nature of DSCs where electron injection, charge transport, and hole carrier are achieved by different components, achieving higher efficiency is dependent on the optimization of the components of the device including a dye (sensitizer), TiO_2 and an electrolyte. A sensitizer is one of the most critical components within a DSC; it determines not only the light harvesting efficiency, but also mediates the interaction between the redox shuttle and TiO_2 .^{11,12} Thus the chemical nature of the sensitizer not only determines the operational efficiency of DSCs but also sets the standards for long term stability as reported for

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Neutral and anionic tetrazole-based ligands in designing novel ruthenium dyes for dye-sensitized solar cells

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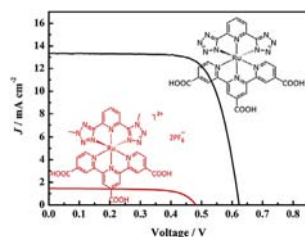
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HIGHLIGHTS

- Novel anionic and neutral tetrazolate ligands based Ru(II) dyes were designed.
- It is the 1st time to study the effect of different charges on the tetrazole unit.
- Ru dye with anionic tetrazolate ligand showed significantly better DSSC property.
- The highest efficiency (6.1%) is reported for Ru dyes with tetrazolate ligand.

GRAPHICAL ABSTRACT



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ABSTRACT

Two novel thiocyanate-free Ru(II) complexes have been synthesized, characterized and evaluated as dyes for dye-sensitized solar cells. Both complexes have two tridentate ligands: one is the tricarboxyterpyridine as an anchoring ligand and the other is one of the two bis(tetrazolyl)pyridine derivatives. One of the bis(tetrazolyl)pyridine ligand coordinates to the Ru(II) ion as a doubly deprotonated tetrazolate anion with a formal charge of -2 to form a neutral complex, which is coded as BTP dye, while the other bis(methyltetrazolyl)pyridine ligand coordinates to the Ru(II) ion as a neutral ligand forming a divalent cationic complex, coded as BMTP dye. Unexpectedly, the oxidation potentials for these two compounds are similar, implying similar electron-donating effects of the anionic tetrazolate ligand and the neutral methyltetrazole ligand to the Ru(II) ion. Despite similar HOMO/LUMO levels, BTP dye performs much better, recording 6.10% efficiency, than BMTP dye for DSSCs. Electrochemical impedance spectroscopy as well as nanosecond transient absorption spectroscopy indicates that the differences in the electron injection and electron recombination processes, which may be the consequences of the difference in the localization of LUMO as suggested by DFT calculations, are the main causes for the differences in performance.

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Study of Donor–Acceptor– π –Acceptor Architecture Sensitizers with Benzothiazole Acceptor for Dye-Sensitized Solar Cells

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Dedicated to Dr. Swaminathan Sivaram, CSIR-Bhatnagar Fellow, on the occasion of his 70th birthday

A new additional benzothiazole (BT) acceptor has been introduced into metal-free organic dyes (**MCG1–MCG4**) to construct donor–acceptor– π –acceptor (D–A– π –A) architecture with the systematic replacement of diheteroanthracene donors and heteroaromatic π -bridge components. BT not only facilitates effective electron transfer from the donor to the anchoring group, but also lowers the band gap. The planarity of the sensitizers induces J aggregation on TiO₂, causes the redshift on TiO₂, and enhances the light-harvest-

ing efficiency up to $\lambda=750\text{--}800\text{ nm}$. Transient absorption spectroscopy and electrochemical impedance spectroscopy have been used to understand the trends in short-circuit current (J_{sc}) and open-circuit voltage (V_{oc}). Dye **MCG4** showed a superior efficiency of 6.46 %. DFT has been complemented with experimentally determined photoelectrochemical properties. These molecules are new and support π -bridge extension with BT for better performance of D–A– π –A organic sensitizers.

Introduction

Since early reports by Grätzel and co-workers and others,^[1–5] dye-sensitized solar cells (DSSCs) have attracted great attention among all solar energy harnessing devices because of their low cost; high efficiency; facile fabrication; and attractive, unique features. Sensitizers are one of the critical components in DSSCs that can be easily designed and modified to significantly influence the power conversion efficiency (PCE) of the device. Zinc porphyrin based sensitizers, in combination with the cobalt bipyridine ([Co(bpy)₃]^{2+/3+}) redox couple, proved to be highly efficient to yield a PCE of 13 %.^[6–8] Recently, organic–inorganic hybrid perovskite sensitizers (MAPbI₃, in which MA = methylammonium or other derivatives) have shown a maximum of 20.1 % efficiency in solid-state devices.^[9–12] However, these devices are associated with several health hazards that may undermine their large-scale applications due to the presence of the poisonous element lead. This dilemma encourages scientists to continuously improve on traditional DSSCs.

Ruthenium-based DSSCs have achieved remarkable PCEs of more than 11 %.^[13–15] However, the large-scale application of ruthenium dyes is limited due to their complicated synthetic routes, higher production costs, and non-eco-friendly concerns. To overcome the prohibitive issues of ruthenium complexes, metal-free organic dyes have been investigated as alternative sensitizers owing to their high molar absorption coefficients, ease of synthesis, low cost, and easy structural modifications.^[16] One of the most important features of these organic dyes is their D– π –A structure, which has been explored to improve the absorption properties, adjust the

HOMO and LUMO levels, and to realize intramolecular charge separation. Our group has been engaged in the synthesis of several ruthenium complexes^[17–19] and organic molecules as sensitizers in DSSC applications, particularly metal-free organic molecules. Recently, we achieved a certified record efficiency by using the coadsorbant Y1 with N749 dye.^[20] Additionally, we have tried to engineer molecules based on carbazole–phenothiazine dyes^[21,22] with A– π –D– π –A^[23] or π –D–A^[24] architectures. To extend the harvesting power of the sensitizer, the D–A– π –A backbone proves to be a promising architecture. The additional acceptor incorporat-

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Near-infrared squaraine co-sensitizer for high-efficiency dye-sensitized solar cells

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A combination of squaraine-based dyes (SPSQ1 and SPSQ2) and a ruthenium-based dye (N3) were chosen as co-sensitizers to construct efficient dye-sensitized solar cells. The co-sensitization of squaraine dyes with N3 enhanced their light-harvesting properties as a result of the broad spectral coverage in the region 350–800 nm. The co-sensitized solar cells based on SPSQ2 + N3 showed the highest short circuit current density of 17.10 mA cm⁻², an open circuit voltage of 0.66 V and a fill factor of 0.73, resulting in the highest power conversion efficiency of 8.2%, which is higher than that of the dye-sensitized solar cells based on the individual SPSQ1 and SPSQ2 dyes. The high power conversion efficiency of SPSQ2 + N3 was ascribed to its good light-harvesting properties, which resulted from its broader incident photon current conversion spectrum than that of the individual dyes. The high electron life time and electron recombination, which were the main causes of the higher efficiency of the device, were successfully analysed and correlated using transient absorption spectrometry and intensity-modulated photovoltage spectrometry.

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Introduction

Dye-sensitized solar cells (DSSCs) are promising sources of renewable energy as a result of their relatively high performance and inexpensive production costs, uncomplicated molecular tuning, intense absorption wavelengths and ease of fabrication in various colours.¹ For more than two decades ruthenium-based dyes were the only candidates for DSSCs as a result of their strong metal to ligand charge transfer transition and power conversion efficiency (PCE) >11%.² However, ruthenium-based dyes have a number of disadvantages, such as the absence of absorption in the near-IR region (NIR), low molar extinction coefficients and high-cost, tedious purification methods.^{1,2} In this context, porphyrins,³ phthalocyanines⁴ and many metal-free organic dyes such as indoline,⁵ triarylamine,⁶ dithieno-fused heterocycles⁷ and squaraine dyes⁸ have been developed to harness photons in the NIR region. However, it is difficult to synthesize organic dyes covering a broad absorption range over the whole UV-visible–NIR region. The use of a photo anode (TiO₂ electrode) in a solution containing two or more dyes with complementary absorption is referred to as co-sensitization and has been shown

to be a more promising way to obtain a broad spectral response over the UV-visible–NIR region for use in DSSCs.^{9,10}

In principle, co-sensitization requires the complementary absorption of two or more dyes and a good understanding of the molecular orientation, size and shape of the dyes. Grätzel and co-workers¹¹ showed that the co-sensitization of metal-containing dyes and metal-free dyes of different molecular sizes allowed a better surface coverage, yielding a high short circuit current density (J_{SC}) and open circuit voltage (V_{OC}) and resulting in a high PCE. Zhu and co-workers¹² also tested this model using two different organic dyes with different molecular sizes and achieved a high PCE of 10.4%. Pauporté and co-workers¹³ used indoline-based organic dyes for co-sensitization and improved the PCE as a result of the enhancement of the light-harvesting properties of the co-sensitized solar cell.¹³ Porphyrin dyes or ruthenium-based dyes used as co-sensitizers with complementary absorbing small molecules showed the highest the PCE of 10–13%, which was attributed to the broad incident photon-to-current conversion efficiency (IPCE) and produced a high J_{SC} and high PCE.^{3,9,10}

Squaraine dyes have attracted much attention as a result of the simple synthetic protocols for symmetrical and asymmetrical squaraine dyes.¹⁴ Squaraine dyes are promising NIR co-sensitizers as a result of their high molar extinction coefficients and absorption at longer wavelengths, which produces broad IPCE conversion, leading to a high PCE.¹⁵ Grätzel *et al.* reported a stepwise co-sensitization procedure based on a squaraine dye (SQ1) with JK-2 and improved the PCE from 4.2 to 7.4% for DSSCs based on liquid electrolytes and from 3.8 to 6.4% for DSSCs based on ionic liquid electrolytes.¹⁶

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Thiocyanate-free asymmetric ruthenium(II) dye sensitizers containing azole chromophores with near-IR light-harvesting capacity

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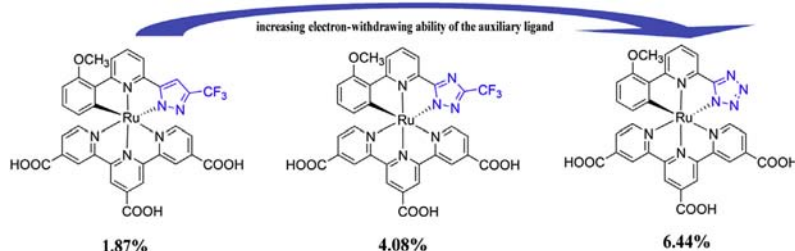
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HIGHLIGHTS

- Three novel thiocyanate-free Ru complexes with a Ru—C bond were designed.
- Three dyes exhibited similar panchromatic absorption features.
- All the dyes exhibited the IPCE boundary to a near-IR region (~1000 nm).
- The more electron withdrawing the auxiliary ligand is, the better the performance.
- TEZ dye showed a good light soaking stability for 1000 h.

GRAPHICAL ABSTRACT



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ABSTRACT

A new series of thiocyanate-free bis-tridentate Ru(II) complexes containing azole ligands as well as an organometallic Ru—C bond are synthesized, characterized, and evaluated in dye-sensitized solar cells (DSSCs). CF₃-substituted pyrazolyl, CF₃-substituted triazolyl, and tetrazolyl derivatives are employed as ligands in the three neutral complexes PYZ, TRZ, and TEZ dyes, respectively. Despite their different structures, all the three complexes exhibit similar absorption features and panchromatic absorption covering the visible and near-IR regions. By switching from a pyrazolyl via triazolyl to tetrazolyl moiety in the ligand, the photocurrent value, open-circuit voltage, and overall efficiency are increased accordingly under the same conditions. Among them, photon-to-current conversion efficiency (η) of TEZ dye reaches the maximum of 6.44% with a short-circuit photocurrent density (J_{sc}) of 17.8 mA cm⁻², an open-circuit photovoltage (V_{oc}) of 0.54 V and fill factor (FF) of 0.67 under illumination of an AM1.5G solar simulator. TEZ dye shows a good long term light soaking stability and maintains up to more than 90% of the initial power conversion efficiency after 1000 h.

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1. Introduction

The third-generation photovoltaics, namely dye-sensitized solar cells (DSSCs), represents one of the most promising alternatives owing to the low cost and high efficiency [1,2]. Besides the

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Stable and charge recombination minimized π -extended thioalkyl substituted tetrathiafulvalene dye-sensitized solar cells†

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Two new metal-free organic sensitizers have been designed based on tetrathiafulvalene scaffolds by implementing a donor- π -acceptor (D- π -A) approach in which thioalkyl substituted tetrathiafulvalene acts as a donor, substituted anthracene as a π -spacer and cyanoacrylic acid acts as an acceptor as well as an anchoring group. Spectroscopic, electrochemical and DFT studies confirmed the molecular integrity of both sensitizers. The onset of absorption of both sensitizers extends up to 600 nm in solution and up to 700 nm on nanocrystalline TiO₂. DFT studies specified that the HOMO is delocalized over the anthracene as well as the dithiole units, and the LUMO is delocalized over the anchoring group in both sensitizers. The new sensitizers have shown an improved efficiency of 7.15% in dye-sensitized solar cells using an I⁻/I₃⁻ redox couple. The enhanced efficiency might be due to the thioalkyl group wrapping over the anthracene π -spacer to prevent the recombination of electrons in the TiO₂ conduction band. Recombination studies indicate the regeneration of the oxidized dye due to the redox couple.

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Introduction

Dye-sensitized solar cells (DSSCs) have attracted interest for nearly two and half decades due to their low cost, easy fabrication and low environmental impact compared to conventional silicon photovoltaics.^{1–6} The chemical nature and structure of a sensitizer play a crucial role in the development of high efficiency DSSCs. Since their first report in the 1990s, polypyridyl ruthenium(II) complexes have been the most commonly used sensitizers, leading to excellent photovoltaic performance, particularly with a high efficiency of over 11%.^{7–9} However, ruthenium(II) complexes are very expensive due to the rarity of the metal in the Earth's crust, intricate synthetic steps and purification methods, and are less durable due to the presence of -NCS groups in their molecular structure.¹⁰ Metal-free organic dyes, however, have attracted significant attention as promising alternatives by virtue of their large diversity in molecular structure, that can tune absorption

and HOMO-LUMO properties *etc.*, in a desired manner through suitable molecular design strategies.^{11,12} The most efficient organic sensitizers are composed of a donor (D) and an acceptor (A) linked through a π -bridge, whereby an effective intramolecular charge transfer can occur leading to the appearance of a broad and intense absorption band in the visible region. Among D- π -A sensitizers, a variety of organic donors including triphenylamine, phenothiazine, carbazole, porphyrin and indoline have been explored.^{13–16} To date, the best DSSC based on organic sensitizers showed an efficiency of *ca.* 10%.¹⁷

Because of the strong π -donor property of the tetrathiafulvalene scaffold, it has been widely used in materials chemistry and is predominantly used for optoelectronic applications.^{18,19} Essentially, TTF-based D- π -A systems have found numerous potential applications as their electrochemical and optical properties can be finely tuned by molecular engineering.^{20,21} In spite of this, only few examples were reported in the literature on extended π -conjugated tetrathiafulvalene (exTTF) based sensitizers for DSSCs.^{22–24} As the first example, exTTF-sensitized solar cells showed a moderate efficiency up to 3.8%.²² The low efficiency of these exTTF based sensitizers is probably due to the fact that they absorb only in the UV region and have an energetically high-lying HOMO, and therefore dye-regeneration after electron-injection is thermodynamically unfavourable. On the other hand, Liu and co-workers have designed a quinoxaline-fused tetrathiafulvalene based sensitizer with red-shifted absorption and show an overall conversion

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A Detailed Investigation into the Electrical Conductivity and Structural Properties of [Poly(ethylene oxide)-succinonitrile]-Li(CF₃SO₂)₂N Solid Polymer Electrolytes

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A solid polymer electrolyte (SPE) was prepared via a solution casting method from a blend of equal weight fractions of poly(ethylene oxide) (PEO) and succinonitrile, used as the polymer matrix, and a salt, Li(CF₃SO₂)₂N ($x = 0-0.3$ in weight fraction). A plot of the electrical conductivity ($\sigma_{25^\circ\text{C}}$) vs. x showed an upturned U-shape, with the highest value being $\sim 3.9 \times 10^{-4}$ S/cm for $x = 0.25$ (EO/Li⁺ = 9.8; the optimum conducting composition). The electrolytes with x ranging from 0.15 to 0.3 showed a linear trend in their $\log(\sigma T^{0.5}) - (T - T_0)^{-1}$ curves with low pseudo-activation energy values, suggesting the presence of highly conductive amorphous domains, as confirmed by X-ray diffractometry measurements, Fourier-transform infrared (FT-IR) spectroscopy, polarized optical microscopy, and differential scanning calorimetry studies. The change in PEO chain conformation with x is discussed in detail using FT-IR spectroscopy in the light of earlier results reported for PEO – Li(CF₃SO₂)₂N SPEs.

Keywords: Polymer electrolyte, Poly(ethylene oxide), Succinonitrile, Electrical conductivity
Fourier-transform infrared spectroscopy

Introduction

Lithium-ion conducting solid polymer electrolytes (SPEs) are highly attractive materials for solid-state electrochemical devices because of their compactness, ruggedness, chemical and mechanical stability, and safety.^{1–7} Poly(ethylene oxide), commonly abbreviated as PEO, is used in the preparation of SPEs for the investigation of all-solid-state batteries. PEO is thermally stable up to 200°C, environmentally friendly, and non-toxic; moreover, it is inexpensive. PEO solvates salts owing to its high dielectric constant (ϵ , 5–8) and, at temperatures greater than the glass transition temperature (T_g), aids ion transport via interactions between the ions and the ethereal oxygen of the polymeric chains.⁶ PEO–LiX electrolytes, where X is an anion, show poor electrical conductivity ($\sigma_{25^\circ\text{C}} < 10^{-5}$ S/cm) at the optimum conducting composition (OCC). This is because of the very high crystallinity of PEO, which results from the highly crystalline PEO domains containing long and linear polymeric chains at the OCC. In other words, only a few highly conductive amorphous domains form at the OCC on salt solvation/complexation. In addition, the amorphous domains are also poorly interconnected, resulting in relatively low ionic mobility.

The crystallinity of PEO has been reduced in PEO-based SPEs by modifying the polymer chains via grafted polymers, block copolymers, and cross-linked polymer networks.^{1–9} These modifications increase the size and

interconnectivity of the amorphous domains, resulting in $\sigma_{25^\circ\text{C}}$ values of $\sim 10^{-4}$ S/cm.

A simple and cost-effective methodology, the blending of two polymers, has also been used to reduce the crystallinity of PEO. For example, PEO has been blended with polymers such as poly(vinylidene fluoride)¹⁰ and polydimethylsiloxane.¹¹ However, these blends have $\sigma_{25^\circ\text{C}}$ values less than 10^{-4} S/cm. Succinonitrile (SN), a low-molecular-weight plastic crystal, has also been used as a blender to reduce the crystallinity of PEO.^{12–24} For PEO – SN – LiX SPEs, SN acts as a plasticizer. These SPEs exhibit $\sigma_{25^\circ\text{C}}$ values ranging from 10^{-5} to 10^{-3} S/cm, where X indicates Cl, BF₄, PF₆, ClO₄, CF₃SO₃, (CF₃SO₂)₂N, (C₂F₅SO₂)₂N, B(C₂O₄)₂, or C₆F₃N₄.^{12–24} The SN acted as a solid solvent because of its low melting temperature ($T_m \sim 54^\circ\text{C}$) and high ϵ (~ 55), which enables the dissolution of various types of salts with a better shape situation.^{25–27} SN also offers high molecular diffusivity between the crystal to plastic crystal phase transition temperature (T_{pc} , -35°C) and melting temperature,^{25–27} which is mediated by the trans-gauche isomerization (involving rotation about the central C–C bond) of the molecules and molecular jumps from one diagonal position of the body-centered cubic structure to another. The plastic phase has a high concentration of “trans” isomers as an impurity, and these are responsible for the high ionic conductivity.^{12–24}

A nearly equal weight fraction of PEO and SN results in PEO–SN blend with electrical conductivity better than that



Cyclometalated ruthenium complexes with 6-(*ortho*-methoxyphenyl)-2,2'-bipyridine as panchromatic dyes for dye-sensitized solar cells

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ABSTRACT

A cyclometalated ruthenium complex with 6-(*ortho*-methoxyphenyl)-2,2'-bipyridine (MeO-L) and tri-carboxyterpyridine (tpy(CO₂H)₃) (**RuCC-PF₆**) was prepared, characterized, and evaluated as a dye for dye-sensitized solar cells (DSSCs). The first oxidation and reduction potentials are +0.99 V and −0.81 V vs NHE, respectively. This complex exhibits panchromatic absorption spectrum extending up to 800 nm. The transitions upon visible light excitation were mixtures of metal-to-ligand (Ru → tpy(CO₂H)₃) and interligand (MeO-L → tpy(CO₂H)₃) charge transfer transitions. Adsorption of the ruthenium complex on TiO₂ was carried out from solutions of **RuCC-PF₆** in the free acid form or solutions of **RuCC-(NBu₄)₂** in a deprotonated carboxylate form. The DSSC devices employing these complexes as the dye sensitizers generate electricity in response to light over the whole visible range and into the near infrared region over 900 nm. Remarkably, **RuCC-(NBu₄)₂** recorded higher short-circuit current density than a benchmark N719, while the open-circuit voltage was lower, resulting in a modest overall photon-to-current conversion efficiency of 6.4%. The transient absorption and electrochemical impedance spectroscopy have been conducted to get insight into the mechanistic details of the DSSC cells, which suggested that the presence of NBu₄ cation was beneficial in retarding the unwanted recombination reaction. Considering the efficient charge injection and regeneration as manifested by the large short-circuit current, modification based on the present structure would be a promising strategy toward higher efficiency dyes for DSSCs.

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1. Introduction

Developing better solar cells is an important issue for wider harvesting of solar energies [1]. Dye-sensitized solar cells (DSSCs) are one of the strong candidates for next-generation solar cells [2–4]. Although DSSCs with organic dyes have made efficiency records recently [5,6], ruthenium polypyridyl complexes still occupy the special position due to the accumulated studies and high efficiencies. The benchmark ruthenium dyes, N719 [7] and Black Dyes [8], however, are not without weakness. The thiocyanate ligand used in these dyes is monodentate and thus prone to

dissociation under operating conditions, thus leading to degradation in long-term use [6,9]. To overcome this problem, cyclometalated [10,11] and other multidentate ruthenium complexes [12,13] have attracted attention. Multidentate ligands are potentially more inert to dissociation and, as a bonus, the chemically modifiable to tune the properties, which is impossible for the thiocyanate ligand.

With applications to DSSCs in mind, we have previously studied the heteroleptic ruthenium complexes carrying 6-(*ortho*-methoxyphenyl)-2,2'-bipyridine (MeO-L) as one of the ligands and 4'-(4-tolyl)-2,2';6',2''-terpyridine as the other [14]. We obtained two types of complexes with MeO-L, one in which a carbon coordinates to the metal and the other in which the oxygen coordinates to the metal. We speculated that former complex would be promising for application to DSSCs on the basis of its HOMO and LUMO levels. In the present study, we have prepared a new ruthenium complex (**RuCC-PF₆**, Chart 1) with MeO-L and 2,2':6',2''-terpyridine-4,4',4''-

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Donor- π -Acceptor Based Stable Porphyrin Sensitizers for Dye-Sensitized Solar Cells: Effect of π -Conjugated Spacers

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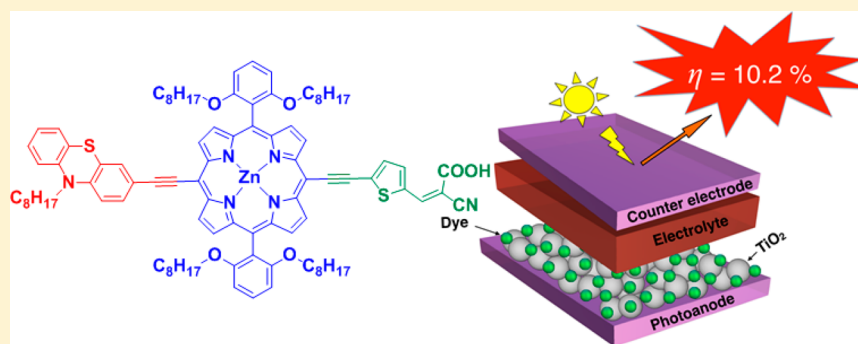
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S Supporting Information



ABSTRACT: Porphyrins are major sensitizers in dye-sensitized solar cells (DSSCs) and result in very high power conversion efficiency; however, aggregation tendency and visible range absorption prevent realistic applications. Thus, designing of novel porphyrins based sensitizers is essential to resolve the current existing issues. In this context, seven D- π -A porphyrin dyes (LG1–LG7) engineered with 3-ethynyl phenothiazine tethered at the meso-position and π -spacers, such as 4-ethynyl phenyl (LG1), 5-ethynylthiophene (LG2), 5-ethynyl furan (LG3), 2,1,3-benzothiadiazole (BTD)–phenyl (LG6), and BTD–thiophene (LG7), were incorporated between porphyrin macrocycle and anchoring carboxylic acid. Similarly, π -spacers 4-ethynyl phenyl (LG4) and 4-ethynylthiophene (LG5) were functionalized between porphyrin and anchoring cyanoacrylic acid. LG5 and LG6 showed significant near-infrared absorption resulting in the highest efficiency of 10.20% and 9.64% among other derivatives. UV–vis–NIR absorption, cyclic voltammetry, and density functional theory calculations of LG1–LG7 suggested that LG5 exhibits strong absorption, and optimized lowest unoccupied molecular orbitals aid to inject electrons very effectively from the excited state of dye into the TiO₂ conduction band. Current density–voltage (J – V) of LG1–LG7 revealed that LG5 exhibits the highest short-circuit current density of 21.01 mA cm^{−2}, resulting in a power conversion efficiency of 10.20% in a liquid I[−]/I₃[−] redox couple electrolyte. Panchromatic incident photon-to-current conversion efficiency response of LG5 was observed between 400 and 900 nm, when compared to other derivatives. Thus, these results suggest that LG5 attained the highest efficiency in liquid electrolyte based DSSCs. Subsequently, durability studies of LG5 performed by continuous light exposure have shown that this sensitizer retained 80% initial efficiency after 1000 h. Therefore, the effect of spacer length and anchoring significantly contributed to improve the efficiency in liquid electrolyte, which is very useful to make efficient future generated DSSCs.

1. INTRODUCTION

With the potential of becoming a clean and renewable energy source, dye-sensitized solar cells (DSSCs) have drawn much attention because of their relatively high photovoltaic efficiencies, lower production cost, and aesthetic features of vivid color and transparency.^{1–8} Even though DSSCs have crossed a certified efficiency of >11%, almost all components of the device have to be redesigned to enhance the durability and lead to the effectiveness of the device cost. The sensitizer is one of the indispensable components of the device, and extensively used

sensitizers are Ru(II) polypyridyl complexes.^{9–13} Irrespective of their high conversion efficiency, the main drawbacks of Ru(II) polypyridyl complexes are their expense due to the rarity of the metal in the Earth's crust, and the lack of absorption in the near-IR region of the visible spectrum, where the solar flux of photons is still significant, thus limiting the realization and usability of

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Effect of spacers and anchoring groups of extended π -conjugated tetrathiafulvalene based sensitizers on the performance of dye sensitized solar cells†

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Four new extended π -conjugated tetrathiafulvalene (ex-TTF) based dyes featuring a donor- π -acceptor (D- π -A) configuration with varying π -spacers and anchoring groups were synthesized and characterized. The sensitizer having the 4-ethynyl phenyl π -spacer (G4) shows red shifted absorption maxima in comparison with the sensitizer having only the phenyl π -spacer (G2). All four sensitizers undergo reversible oxidations to form stable radical cations. TDDFT calculations highlighted that the LUMO of the G4 sensitizer is more stabilized by the incorporation of the ethynyl group between the π -spacer and the cyanoacrylic acid anchoring group that aid to inject electrons efficiently into TiO₂ thereby resulting in an enhanced power conversion efficiency of 6.36% when compared to the other derivatives, which is also confirmed by the intensity-modulated photovoltage spectroscopy (IMVS) method. Kinetic studies demonstrated that fast regeneration of the oxidized dye by the redox couple is an important factor behind enhanced efficiencies in solar cells. Finally, the performance of the present sensitizers is compared to that of previously reported sensitizers.

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Introduction

Dye-Sensitized Solar Cells (DSSCs) have attracted interest for over two and half decades because of their ease of fabrication, flexibility and low environmental impact compared to conventional solid-state p-n junction photovoltaic devices.^{1–8} The sensitizer is one of the vital components in achieving high efficiency and durability of the device. Among various classes of sensitizers, Ru(II) polypyridyl complexes are widely used in view of their broad absorption through the metal-to-ligand charge transfer (MLCT) transition and their long excited state lifetimes.^{9–11} However, the rarity of Ru metal in the Earth's crust and cost due to intricate synthesis and purification steps might impede commercialization of the technology. Recently, a new class of compounds *i.e.*, metal-free organic dyes have been found to be alternatives based on the tunability of their optical and electrochemical properties in a desired manner through suitable molecular design strategies.^{12–15} Organic dyes showing good efficiencies are composed of a donor (D) and an acceptor

(A) linked through a π -bridge and one can efficiently tune their optical properties.^{16–18} By adopting the D- π -A approach, great varieties of metal-free organic dyes have been reported with a record efficiency of 14%.¹⁹

Tetrathiafulvalene (TTF) scaffolds have a wide range of applications in materials chemistry towards molecular optoelectronics.^{20,21} A few TTF scaffold based sensitizers have been reported in the literature.^{22–24} Grätzel and co-workers reported extended π -conjugated tetrathiafulvalene (ex-TTF) based sensitizers for DSSCs with an efficiency of 3.8%.²⁴ The low efficiency of ex-TTF sensitizers is due to their energetically unfavourable HOMO level, in which dye-regeneration after electron-injection is thermodynamically not feasible. Geng *et al.* studied the effect of π -linkers between the donor tetrathiafulvalene scaffold and anchoring groups on optical and electronic properties, achieving an overall device conversion efficiency of 0.87%.²² Recently, our group have reported ex-TTF based sensitizers by introducing long alkyl chains and changing the π -linker, achieving an overall conversion efficiency of 7.15%.²⁵ Motivated by these results, we have designed four new D- π -A sensitizers constituted with ex-TTF as the donor and either cyanoacrylic acid or rhodanine acetic acid as the acceptor. The change of π -linkers between the donor and acceptor units of dyes might tailor their frontier orbital energy levels to be beneficial to red shift the charge-transfer transition. In the present manuscript, we report the synthesis, characterization, optical and electrochemical properties, and recombination/dye regeneration kinetic study of four dyes as well as their application in DSSCs.

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Effect of different auxiliary ligands and anchoring ligands on neutral thiocyanate-free ruthenium(II) dyes bearing tetrazole chromophores for dye-sensitized solar cells



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ABSTRACT

Four new bistridentate Ru(II) complexes having a combination of ligands, 4,4'-dicarboxy-2,2':6,2''-terpyridine or its 2-hexylthiophene-substituted derivative as the anchoring ligand on one hand and one of tetrazolylpyridine-based ligands having a N⁺N⁺N⁺ coordination pattern or C⁺N⁺N⁺ coordination pattern as the auxiliary ligand on the other are reported as sensitizers for dye-sensitized solar cells (DSSCs), along with their spectroscopic, electrochemical, and theoretical characterizations. For the anchoring ligand, the introduction of 2-hexylthiophene unit leads to narrower spectral response and lower molar extinction coefficients and a smaller driving force for dye regeneration. For the ancillary ligand, the cyclometalating Ru–C bond induces a red shift in absorption compared with a Ru–N bond and thus affords a photocurrent generation at wavelengths of up to 950 nm. Further, the overall efficiencies of DSSCs are higher with the N⁺N⁺N⁺ complexes than with the C⁺N⁺N⁺ complexes, mainly due to higher open-circuit voltages (V_{oc}). Overall, the DSSC based on the bistetrazolate dye without the hexylthiophene unit for the anchoring ligand and having the N⁺N⁺N⁺ coordination pattern for the auxiliary ligand exhibited the highest efficiency of 5.9% when employing 0.5 M *t*-butylpyridine in the electrolyte.

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1. Introduction

Since dye-sensitized solar cells (DSSCs) based on modified nanocrystalline TiO₂ surfaces first appeared in a quarter century ago [1], bidentate 4,4'-dicarboxy-2,2'-bipyridine and tridentate 4,4',4''-tricarboxy-2,2':6,2''-terpyridine were extensively employed as the typical anchoring ligand in thiocyanate (NCS) based [2–10] and NCS-free [11–18] ruthenium complexes. In comparison with Ru(II) dyes with the bidentate structure, those with the tridentate structure exhibited superior absorption response in the near IR region.

It has been recently demonstrated that only two carboxy groups each substituted on a pyridine ring in the terpyridine-based anchoring ligand are sufficient for stable adsorption of the complex on TiO₂ surface [19]. For the dicarboxyterpyridine anchor, the two carboxy groups can be substituted on the terminal pyridine rings [20] leaving the central pyridine ring open or one on the terminal and the other on the central pyridine ring leaving a terminal ligand open [5,21–23]. In these two molecular designs, the remaining pyridine group without the carboxy group becomes available for further functionalization. The Ru(II) complexes with the former anchoring ligand substituted with dicarboxy groups on the terminal pyridine rings showed higher fill factor values but achieved only moderate efficiencies even if functional units were introduced on the middle pyridine ring to provide electron donating abilities and expand the π -conjugation system [20]. In the latter molecular design, functional units have been attached to the 3, 4, 5, and 6-positions of the terminal pyridine unit of 4,4'-dicarboxy-2,2':6,2''-terpyridine, such as

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Heteroleptic Ru(II) cyclometalated complexes derived from benzimidazole-phenyl carbene ligands for dye-sensitized solar cells: an experimental and theoretical approach†

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We have designed and synthesized two new ligands based on N-heteroleptic/phenyl carbene (NH-phenyl C) i.e., 1-benzyl-2-(3,5-bis(trifluoromethyl)phenyl)-1H-benzodimidazole (**L1**) and 3-(1-benzyl-1H-benzol-2-yl)-10-hexyl-10H-phenothiazene (**L2**), used as ancillary ligands to heteroleptic Ru(II) complexes for dye-sensitized solar cells. Both NCS groups of the **N719** sensitizer are replaced with **L1** (**TC-1**) and **L2** (**TC-3**) to obtain cyclometalated Ru(II) complexes and one of 4,4'-dicarboxylato-2,2'-bipyridine (dcbpy) with **L1** to obtain a heteroleptic Ru(II) complex (**TC-2**). The presence of two trifluoromethyl groups of the **L1** ligand stabilizes the HOMO level of Ru(II) complexes and the presence of a phenothiazine moiety of the **L2** ligand alters the absorption properties of the **TC-3** complex. Both the ligands and the heteroleptic Ru(II) complexes are characterized by elemental analyses, ESI-MS, ¹H NMR, absorption and emission spectroscopy as well as electrochemical methods. The absorption spectra of **TC-1** and **TC-3** are blue shifted, when compared to the standard **N719** sensitizer. The assessment of these newly designed cyclometalated and heteroleptic Ru(II) complexes has revealed that **TC-2** exhibits an efficiency of 7.63%, whereas **TC-1** has an efficiency of 6.39% using an I⁻/I₃⁻ redox couple. DFT and nanosecond transient absorption kinetic studies have been adopted to understand the low efficiency of the **TC-3** complex.

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Introduction

Dye-sensitized solar cells (DSSCs) are being investigated extensively for their use in renewable energy technologies because of their great potential in terms of low fabrication cost, and flexible and high light-to-electrical energy conversion efficiency.^{1–8} DSSCs have achieved power conversion efficiencies of over 11%, which was demonstrated using a prototype device with

bis(tetrabutylammonium)-*cis*-di(thiocyanato)-*N,N'*-bis(4-carboxylato-4'-carboxylic acid-2,2'-bipyridine)ruthenium(II) (the **N719** dye) and trithiocyanato-4,4',4''-tricarboxy-2,2':6',2''-terpyridine ruthenium(II) (the black dye) sensitizers.^{9–12} In spite of this, these sensitizers show insufficient light-harvesting efficiencies in the near-IR region of the absorption spectra. The sensitizers are one of the key components in DSSCs as they absorb sunlight and induce intramolecular charge transfer from the ancillary ligand to the anchoring ligand with consequent electron injection into the conduction band of the TiO₂ semiconductor. For this reason, numerous heteroleptic ruthenium complexes have been probed, where one of the two 4,4'-dicarboxylato-2,2'-bipyridine (dcbpy) anchoring ligands has been replaced by a functionalized 2,2'-bipyridine (bpy) ligand with either hydrophobic chains to improve the device stability or with extended π -conjugated systems that include thiophene, carbazole, triphenylamine, coumarine *etc.*, to enhance the optical properties.^{13–22} Despite their stability and efficiency, modification of *N,N'* ancillary ligands involves tedious synthetic protocols that will affect the cost of the sensitizer. In contrast, Grätzel and co-workers reported cyclometalated ruthenium polypyridyl complexes by replacing the NCS ligand with an anionic carbon atom, C⁻N as an alternative

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Cationic effect on dye-sensitized solar cell properties using electrochemical impedance and transient absorption spectroscopy techniques

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Abstract

Redox-couple polymer electrolytes, (poly(ethylene oxide)-succinonitrile) blend/MI-I₂, where M = Li or K, were prepared by the solution cast method. Owing to the plasticizing property of K⁺ ions, the K⁺ ion-based electrolyte exhibited better electrical conductivity than the Li⁺ ion-based electrolyte, which did however exhibit better photovoltaic properties.

Electrochemical impedance spectroscopy revealed faster redox species diffusions and interfacial processes in the Li⁺ ion-based dye-sensitized solar cells than in the K⁺ ion-based ones. Transient absorption spectroscopy ascertained faster dye-regeneration by the Li⁺ ion-based electrolyte than the K⁺ ion-based electrolyte.

Keywords: dye-sensitized solar cell, cationic effect, electrochemical impedance spectroscopy, transient absorption spectroscopy

 Supplementary material for this article is available [online](#)

(Some figures may appear in colour only in the online journal)

1. Introduction

The research on photovoltaic (PV) cells is currently gaining impetus worldwide due to global warming and pollution problems, energy crises and the abundant availability of sunlight. The area of dye-sensitized solar cells (DSSCs) is becoming more attractive because of their simple cell structure and cost-effectiveness regarding materials and manufacturing [1, 2]. A conventional DSSC—also known as a Gratzel cell—has the following structure: current collector (CC)/dye-sensitized nanostructured mesoporous semiconducting layer/redox mediator/counter electrode (CE, which is usually a platinum layer)/CC [1, 2]. The CC is a fluorine-doped tin oxide (FTO) conducting and transparent layer on a glass plate. The semiconductor is an n-type material, e.g. TiO₂. Because of the n-type nature of the semiconductor, the conventional cell is also known as n-type DSSC. The photon of the sunlight is

absorbed by a thin layer of dye molecule on the mesoporous TiO₂. The redox mediator is, in general, an I[−]/I₃[−]-based redox-couple liquid electrolyte that exhibits a maximum photon-to-current conversion efficiency (η) of 11.3% [3]. Recently, a Co^{3+/2+}-based redox-couple liquid electrolyte showed a record efficiency of 13% [4]. As shown in figure 1, the n-type DSSC works through the reactions, R0–R7 [1, 2, 5, 6]. The absorption of a photon by a dye molecule (*S*) results in a dye molecule (*S*^{*}) with an excited state (R0), followed by its oxidation (*S*⁺) and the injection of an electron (*e*[−]) to the conduction band (CB) of the TiO₂ (R2). The *S*⁺ at the excited state returns immediately back to the ground state by a process, R1. The generated electron (*e*_{CB}) migrates through mesoporous TiO₂ (R4) to CC and then a load, and finally reaches CE through FTO glass. At the CE/electrolyte interface, the electron reduces I₃[−] and regenerates I[−] (R7). The dye regeneration (ground state *S*⁺ to *S*) takes place via oxidation of I[−],