

Ag⁺ ION MOBILITY IN AgI AND AgCl BY TRANSIENT IONIC CURRENT (TIC) TECHNIQUE

R.C. Agrawal*, Kuldeep Kathal, Rakesh Chandola & R.K. Gupta
Solid State Ionic Research Laboratory
School of Studies in Physics
Pt. Ravishankar Shukla University
RAIPUR - 492010, M.P., India

And

Ajay Kumar
Department of Physics
Banaras Hindu University
VARANASI-221005, U.P., India

ABSTRACT

Silver ion mobility in AgI and AgCl was measured using transient ionic current (TIC) method. The ionic mobility μ_{Ag} is $\sim 3 \times 10^{-3}$ and $\sim 2.5 \times 10^{-3}$ cm²/V.sec at room temperature, respectively for AgCl and AgI. The mobility in AgI increases slowly and smoothly with temperature in both phases independently with a little jump ($\sim 10^{-1}$) in the transition region while the conductivity changes abruptly at $\beta \rightarrow \alpha$ transition ($\sim 147^\circ\text{C}$). Therefore, it can be safely concluded that the large increase in σ at the $\beta \rightarrow \alpha$ transition is because of change in the number of mobile carriers rather than the mobility. Ag⁺ mobility in AgCl is almost independent of temperature which indicates that the ionic conductivity is predominantly governed by mobile ion concentration.

1. Introduction

AgI is well-known for the characteristic $\beta \rightarrow \alpha$ structural transition at $\sim 147^\circ\text{C}$. The ionic conductivity increases abruptly from $\sim 10^{-5}$ S/cm in the β -phase to a very high value $\sim 10^{-1}$ S/cm in the α -phase^{2,3}. This high conducting α -AgI is most suitable to develop solid state electrochemical devices viz. solid state batteries, coulometer-timers, electrochromic displays etc. with the only major disadvantage, as these devices are to be operated at temperatures above 147°C . Tremendous efforts were made in the past to obtain the α -phase at ambient temperature which includes the substitution of impurity ions either in cation or in anion or in both sites of AgI lattice. The first major breakthrough was achieved in the year 1967, when Bradley & Greene⁴ and Owens & Argue⁵ reported exceptionally high ionic conduction $\sim 10^{-1}$ S/cm at room temperature in M Ag₄I₅ group of solids (where M = NH₄, K, Rb). This discovery, in fact, marked the beginning of AgI-based solid electrolytes. A large number of solids in crystalline/ polycrystalline/ glassy phase have been reported since then to have very high Ag⁺ ion conduction⁶⁻⁹.

The ionic conductivity of superionic solids is governed by well-known expression:

$$\sigma = nq\mu$$

where n is the mobile charge concentration, q is the mobile ion charge and μ is the ion mobility. The increase in the ionic conductivity can be attributed to the increase either in the carrier concentration or in the carrier mobility or both. In the case of AgI, the question of fundamental importance is to see, during $\beta \rightarrow \alpha$ transition which factor (n or μ) dominates the conductivity behaviour.

* For future correspondence.

SOLID STATE BATTERY USING ALL HALIDE GLASSY ELECTROLYTE
0.45 AgI.0.35 AgCl.0.20 CsCl

R.C.Agrawal*, Kuldeep Kathal, & R.K. Gupta
Solid State Ionic Research Laboratory
School of Studies in Physics
Pt. Ravishankar Shukla University
RAIPUR - 492010, M.P., India

And

M. Saleem
Department of Applied Physics
K.D.K. Engineering College, Nandanvan
NAGPUR, M.S., India

ABSTRACT

All halide glass system with composition 0.45 AgI. 0.35 AgCl.0.20 CsCl was prepared by quenching the sample to room temperature between two steel plates and by roller quencher at 10°C. The electrical conductivity was measured below T_g by impedance spectroscopy (IS) technique in the frequency range 40 Hz to 100 KHz. The sample prepared by quenching in roller quencher or between steel plates shows similar conductivity values. Ionic transference number (t_{Ag^+}) approximately equal to 1, was measured by Wagner's D.C. polarization method. The Ag^+ ion mobility was measured using Transient Ionic Current (TIC) technique. The ionic mobility μ_{Ag^+} was found to be $\sim 10^{-2}$ cm²/V sec. at room temperature. Our TIC measurements on this system suggested the presence of two different kinds of mobile Ag^+ ions with fairly close mobility values. Solid state battery with the configuration Ag (anode)/ Ag^+ (glass electrolyte)/ KI_3 + C (cathode) was prepared and the discharge characteristic has been studied at room temperature using different loads.

1. Introduction

The field of high conductivity solid electrolytes involving the study of ion transport in solids has been drawing considerable attention in the recent years¹⁻⁴. Initially the studies were mainly concentrated to the crystalline and polycrystalline phases, however, greater efforts are now being directed towards obtaining these solids in the glassy/amorphous phase. Glassy phase has many material properties superior to other phases mentioned above, viz. isotropic conduction; absence of grain boundaries; ease of preparation, fabrication and possibility to obtain thin film; continuous variation of composition for optimization of the material properties; high ionic with extremely low electronic conductivity etc. A large number of glasses with Ag^+ , Cu^+ , Li^+ etc. have been reported so far, however, Ag^+ ion - based glasses are perhaps the best, exhibiting very high ionic conductivity ($\sim 10^{-2}$ - 10^{-4} S/cm) at room temperature. Majority of the fast Ag^+ ion conducting glasses are prepared by rapidly quenching the mixture of AgI + Ag - oxyanion melt to low to very low temperatures (See for review: Ingram⁵, Tuller⁶, Minami⁷, Levasseur⁸).

* For future correspondence.

Ionic drift velocity and mobility measurements on a quenched [0.75AgI:0.25AgCl] mixed-system or solid solution

R.C. Agrawal^{*1}, R.K. Gupta^{*} and R.K. Pandey^{**}

^{*}Solid State Ionics Research Laboratory, School of Studies in Physics,
Pt. Ravishankar Shukla University, Raipur 492010, INDIA

^{**}Department of Physics, Barkatullah University, Bhopal, INDIA

ABSTRACT

Ionic drift velocity (v_d) measurements as a function of temperature on *quenched* [0.75AgI:0.25AgCl] mixed-system/solid solution are reported. Wagner's dc polarization method, originally used to determine the ionic transference number (t_{ion}), was employed for v_d -measurements. This study revealed that the system remained purely ionic (i.e. $t_{ion} \sim 1$) with Ag^+ ions as the sole charge carriers in the entire range of temperature of measurement. The energy E_d , involved in the thermally activated process, was computed from the $\log v_d$ vs $1/T$ Arrhenius plot. At a fixed value of applied dc field, ionic drift velocity is directly proportional to the ionic mobility (μ) at all temperatures. Thus, energy E_d should be equal to energy of migration E_m , involved in $\log \mu$ vs $1/T$ thermally activated processes. E_d : ~ 0.186 & -0.189 eV, computed in temperature regions (I & II) below and above the transition region, are very close to the E_m : ~ 0.17 & -0.18 eV respectively obtained earlier in the same temperature regions (I & II).

1. Introduction

Solid State Ionics is relatively a new branch of material science which deals with fast ion transport in solids. Ion transport in majority of these solids is governed, in general, by hopping mechanism. Characterization of various ionic transport properties are very essential to understand the ion transport mechanism in these solids. These studies mainly encompass experimental measurements of ionic transport parameters viz. electrical conductivity (σ), ionic mobility (μ), mobile ion concentration (n), ionic drift velocity (v_d) and ionic transference number (t_{ion}). σ is an important parameter representing the power of ionic transport. Impedance spectroscopy is a widely adopted technique to determine the true bulk conductivity of the system [1]. σ is related to μ and n by following well-known equation:

$$\sigma = \sum_i n_i q_i \mu_i \quad (1)$$

where q is the charge on the mobile ion species. As obvious from the eq.(1), transport phenomenon can be well understood if n and μ are characterized correctly for these systems.

¹For future correspondence

Thermoelectric power study on a new Ag^+ ion conducting composite electrolyte system $0.8[0.75\text{AgI}:0.25\text{AgCl}]:0.2\text{SnO}_2$

M. Saleem^{*1}, R.K. Gupta^{**} and R.C. Agrawal^{**}

^{*}K.D.K. Engineering College, Nandanvan, Nagpur 440090, INDIA

^{**}Solid State Ionics Research Laboratory, School of Studies in Physics,
 Pt.Ravishankar Shukla University, Raipur 492010, INDIA

ABSTRACT

Thermoelectric power (TEP) θ measurements on a new Ag^+ ion conducting composite electrolyte system $0.8[0.75\text{AgI}:0.25\text{AgCl}]:0.2\text{SnO}_2$ are reported. This composite system was explored recently by dispersing SnO_2 dispersoid particles (size $\sim 10 \mu\text{m}$) into an alternate first phase host-matrix: a *quenched/annealed* $[0.75\text{AgI}:0.25\text{AgCl}]$ *mixed-system/solid solution*, in place of conventional host AgI. The temperature variation of θ was studied in two temperature regions (I & II) separated by a transition region. The heats of Ag^+ ion transport (q^*) ~ 0.148 & 0.048 eV, evaluated from the slopes of θ vs $1/T$ plot in the temperature regions (I & II) respectively, are very close to the activation energy (E_a) values: ~ 0.147 & 0.052 eV respectively obtained earlier from $\log \sigma$ vs $1/T$ Arrhenius plots in the same regions (I & II). The results well espoused the Rice and Roth's free-ion theory proposed for superionic solids possessing an average structure and free-ion like state.

1. Introduction

Conductivity enhancements of ~ 1 -3 orders of magnitude have been reported in many two-phase composite electrolyte systems [1-6]. Liang reported ~ 50 times increase in Li^+ ion conduction at room temperature simply by dispersing submicron size particles of an inert and insulating Al_2O_3 second phase dispersoid into a moderately conducting first phase ionic salt LiI [7]. Shahi and Wagner [8] reported ~ 2500 times enhancement in the Ag^+ ion conduction at room temperature in $\text{AgI}:\text{Al}_2\text{O}_3$ composite system. A large number of composite electrolyte systems with various ion conduction such as Li^+ , Ag^+ , Cu^+ , F^- etc. have been reported since then. Many theoretical models have been proposed to explain the phenomenon of conductivity enhancement in these two-phase composite systems [9-14]. Majority of the theories suggested some common features, like increase in the mobile ion defect concentration at the host/dispersoid interfacial space-charge region and/or increased mobility due to the creation of intergrain high conducting paths, as the reason for enhancement. Volume fraction and particle size of the dispersoid phase play very

¹For future correspondence

Transport property studies on Ag^+ ion conducting composite electrolyte system $(1-x)\text{AgI}:x\text{SnO}_2$

R.K. Gupta ^{*1}, R.C. Agrawal^{*}, and R.K. Pandey^{**}

^{*}Solid State Ionics Research Laboratory, School of Studies in Physics,
Pt. Ravishankar Shukla University, Raipur 492010, INDIA

^{**}Department of Physics, Barkatullah University, Bhopal, INDIA

ABSTRACT

Investigations on various ionic transport parameters viz. electrical conductivity (σ), ionic mobility (μ), mobile ion concentration (n), ionic transference number (t_{ion}), activation energy (E_a), are reported for a new Ag^+ ion conducting composite electrolyte system $(1-x)\text{AgI}:x\text{SnO}_2$, where $0 \leq x \leq 50$ in wt(%). The system was prepared by dispersing SnO_2 particles into the host-matrix AgI . σ vs x variation showed an order of magnitude enhancement in the room temperature conductivity for the composition $0.8\text{AgI}:0.2\text{SnO}_2$. This has been referred to as *optimum composition*. σ as a function of x & temperature were measured by impedance spectroscopy (IS). μ and t_{ion} measurements were done on the optimum composition at room temperature using transient ionic current (TIC) technique and Wagner's dc polarization method respectively. While, n was evaluated from σ and μ data. The room temperature values of various ionic parameters (σ , μ , n & t_{ion}) obtained for the optimum composition were compared with those of host-matrix AgI . The increase in the ionic mobility has been the reason attributed to the conductivity enhancement in the composite system. The result has been well supported by the activation energy (E_a) values obtained from the $\text{Log } \sigma$ vs $1/T$ Arrhenius plots for the optimum composition and the host salt. E_a for the optimum composition decreased substantially as compared to that for the host salt.

1. Introduction

Composite electrolytes are new class of solid state ionic materials which show a number of promising technological applications in electrochemical devices such as solid state batteries, fuel cells, sensors, electrochromic display devices etc. Composite electrolytes are normally two-phase solid mixtures in which enhancements of ~ 1 -3 orders of magnitude in the room temperature conductivity have been reported [1-6]. These systems are prepared, in general, by dispersing submicron size particles of insulating and chemically inert material, namely Al_2O_3 , Fe_2O_3 , SiO_2 etc. (termed as second phase *dispersoid*) into a moderately conducting ionic salt like AgI , AgCl , LiI , CuI , HgI_2 etc. (termed as first phase *host-matrix*). A large number of two-phase composite systems with various ion conducting species such

¹For future correspondence

**ESTIMATION OF MOBILE ION CONCENTRATION IN
SOME SILVER ION CONDUCTING SOLID ELECTROLYTE SYSTEMS
BY DC POLARIZATION /DEPOLARIZATION STUDIES**

R.C. AGRAWAL, MOHAN L. VERMA, R.K. GUPTA, R. KUMAR[†], M.L. VERMA* and
S.K. PANDEY

Solid State Ionics Research Laboratory, School of Studies in Physics,
Pt. Ravishankar Shukla University, RAIPUR 492 010, INDIA

[†]Department of Physics, Dr. H.S. Gour University, SAGAR 470003, INDIA

* Govt. D.B. Girls PG College, Raipur 492001, INDIA.

ABSTRACT

A novel experiment, based on dc polarization/self-depolarization technique, has been suggested for the direct estimation of mobile ion concentration (n) in ionic/superionic systems. ' n ' can be determined conveniently from the theoretical fit of the 'depolarization current vs time' plot. The present paper reports the estimation of ' n ' at various temperatures in some Ag^+ ion conducting solids viz. AgI , 'a quenched $[\text{0.75AgI:0.25AgCl}]$ mixed-system/solid solution' and superionic glass/composite systems. The ' n ' - values obtained in the present study are in very good agreement with those reported earlier by us using an entirely independent technique.

1. INTRODUCTION

Solid State Ionics is truly an interdisciplinary subject as it deals with the physics, chemistry & technological aspects of the materials exhibiting high ionic conductivity. These materials, termed as *Superionic Solids* or *Fast Ion Conductors* or *Solid Electrolytes*, show tremendous technological potential to develop variety of solid state electrochemical devices viz. mini/micro batteries, sensors, fuel cells, memory devices, electrochromic displays (ECD's), supercapacitors etc. [1-5]. The characteristic high ionic conductivity (σ) of the solid electrolyte systems is predominantly governed by two basic ionic parameters : mobile ion concentration (n) and ionic mobility (μ). Number of experimental techniques are employed to study the macroscopic and/or microscopic behaviour of transporting ions in these systems [1]. Some of the techniques, widely adopted for the characterization of basic ion transport parameters viz. ' σ ', ' μ ', ' n ', are :

- *Impedance spectroscopy* (IS) for the measurement of ionic conductivity (σ). Hence, computation of the activation energy (E_a) from the ' $\log \sigma$ vs $1/T$ ' Arrhenius plot [6];
- *Transient ionic current* (TIC) technique for direct determination of ionic mobility (μ) [7, 8]. Subsequently, calculation of mobile ion concentration (n) using ' σ ' and ' μ ' data. Hence, computation of energies of migration (E_m) and formation (E_f) from the ' $\log \mu$ vs $1/T$ ' and ' $\log n$ vs $1/T$ ' plots respectively [9];
- *Wagner's dc polarization* method for the measurement of ionic transference number (t_{ion}) [10]. Consequently, estimation of ionic drift velocity (v_d) of the mobile species from the ' I_t '-data, obtained from the Wagner's 'current vs time' plot, and ' n '-data [11].

In addition to the above mentioned techniques, a novel experimental method, based on dc polarization/self-depolarization, has recently been developed in the present laboratory [12]. This technique can be employed to demonstrate the role played by the mobile ions in ionic/superionic systems. The method is specifically useful to pure silver ion conducting

**THERMOELECTRIC POWER AND BATTERY DISCHARGE CHARACTERISTIC
STUDIES ON A NEW SILVER ION CONDUCTING
COMPOSITE ELECTROLYTE SYSTEM**

R.C. AGRAWAL, MOHAN L. VERMA, R.K. GUPTA & S. THAKER*

Solid State Ionics Research Laboratory, School of Studies in Physics,
Pt. Ravishankar Shukla University, Raipur 492 010, INDIA

* Govt. Science College, Raipur 492 010, INDIA

ABSTRACT

Thermoelectric power (θ) and battery discharge characteristic studies on a new Ag^+ ion conducting two-phase composite electrolyte system : $0.9[0.75\text{AgI}:0.25\text{AgCl}]:0.1\text{SiO}_2$ are reported. The composite electrolyte system was prepared by dispersing nano-size (~ 8 nm) particles of fumed SiO_2 into a new and alternate first phase host matrix salt : a quenched $[0.75\text{AgI}:0.25\text{AgCl}]$ mixed-system/solid-solution, recently investigated in the present laboratory, instead of the conventional host AgI. The heat of Ag^+ ion transport (q^*), evaluated from the slope of ' θ vs $1/T$ ' plot, is very close to the conductivity activation energy (E_a). This in turn indicated the fact that the composite system possesses Rice & Roth's 'free-ion' like states. We also report the discharge characteristic studies on all solid state battery, fabricated in the cell configuration : (Ag-metal) Anode | $0.9[0.75\text{AgI}:0.25\text{AgCl}]:0.1\text{SiO}_2$ | (Graphite + Iodine) Cathode, under different load conditions and cathode preparations viz. $\{\text{C}+\text{I}_2\}$, $\{\text{C}+\text{KI}_3\}$, $\{\text{C}+(\text{CH}_3)_4\text{NI}_3\}$, $\{\text{C}+(\text{C}_2\text{H}_5)_4\text{NI}_3\}$. The battery with $\{\text{C}+\text{I}_2\}$ cathode performed more satisfactorily under low current drain states. The ionic transference number (t_{ion}) measurement was also carried out at room temperature using electrochemical cell potential method. ' t_{ion} ' ~ 1 , obtained in the present study, is close to the value reported earlier using Wagner's dc polarization method.

1. INTRODUCTION

Two-phase composite electrolyte systems are new class of superionic solids which exhibit ~ 1 -3 orders of enhancement in the room temperature conductivity simply when sub-micron size particles of an insulating and inert material viz. Al_2O_3 or SiO_2 or SnO_2 or ZrO_2 or Fe_2O_3 etc. (termed as second phase dispersoid) are heterogeneously mixed with a moderately ion conducting first phase host-matrix salt such as AgI or AgCl or CuI or PbF_2 etc. The conductivity enhancement phenomenon in such systems was observed for the first time in 1973 by C.C. Liang who reported ~ 50 times enhancement of Li^+ ion conductivity in $\text{LiI}-\text{Al}_2\text{O}_3$ composite electrolyte [1]. A large number of composite electrolyte systems with high Ag^+ , Cu^+ , Li^+ , F^- etc. ion conduction have been investigated since then [2]. Agrawal & Gupta [3] have recently made an extensive survey on these systems incorporating various aspects such as material, transport phenomena *vis-a-vis* phenomenological models explaining the conductivity enhancements in these systems. Amongst the known 2-phase composite electrolyte systems, maximum enhancement in the room temperature conductivity is generally achieved when AgI is used as first phase host-matrix salt. Shahi & Wagner [4] reported ~ 2500 times enhancement (highest so far) of Ag^+ ion conduction in $\text{AgI}-\text{Al}_2\text{O}_3$ composite system. Recently, a new compound : "a quenched/annealed $[0.75\text{AgI}:0.25\text{AgCl}]$ mixed system/solid solution" has been investigated in the present laboratory [5, 6] which has been proved to be a better alternate to the conventional host-matrix salt AgI in the preparation of fast Ag^+ ion conducting composite/glass systems. In fact, several new Ag^+ ion conducting 2-phase composite electrolytes : $0.7[0.75\text{AgI}:0.25\text{AgCl}]$:

**SOLID STATE BATTERY DISCHARGE CHARACTERISTIC
STUDIES ON A NEW Ag^+ ION CONDUCTING GLASS SYSTEM :
 $0.7[0.75\text{AgI}:0.25\text{AgCl}]:0.3[\text{Ag}_2\text{O}:\{0.7\text{B}_2\text{O}_3:0.3\text{MoO}_3\}]$**

R. C. Agrawal^a, M. L. Verma^b, R. K. Gupta^a, R. Kumar^c

^a Solid State Ionics Research Laboratory, School of Studies in Physics,
Pt. Ravishankar Shukla University, Raipur 492010, INDIA.

^b Govt. D. B. Girls P. G. College, Raipur 492001, INDIA.

^c Department of Physics, Dr. H. S. Gaur University, Sagar 470003, INDIA.

Solid state batteries with the cell configuration : [Anode]/ $0.7[0.75\text{AgI}:0.25\text{AgCl}]:0.3[\text{Ag}_2\text{O}:\{0.7\text{B}_2\text{O}_3:0.3\text{MoO}_3\}]/[\text{Cathode}]$, have been fabricated using $0.7[0.75\text{AgI}:0.25\text{AgCl}]:0.3[\text{Ag}_2\text{O}:\{0.7\text{B}_2\text{O}_3:0.3\text{MoO}_3\}]$ as electrolyte. Ag-metal was used as anode while elemental iodine (I_2)/chelated iodine (KI_3 or $(\text{CH}_3)_4\text{NI}_3$ or $(\text{C}_2\text{H}_5)_4\text{NI}_3$) mixed with electronically conducting graphite in 1 : 1 weight ratio was used as cathode. Fast Ag^+ ion conducting glass system : $0.7[0.75\text{AgI}:0.25\text{AgCl}]:0.3[\text{Ag}_2\text{O}:\{0.7\text{B}_2\text{O}_3:0.3\text{MoO}_3\}]$ was recently investigated in our laboratory using an alternate host matrix salt : 'an quenched $[0.75\text{AgI} : 0.25\text{AgCl}]$ mixed-system/solid solution' in place of traditional salt AgI. The battery discharge characteristic studies carried out under different load conditions revealed that the batteries fabricated with $(\text{C} + \text{I}_2)$ cathode performed most satisfactorily specially during low current drain applications. Ionic transference number (t_{ion}) ~ 1 , obtained using electrochemical cell potential measurement is identical to the value reported earlier by Wagner's dc polarisation method.

INTRODUCTION

Fast Ag^+ ion conducting superionic solids in glassy phase have attracted wide-spread attention in recent years due to their high ionic conductivity ($\sim 10^{-1}$ - 10^{-3} S.cm^{-1}) at the room temperature with a negligible electronic contribution. In addition, these materials possess several definite advantages over their crystalline/polycrystalline counterparts viz. isotropic conduction, absence of grain boundary, a continuously variable composition permitting optimisation of electrolyte properties, good workability, and long-term mechanical stability below the glass transition temperature. There distinct properties of glassy electrolytes allow one to use them in solid state electrochemical devices viz. solid state batteries, fuel cells, sensors, super-capacitors, electrochromic display devices etc. (for a review, see [1-5]).

The majority of fast Ag^+ ion conducting glasses are based on AgI where superionic conducting α -AgI phase is stabilised at the room temperature in an appropriate ratio of glass former/modifier [1-5]. Recently, a number of fast Ag^+ ion conducting glass electrolyte systems viz. $0.7[0.75\text{AgI}:0.25\text{AgCl}]:0.3[\text{Ag}_2\text{O}:\text{B}_2\text{O}_3]$ [6], $0.75[0.75\text{AgI}:0.25\text{AgCl}]:0.25[\text{Ag}_2\text{O}:\text{CrO}_3]$ [7] including the present system $0.7[0.75\text{AgI}:0.25\text{AgCl}]:0.3[\text{Ag}_2\text{O}:\{0.7\text{B}_2\text{O}_3:0.3\text{MoO}_3\}]$ [8] have been

**THERMOELECTRIC POWER AND BATTERY DISCHARGE
CHARACTERISTIC STUDIES ON A NEW Ag^+ ION CONDUCTING
2-PHASE COMPOSITE ELECTROLYTE SYSTEM :
0.9 [0.75 AgI: 0.25 AgCl] : 0.1 ZrO_2**

R.C. Agrawal, Mohan L. Verma, R.K. Gupta and S. Thaker*
Solid State Ionics Research Laboratory, School of Studies in Physics
Pt. Ravishankar Shukla University, Raipur 492 010, M.P., INDIA
*Govt. Science College, Raipur 492 010, M.P., INDIA.

Thermoelectric power (TEP) ' θ ' and solid state battery discharge characteristic studies, performed on a new Ag^+ ion conducting 2-phase composite electrolyte system : 0.9 [0.75 AgI: 0.25 AgCl]: 0.1 ZrO_2 , are reported. This system is recently investigated in the present laboratory using an alternate host matrix salt : '*an annealed/quenched [0.75 AgI: 0.25 AgCl] mixed-system/solid solution*' as a first phase in place of traditional host AgI and sub-micron size particles of ZrO_2 as second phase dispersoid. The heat of Ag^+ ion transport (q^*), computed from the slope of ' θ ' versus $1/T$ ' linear plot, is extremely close to the value of conductivity activation energy (E_a) suggesting the existence of Rice & Roth's 'free-ion-like' states in the system with an average structure. Solid state battery studies were also carried out under different load conditions and various cathode preparations. The discharge characteristic study revealed that the batteries fabricated with (C + I_2) cathode performed most satisfactorily under low current drain states. Ionic transference number (t_{ion}) has also been evaluated using electrochemical cell potential measurement.

INTRODUCTION

Enhanced ionic conductivity along with improved mechanical/thermal stability has been reported in several 2-phase composite electrolyte systems. Hence, these materials are the potential candidates as solid electrolytes in various solid state electrochemical devices. Composite electrolytes are prepared, in general, by dispersing sub-micron size particles of an inert and insulating material e.g. Al_2O_3 , SiO_2 etc. (called second-phase dispersoid) into a moderate ion conducting solid viz. AgI, CuI, PbF_2 , ion conducting glass/polymer (called first-phase host matrix salt). The Ag^+ ion conducting 2-phase composite electrolyte systems (ionic conductivity, $\sigma_{27^\circ\text{C}}$, 10^{-4} – 10^{-5} S. cm^{-1}), are prepared, in general, using AgI as a first-phase host matrix salt (for a review, see [1-3]). Recently, Agrawal and co-workers suggested an alternate host salt : '*an annealed/quenched [0.75 AgI: 0.25 AgCl] mixed-system/solid solution*' in place of traditional salt AgI [4]. The new host exhibits several transport property superior to AgI, hence, yields better composite electrolyte systems ($\sigma_{27^\circ\text{C}} \sim 10^{-3}$ S. cm^{-1}) [5-8]. The present paper reports the studies on thermoelectric power and solid state battery application of a newly investigated 2-phase composite electrolyte system: 0.9[0.75AgI: 0.25 AgCl] : 0.1 ZrO_2 where sub-micron size particles of ZrO_2 was used as second

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

R. C. Agrawal, M. L. Verma¹, R. K. Gupta and A. Bhatt

*Solid State Ionics Research Laboratory, School of Studies in Physics,
Pt. Ravishankar Shukla University, Raipur – 492010, C. G.*

¹ *Govt. D.B. girls PG College, Raipur – 492001, C. G.*

Abstract

Ion transport characterization has been done on 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. The glass samples were prepared using twin-roller at a quenching rate $\sim 10^3$ K/s. An alternate host compound "a quenched $[0.75\text{AgI}:0.25\text{AgCl}]$ mixed system/ solid solution" has been used in place of traditional host AgI. Silver molybdate glass systems: $x\text{AgI}:(1-x)[\text{Ag}_2\text{O}:\text{MoO}_3]$, were also prepared using AgI, in the identical manner for direct comparison of room temperature conductivity. Compositional variation of conductivity exhibited a peak at $x = 0.8$ in the room temperature conductivity for both the systems. However, the new host yielded a better glass electrolyte with higher room temperature conductivity ($\sim 6 \times 10^{-3} \text{ Scm}^{-1}$). The composition: $0.8[0.75\text{AgI}:0.25\text{AgCl}]:0.2[\text{Ag}_2\text{O}:\text{MoO}_3]$, has been referred to as optimum conducting composition (OCC). A direct determination of ionic mobility (μ) as a function of composition (x) was carried out using TIC technique and subsequently, mobile ion concentration (n) was evaluated from σ & μ data. These studies revealed the fact that the increased mobile ion concentration (n) has been predominantly responsible for the overall increase in the conductivity of OCC. The phase identification was done on the OCC using XRD technique.

1. Introduction

Amongst the known superionic glasses, Ag^+ ion conducting systems attracted widespread interest in the recent years. They exhibit several advantageous material properties over their crystalline/ polycrystalline counterparts, including a very high isotropic ionic conductivity (10^{-2} - 10^{-4} Scm^{-1}) at room temperature [1-5]. Majority of Ag^+ ion conducting superionic glasses, reported in the past, have been prepared, in general, by melt quenching the appropriate molar compositions of host salt AgI and glass modifier Ag_2O , in common, with any one of the glass formers such as B_2O_3 , MoO_3 , CrO_3 , WO_3 etc. [5-8]. However, in the present investigation, we report 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, using "a quenched $[0.75\text{AgI}:0.25\text{AgCl}]$ mixed system/ solid solution" as an alternate host compound in place of the traditional host salt AgI. The new host exhibits transport characteristic analogous to AgI with an improved ionic transport parameter values at room temperature [8,9]. It has also been observed that the new host yields superior glass/ composite electrolyte systems as compared to those prepared using traditional host AgI [10-18]. For direct comparison of the room temperature conductivity of the new system, silver molybdate glass: $x\text{AgI}:(1-x)[\text{Ag}_2\text{O}:\text{MoO}_3]$ has been prepared in the identical manner using AgI. To identify the optimum conducting composition (OCC) as well as to explore the reason for the enhancement in the conductivity, the compositional variation of conductivity (σ), ionic mobility (μ) and mobile ion concentration (n) were carried out using various experimental techniques. X-ray diffraction was done to identify the phase of the OCC.

Investigation on a new Ag^+ ion conducting two-phase composite electrolyte system: $(1-x)[0.75\text{AgI}: 0.25\text{AgCl}]: (x)\text{Fe}_2\text{O}_3$

R. C. Agrawal, R. K. Gupta, C. K. Sinha, R. Kumar

*Solid state ionics research laboratory, School of studies in physics
Pt. Ravishankar Shukla University Raipur (CG) 492010.*

¹Dr. H.S. Gaur University, Sagar (M.P.)

Abstract

Investigation on ionic transport properties of a new Ag^+ ion conducting two-phase composite electrolyte system: $(1-x)[0.75\text{AgI}: 0.25\text{AgCl}]: x\text{Fe}_2\text{O}_3$ has been reported. An "annealed $[0.75\text{AgI}: 0.25\text{AgCl}]$ mixed-system/ solid solution", investigated in the present laboratory, has been used as the first phase host matrix in place of the traditional host AgI , while the insulating and inert Fe_2O_3 (particle size $< 1 \mu\text{m}$) has been dispersed as a second phase dispersoid. Homogeneous mixtures of two phases in different wt (%) compositions, kept in separate silica tubes, were heated $\sim 750^\circ\text{C}$ for 15 min (soaking time), then cooled rapidly. The compositional dependence of conductivity (σ) was carried out on the composite electrolyte system: $(1-x)[0.75\text{AgI}: 0.25\text{AgCl}]: x\text{Fe}_2\text{O}_3$ as well as on the system: $(1-x) \text{AgI}: x\text{Fe}_2\text{O}_3$, prepared in the identical manner for direct comparison of room temperature conductivity. The new host salt yielded better solid electrolytes as compared to those prepared with AgI . The composition: $0.8[0.75\text{AgI}: 0.25\text{AgCl}]: 0.2\text{Fe}_2\text{O}_3$ exhibited the highest conductivity ($\sim 1.5 \times 10^{-3} \text{Scm}^{-1}$) at room temperature and has been referred to as 'optimum conductivity composition' (OCC). An enhancement of more than an order of magnitude from the pure annealed host has been achieved in the OCC. In order to assign the reason for the enhancement in the room temperature conductivity, a direct determination of μ was done using TIC technique and subsequently, n was evaluated using equation: $\sigma = nq\mu$. The temperature dependence of ionic conductivity was carried out on the OCC and the activation energy (E_a) was computed from the 'log $\sigma - 1/T$ ' Arrhenius plot. The ionic transference number (t_{ion}), measured on OCC, has been very close to unity. This clearly indicated that Ag^+ ions are the sole charge carriers in the OCC.

1. Introduction

Fast Ag^+ ion conducting two phase composite electrolytes are interesting systems to develop potential solid state electrochemical devices such as solid state batteries, fuel cells, sensors, supercapacitors etc. These systems exhibit superionic conduction ($\sim 10^{-2}$ - 10^{-3}S/cm) at room temperature. They are prepared, in general, by dispersing submicron size particles of an inert and insoluble compounds like Al_2O_3 , SiO_2 , ZrO_2 etc., known as second phase dispersoid, into a moderately ion-conducting first phase host matrix salts like AgI , AgCl , AgBr etc. [1-6]. A conductivity enhancement of 1-3 orders of magnitude, as compared to that of the pure host, is normally achieved at room temperature. It has been observed that AgI composites normally exhibit high enhancement in the room temperature conductivity [1-4]. Recently, at the present laboratory a new host: 'a quenched/annealed $[0.75\text{AgI}: 0.25\text{AgCl}]$ mixed system/solid solution', has been investigated as an alternate to the traditional host AgI , which yielded several glass/composite systems with superior electrolyte properties [7-15]. In the present paper, we report the preparation of an another two phase composite electrolyte system: $(1-x)[0.75\text{AgI}: 0.25\text{AgCl}]: x\text{Fe}_2\text{O}_3$, in the series, where Fe_2O_3 particles (size $< 1 \mu\text{m}$) were dispersed into the new host. The characterization of ionic transport properties was done on the basis of various experimental measurements viz. compositional and temperature dependence of conductivity using impedance spectroscopy, direct determination of ionic mobility (μ) using TIC technique and then

**ELECTRICAL AND STRUCTURAL PROPERTIES OF NEW Li^+ ION
CONDUCTING SOL-GEL DERIVED ORMOLYTES: $(\text{SiO}_2\text{-PEG})\text{-LiCF}_3\text{SO}_3$**

R. K. GUPTA, H. Y. JUNG, C. J. WI AND C. M. WHANG

Institute of Advanced Materials and School of Materials Science and Engineering,

Inha University, 253 Youghyun-dong, Incheon 402-751, South Korea

E-mail: cmwhang@inha.ac.kr

A new fast Li^+ ion conducting ORMOLYTE system: $(\text{SiO}_2\text{-10wt\% PEG})\text{-[Li/O] LiCF}_3\text{SO}_3$ with $[\text{Li/O}] = 0$ to 0.1 mole, was synthesized via traditional and sono-catalysis routes of sol-gel method, and bulk samples have been referred to as classic and sono ormolytes, respectively. The highest electrical conductivity ($\sigma_{25^\circ\text{C}} \sim 10^{-4} \text{ Scm}^{-1}$) at $[\text{Li/O}] = 0.04$ and 0.05 mole was achieved for classic and sono ormolytes, respectively, with enhancement of 10^3 times from the host matrix: $\text{SiO}_2\text{-PEG}$ xerogels. The ionic transport parameters of the sono ormolytes were found slightly superior to the classic ormolytes. The results have been explained on the basis of scanning electron microscopy and Fourier-Transform infrared spectroscopy studies and found supportive to the theoretical models especially the morphological model proposed for two-phase composite electrolyte systems.

1. Introduction

Li^+ ion conducting polymer electrolytes offering wide range of electrochemical window (0–5 V), light weight, transparency, flexibility, elasticity, thin-film formation, etc., attract widespread attention as solid-state alternatives to liquid and crystalline electrolytes for device applications, namely, high and low energy density batteries, fuel cells, sensors, supercapacitors, electrochromic devices etc. Ionic conductivity $\sim 10^{-3} \text{ Scm}^{-1}$ has already been achieved for polymer gel electrolytes, however, exhibiting poor mechanical property. The solvent-free polymer electrolytes have also been investigated extensively. However, they have been found less ion conducting than the gel electrolytes. The heterogeneous doping of inorganic filler, e.g. SiO_2 , into polymer electrolyte has also been attempted to enhance the ionic conductivity and to improve upon the mechanical property. However, the ionic conductivity has been found limited to $\sim 10^{-4}\text{-}10^{-5} \text{ Scm}^{-1}$. For review, refer to [1-3]. Following the work of

The 26th
International Japan-Korea
Seminar on Ceramics

2009.11.24 [TUE] - 11.26 [THU]

Tsukuba International Congress Center "Epochal Tsukuba"
(Tsukuba, Ibaraki, Japan)

Extended Abstracts



Organized by
Organizing Committee of the 26th International Japan-Korea Seminar on Ceramics
Executive Committee of the 26th International Japan-Korea Seminar on Ceramics

Improved Flatness of Tape-casted and Cofired (NiO–CGO)/ CGO Multi-layers for Anode-Supported Planar Solid Oxide Fuel Cells

Ravindra K. GUPTA, Ik Jin CHOI and Yong Soo CHO*

Department of Materials Science and Engineering, Yonsei University, Seoul 120-749, Korea

*Corresponding author: ycho@yonsei.ac.kr

Keywords: SOFC, Tape-casting, Cofiring, Flatness

1. Introduction

The problems of energy crises and global warming demand to develop environmentally benign and cost-effective power sources, e.g., anode-supported planar solid oxide fuel cells (AS-SOFCs). The AS-SOFC offers simple cell design and electrical power of multi-mega Watt [1]. The particular advantage of the AS-SOFC is the potential to reduce the operating temperature of the SOFC to ~500-800°C via decreasing the electrolyte thickness to ~10 μm. 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.

The tape-casting followed by cofiring is applied, in general, for reducing the manufacturing cost of the AS-SOFC [2, 3]. The tape-casting offers low-cost and large-scale manufacturing with large area and flat sheets. However, manufacturing with high precision, reproducibility, and tapes of micron-thickness are the typical challenges to solve. The cofiring reduces the processing time and cost of manufacturing. However, it results in a camber with curvature (k) due to the differential shrinkage ($\Delta\epsilon$) of the layers. For an asymmetric laminate consisting of layers 1 and 2, the rate of change of normalized curvature can be expressed as [4],

$$\frac{dk}{dt} = \frac{d}{dt} \left(\frac{h_1 + h_2}{r} \right) = \left[\frac{6(m+1)^2 mn}{m^4 n^2 + 2mn(2m^2 + 3m + 2) + 1} \right] \frac{d}{dt} (\Delta\epsilon), \quad (1)$$

where h stands for the thickness of a layer and r for the radius of curvature of the cofired sample. In addition, the layer thickness ratio (m) = h_1/h_2 and elastic constant ratio (n) = $[\eta_1/(1-\nu_1)]/[\eta_2/(1-\nu_2)]$, where η denotes the viscosity of a layer and ν corresponds to its Poisson's ratio. The equation (1) infers that the m , n and $\Delta\epsilon$ are the crucial parameters to control the curvature of a sample. This also indicates that a sample can be made completely flat (curvature = 0) by setting up the differential shrinkage to zero for any values of m and n .

In the present paper, the flatness of an asymmetric (NiO–Ce_{0.9}Gd_{0.1}O_{1.95})/ Ce_{0.9}Gd_{0.1}O_{1.95} multi-layers is reported for the first time. The flatness is quantified by the maximum height of the camber of the cofired sample. The Ce_{0.9}Gd_{0.1}O_{1.95} (CGO) is used as a solid electrolyte because of its sufficiently high ionic conductivity at ~500-600°C. The NiO and Ce_{0.9}Gd_{0.1}O_{1.95} with 40/ 60 volume ratio is used as an anode. Various processing parameters, such as the lamination structure, use of sacrificial layers (Al₂O₃, CeO₂, Y₂O₃, and ZrO₂) and heating rate, are studied. The sample thickness is kept nearly 550 μm with the electrolyte (h_1) to anode (h_2) thickness ratio (m) of ~0.033 for reducing the materials cost, and start up and turn off time of the device.

2. Experimental procedure

The commercially-available chemicals were utilized to prepare the slurry of sacrificial layers, electrolyte and anode for the tape-casting. For example, CGO (surface area ~6.5 m²g⁻¹, particle size ~0.3 μm, Anan Kasei Co. Ltd., Japan) was used as a solid loading for the electrolyte. For the anode, the solid loading

The 26th
International Japan-Korea
Seminar on Ceramics

2009.11.24 [TUE] - 11.26 [THU]

Tsukuba International Congress Center "Epochal Tsukuba"
(Tsukuba, Ibaraki, Japan)

Extended Abstracts



Organized by
Organizing Committee of the 26th International Japan-Korea Seminar on Ceramics
Executive Committee of the 26th International Japan-Korea Seminar on Ceramics

Structural, Thermal and Electrical Properties of a Perovskite-type Cathode System, $\text{La}_{0.75}\text{Sr}_{0.25}\text{Mn}_{0.95-x}\text{Co}_x\text{Ni}_{0.05}\text{O}_{3+\delta}$

Ravindra K. Gupta, Ik Jin Choi and Yong Soo Cho*

Department of Materials Science and Engineering, Yonsei University, Seoul 120-749, Korea

*Corresponding author: ycho@yonsei.ac.kr

Keywords: Doped LaMnO_3 , Cathode, Thermal property, Electrical conductivity

1. Introduction

Solid oxide fuel cell (SOFC) is one of the most attractive power generating systems. It offers internal reforming of hydrocarbon fuels, low level of pollutants, high energy conversion efficiency and electrical power of multi-mega Watt. However, the high manufacturing cost and challenges related to materials' compatibility demand to reduce the high operational temperature (1000°C) to an intermediate-temperature range, $600\text{--}800^\circ\text{C}$. This requires a highly catalytic active perovskite-type material for replacing the conventional poor catalytic active cathode, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3+\delta}$ [1,2].

A number of cathode materials has been investigated in the past utilizing high electronic conductivity and/ or catalytic activity of Sr^{2+} doped $\text{LaM}'\text{O}_{3-\delta}$ ($\text{M}' = \text{Fe}, \text{Co}$ or Ni) [2]. The doped LSM exhibited electrical conductivity less than that of the pure LSM [3-5]. The doping of Co^{3+} and Fe^{2+} increased and decreased the coefficient of thermal expansion of LSM, respectively [4]. The Ni^{2+} doping did not alter the coefficient of thermal expansion of LSM significantly [5].

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, morphology, electrical properties and reactivity.

2. Experimental Procedure

$\text{La}_{0.75}\text{Sr}_{0.25}\text{Mn}_{0.95-x}\text{Co}_x\text{Ni}_{0.05}\text{O}_{3+\delta}$ ($0.1 \leq x \leq 0.3$) is prepared by the Pechini method [6] using lanthanum (III) acetate hydrate (99.9%), strontium acetate hydrate (97%), manganese (II) acetate tetrahydrate (99%), cobalt (II) acetate tetrahydrate (99%) and nickel (II) acetate tetrahydrate (99%). Metal salts were dissolved in distilled water under stirring. Ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$, 99%) and citric acid ($\text{C}_6\text{H}_8\text{O}_7$, 99.5%) were added drop-wise under stirring. The solution was continuously stirred at $\sim 80^\circ\text{C}$ to obtain polymeric resin. The resin was dried at $\sim 150^\circ\text{C}$ for 8 h to remove the solvent. It was then pre-calcined at $\sim 450^\circ\text{C}$ for 1 h to burn out organic components and finally calcined at $\sim 1100^\circ\text{C}$ for 2 h to produce ceramic oxide in powder form.

The X-ray diffraction (XRD) patterns of the films were obtained by X-ray diffractometer (PANalytical, model X'Pert Pro, Netherlands) using Cu K_α radiation. A Micromeritics pycnometer (Accupye 1330, USA) was used for measuring the density (ρ_m) of the powder sample. Differential thermal analysis-thermo gravimetry (DTA-TG) was carried on the powder sample by a Setaram TG-DTA unit (TGA-92, France). Thermal expansion was recorded using a MAC Science dilatometer

ELECTRICAL, STRUCTURAL, OPTICAL AND THERMAL PROPERTIES OF (1-*X*)BLEND: *X* Li[(CF₃SO₂)₂N] SOLID POLYMER ELECTROLYTE SYSTEM

RAVINDRA KUMAR GUPTA*

CRC, Department of Optometry, College of Applied Medical Sciences, King Saud University, Riyadh 11433, Saudi Arabia

HEE-WOO RHEE

*Department of Chemical and Biomolecular Engineering, Sogang University
Seoul 121-742, Korea*

Effect of Li[(CF₃SO₂)₂N] content ($x = 0 - 0.3$ in weight fraction) on the electrical, structural, optical and thermal properties of (1- x)blend: x Li[(CF₃SO₂)₂N] solid polymer electrolyte system is reported for the first time. The blend consisted of a conventional polymer matrix, poly(ethylene oxide) and a plastic crystal, succinonitrile in equal weight fraction. Salt solvation and plasticization of the poly(ethylene oxide) and succinonitrile helped to improve electrical conductivity ($\sigma_{25^\circ\text{C}}$) via increasing ionic mobility and mobile ion concentration. An increase of x increased the $\sigma_{25^\circ\text{C}}$ -value up to the optimum conducting composition ($x = 0.25$, OCC) with $\sigma_{25^\circ\text{C}} \sim 3.9 \times 10^{-4} \text{ S cm}^{-1}$. The $\log \sigma - 1/T$ curves showed a nearly Arrhenius type pattern for the OCC. The XRD pattern of the OCC was free from the reflection peaks of the constituents. In addition, no poly(ethylene oxide) spherulites was noticed in the polarized optical microscopic image. The differential scanning calorimetry showed significantly low value of the relative crystallinity for the OCC indicating plasticizing effect of the Li[(CF₃SO₂)₂N] salt.

1. Introduction

Lithium ion conducting solid polymer electrolytes (SPEs) with electrical conductivity ($\sigma_{25^\circ\text{C}}$) of $\sim 10^{-3} \text{ S cm}^{-1}$ exhibit potential industrial applications in all-solid-state electrochemical devices [1-3]. The SPE in a form of polymer matrix-LiX ($X = \text{I}, \text{BF}_4, \text{PF}_6, \text{ClO}_4, \text{CF}_3\text{SO}_3, (\text{CF}_3\text{SO}_2)_2\text{N}, (\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}$, etc.) offers various advantageous properties, such as thin-film formation to act as a separator, easy processing, flexibility, chemical and mechanical stability, and a wide electrochemical voltage window. A coordinating polar polymer, poly(ethylene oxide), abbreviated as PEO is the most commonly used polymer matrix. The PEO shows self-standing film formation, thermal stability up to 200

* For correspondence. e-mail rgupta@ksu.edu.sa, Phone: +96611469 8623, Fax: +96611469 3536