Preparation, characterization and ionic conductivity measurements of (1-x) KCl:x ZrO_2 solid electrolyte system

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Solid electrolytes in the system (1-x) KCl : x ZrO_2 were prepared by varying x (mol %) from 0.0 to 0.8 in steps of 0.1. The samples were obtained in the form of pellets by powder compaction followed by the solid state sintering process. The samples were characterized by Scanning Electron Microscope and X-ray Diffractometer for their microstructural behaviour and detection of new phases, if any, that would have formed in the samples. The dc conductivity (\(\sigma\)) of the samples was estimated from the impedance analysis data in the frequency range 100 Hz to 100 kHz. It has been found that the conductivity enhancement starts taking place appreciably from \(x=0.4\) and attains its maximum at around 70 mol% ZrO_2. The enhanced conductivity has been found to be over 3.6x10^{-6} S cm^{-1} which is about 20 times higher than that of the base matrix (KCl).

The increase in conductivity has been attributed to the space charge layer formation at the dispersoid/matrix interface.

Solid electrolytes belong to a class of materials which have high ionic conductivity of the order of 10^{-4} to 10^{-1} Scm^{-1}. The single-phase ionic solids namely alkali halides have limited conductivity as characterized by their crystal structure and the defects present within the structure. The enhancement in conductivity results in different type of materials called composite solid electrolytes. Such materials are formed by dispersing alkali halides (first phase) like LiI, CuCl and AgI, etc., with finely powdered specimens of oxides (second phase) such as Al_2O_3, SiO_2, SnO_2, etc. Conductivity of these two phases compacted solids has been studied earlier. The composite electrolytes have attracted much interest due to their technological applications in solid-state batteries, fuel cells, electrochromic display devices, etc.

Though the conductivity enhancement in two phase electrolytes was known for quite a long time, systematic investigations were made only after Liang when he reported the conductivity behaviour of LiI:Al_2O_3 system in which a 50 times enhancement in Li^+ conductivity was achieved. A large number of two-phase composite electrolyte systems with Ag^+, Li^+, Cu^+, F^-, etc. ion conductors have been reported so far.

Several models have been proposed in order to explain the observed conductivity enhancement. Almost all the models presume the formation of a highly conducting space charge layer at the host (halide matrix)/dispersoid (oxide crystallite) interface. The increase in the mobile ion concentration and/or the ionic mobility due to the creation of highly conducting paths connecting the interface regions may be considered as underlying causes for the conductivity enhancement. The volume fraction and the size of dispersoid particles also play very vital roles in controlling the conductivity enhancement in composite electrolytes.

It is seen from the literature that a considerable amount of work has been carried out on Ag^+ ion conducting composite electrolytes (single and mixed matrix) whereas not much attention has been paid to alkali halide based composite electrolytes with the exception of Li^+ conductors.

In the present study, KCl-based electrolytes in the system (1-x) KCl : x ZrO_2 have been prepared and their transport characteristics (namely conductivity, \(\sigma\), and mobility, \(\mu\)) are reported here.

**Experimental Procedure**

**Preparation of samples**—The raw materials KCl (E Merck, 99%) and ZrO_2 (having particle size 9-10 \(\mu\)m) in the required proportion for various compositions of (1-x) KCl : x ZrO_2 in different mol% were mixed using mortar and pestle and then ground using a centrifugal ball mill (Retsch). The samples were made in the form of pellets (dia=20 mm and thickness=3 mm) at a pressure level of 240 kg/cm\(^2\) in a hydraulic press. The pellets were then sintered in the temperature range 923-1123 K in a muffle furnace.
X-ray diffraction—The X-ray diffraction (XRD) patterns were recorded at room temperature using an X-ray diffractometer (Rigaku, Model D max IlIlc) employing CuKα radiation. The X-ray diffraction studies were carried out for confirming new phase(s), if any, that would have formed during sintering.

SEM photographs—In order to study the microstructure of the samples and to examine the distribution of ZrO₂ particles in the KCl matrix, micrographs were taken using a scanning electron microscope (Jeol, Model 840A).

Electrical conductivity (σ)—The ac conductivity measurements were carried out in the frequency range 100 Hz to 100 KHz using an LCR meter (HP, Model 4274A). The dc conductivity values of the samples were estimated from the plots of imaginary (Z”) vs. real (Z’) obtained from the frequency dependent complex impedance data. The activation energies for the ionic transport have been determined from the temperature dependent conductivity plot (log σ vs. 1/T plot).

 Ionic mobility (μ)—The ionic mobilities of the samples were estimated using the transient ionic current (TIC) technique12,13. The schematic diagram used for the mobility measurement is shown in Fig. 1. A fixed potential V of 2V was applied across the sample through graphite electrodes. Here graphite electrode is treated as a blocking electrode. The sample was polarized for a sufficiently long time (~2 min). After the polarization, the polarity of the electric field was reversed. The time dependent TIC response was monitored using an X-Y-t recorder. Accordingly, the response time (t) at which the current peaks up was noted and hence the ionic mobility estimated using the relation:

\[ μ = \frac{d^2}{tV} \]  

... (1)

Results and Discussion

X-ray diffraction—The X-ray diffraction patterns were obtained for all the samples of the system (1−x) KCl : x ZrO₂ where x varies from 0 to 1.0 in steps of 0.1. Fig. 2 shows the XRD pattern obtained for four typical samples having x=0, 0.5, 0.7 and 1, respectively. It can be seen from Fig. 2 that there is no evidence of new chemical compound/phase formation. The peaks due to the parent phases, i.e., KCl and ZrO₂ are retained in the composite electrolyte system. However, the intensity of the peaks is found to vary with the composition of the system.

SEM photographs—The scanning electron micrographs were taken for all the samples and those obtained for x=0, 0.5, 0.7 are shown in Fig. 3. From these micrographs, the evidence of grain formation
due to sintering is clear and the dispersion characteristics are also clearly seen. Almost uniform grain size is noticed in KCl samples [Fig. 3a].

It is clear from Figs 3b & 3c that though dispersions are clearly visible, the interconnecting interphase regions are significantly high for the sample $x=0.7$ (Fig. 3c). The isolated interfaces are observed for the sample $x=0.5$ (Fig. 3b). As proposed by various researchers,$^6-8$, the microstructural development resulting in interconnecting interface is the key factor to explain the conductivity enhancement in composite solid electrolytes.

**Electrical conductivity ($\sigma$)**—Fig. 4 shows the variation of conductivity ($\sigma$) as a function of dispersoid concentration mol% $\text{ZrO}_2$ in KCl at room temperature. It can be seen from the above figure that with the variation of dispersoid concentration from 0-40 mol%, no appreciable conductivity enhancement has been observed except at 10 mol% where the conductivity enhancement has been found to be about 6.5 times, i.e., $1.19 \times 10^{-6}$ S cm$^{-1}$. 

![Fig. 3—SEM photographs of: (a) KCl, (b) KCl-50 mol% $\text{ZrO}_2$, and (c) KCl-70 mol% $\text{ZrO}_2$ sintered samples

![Fig. 4—Composition dependence of conductivity for KCl-$\text{ZrO}_2$ system at room temperature

![Fig. 5—The variation of conductivity as a function of inverse temperature for KCl and KCl-70 mol% $\text{ZrO}_2$ sintered samples
The significant enhancement in conductivity starts at around 40 mol% and reaches its maximum at 70 mol% before falling down. The highest conductivity for \( x = 0.7 \) has been estimated as about 20 times, i.e., \( 3.66 \times 10^{-6} \text{ S cm}^{-1} \) the base matrix (KCI) conductivity. The conductivity enhancement can be ascribed to the change in the carrier concentration at/or near the interfacial region (region of space charge formation) and the increase in ionic mobility.

From the temperature dependent conductivity measurements (as shown in Fig. 5) for the samples having \( x=0 \) and \( x=0.7 \), the average activation energies are found to be different. The activation energies for KCI and the highly conducting 0.3 KCl:0.7 ZrO\(_2\) samples have been estimated to be 0.35 eV and 0.54 eV, respectively. The difference in activation energy values indicates that the mechanism of conduction in KCI is not only due to the change in carrier (K\(^+\) ion) concentration, but also due to the mobility enhancement.

The enhanced conductivity for the electrolyte composition 0.3 KCl : 0.7 ZrO\(_2\) can further be explained from its microstructural features (Fig. 3c) in which the presence of interconnecting interfacial regions were observed. The requirement of interconnecting interfacial regions for satisfying the percolation theory has also been achieved in the present study.

**Ionic Mobility (\( \mu \))**—Fig. 6 shows the transient ionic current vs. time plot obtained for the determination of the ionic mobility in the samples of highest conducting composition 0.3 KCl:0.7 ZrO\(_2\) at room temperature, i.e., 300 K. From this plot, the mobility \( \mu \) has been estimated as \( 20.8 \times 10^{-2} \text{ cm}^2\text{/Vs} \) and the same has been compared with that of KCl samples for which the value was obtained as \( \mu=5.7 \times 10^{-2} \text{ cm}^2\text{/Vs} \). Therefore, there is about 3.5 times mobility enhancement in the highly conducting composition.

**Conclusions**

The ionic conductivity of solid KCl increases with ZrO\(_2\) particle dispersion and the highest conductivity i.e. \( \sigma=3.66 \times 10^{-6} \text{ S cm}^{-1} \) was obtained with 70 mol% ZrO\(_2\) dispersoid. The conductivity enhancement was not due to the new chemical compound formation as revealed by the XRD pattern but due to the creation of interconnecting interface regions as seen from the SEM micrographs of 0.3 KCl–0.7 ZrO\(_2\) samples.

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**References**