

Short Communication

Fabrication and characterization of solid-state cells using $\text{CuI}_{100-x}-(\text{silver ortho/pyrophosphate})_x$ ($0 \leq x \leq 60$) mixed systems as solid electrolytes

N. Gogulamurali, S.A. Suthanthiraraj, P. Maruthamuthu *

Department of Energy, University of Madras, A.C. College Campus, Madras 600 025, India

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Abstract

Solid-state cells are fabricated using the best conducting compositions found in two different mixed systems, namely, $\text{CuI}-\text{Ag}_3\text{PO}_4$ and $\text{CuI}-\text{Ag}_4\text{P}_2\text{O}_7$. The discharge and polarization studies of these cells are examined. The open-circuit voltage and short-circuit current density exhibited by the two prototype systems are 639 and 635 mV and 1.2 and 2 mA cm^{-2} , respectively. The discharge and polarization studies indicate that the best conducting compositions, for the two systems, i.e., $(\text{CuI})_{0.5}-(\text{Ag}_3\text{PO}_4)_{0.5}$ and $(\text{CuI})_{0.55}-(\text{Ag}_4\text{P}_2\text{O}_7)_{0.45}$, respectively, would act as promising solid electrolytes based on Ag^+ -ion migration. This is because of their excellent physical properties.

Keywords: Solid-state cells; Copper; Iodine; Silver; Silver phosphates

1. Introduction

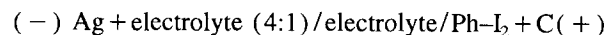
It is well known that solid electrolytes have many advantages over conventional liquid electrolytes. Hence, extensive studies have been carried out on solid-state electrochemical power sources that use various fast ionic conductors as solid electrolytes [1–5]. Most of the Ag^+ -ion conductors have limited practical usage due to the cost factor. In order to achieve cost-effective solid-state batteries, an attempt is being made in the work reported here to use new Ag^+ -ion conducting systems that are obtained by incorporating Cu^+ ions, in the form of CuI , into the lattices of two silver oxysalts, namely, Ag_3PO_4 and $\text{Ag}_4\text{P}_2\text{O}_7$ [6–8]. In earlier work, the authors established that the best conducting compositions of the two mixed systems $\text{CuI}-\text{Ag}_3\text{PO}_4$ and $\text{CuI}-\text{Ag}_4\text{P}_2\text{O}_7$ are 50mol% CuI –50mol% Ag_3PO_4 and 55mol% CuI –45mol% $\text{Ag}_4\text{P}_2\text{O}_7$, respectively. These display Ag^+ -ionic conductivities of the order of 10^{-4} to 10^{-3} S cm^{-1} at room temperature. The present work deals with the application of the above compositions as solid electrolytes in all-solid-state cells.

2. Experimental

The preparation of samples of 50mol% CuI –50mol% Ag_3PO_4 and 55mol% CuI –45mol% $\text{Ag}_4\text{P}_2\text{O}_7$, in the

form of powder specimens, has been described previously [6–8]. Since these two electrolyte compositions have been identified as Ag^+ -ion conducting materials, silver needs to be chosen as the anode. In order to reduce the anode/electrolyte interfacial resistance, a mixture of silver powder and electrolyte material was used as the anode in all the new cells. A charge-transfer complex (CTC), namely, phenothiazine-iodine CTC, ($\text{Ph}-\text{I}_2$), was chosen as the cathode (source of iodine) in view of the fact that pure iodine may sublime and lead to self-discharge of the cells. A small amount of graphite (C) was also incorporated in the cathode compartment for better cell performance, especially with regard to the cathode/electrolyte interface.

The solid-state cells had the configuration:



In cell 1, the electrolyte was 50mol% CuI –50mol% Ag_3PO_4 ; in cell 2, the electrolyte was 55mol% CuI –45mol% $\text{Ag}_4\text{P}_2\text{O}_7$.

A mixture of 0.16 g of AnalaR grade silver powder (400 mesh size) and 0.04 g of the electrolyte powder was taken as the anode layer. Thin layer was pressed together with 0.5 g of the electrolyte powder into a cylindrical pellet of 10 mm diameter at a pelletizing pressure of 4000 kg cm^{-1} . A mixture of 0.2 g of the $\text{Ph}-\text{I}_2$ CTC containing phenothiazine and iodine (in the molar ratio 2:3) and 0.1 g of graphite was pressed into another pellet. The anode-electrolyte and cathode pellets were mounted between two ebonite plates, along

* Corresponding author.

with silver foils at the current collectors at both the ends. The entire cell assembly was pressed tightly using brass bolts on four corners of the ebonite plates. This established an intimate physical contact between the various layers of anode, electrolyte, cathode, and current collectors. The whole cell assembly was encapsulated using epoxy resin, as shown in Fig. 1. It was shielded against atmospheric effects and to prevent iodine liberation from the cathode.

3. Results and discussion

The open-circuit voltage (OCV) values for cells 1 and 2 were 639 and 635 mV, respectively, at room temperature. These values are comparable to the thermodynamically estimated value of 646 mV for a solid-state cell having silver as an anode and Ph-I₂ CTC as a cathode material (as in the present case) [9]. The measured values of the short-circuit current density for cells 1 and 2 were 1.2 and 2 mA cm⁻², respectively. These values suggest that the two cells are capable of delivering current densities of the order of 100 μA cm⁻² at room temperature, i.e., currents similar to other silver batteries [10,11].

3.1. Discharge and polarization studies

The discharge curves for cells 1 and 2 under a constant load of 6.4 kΩ (medium drain) are presented in Figs. 2 and 3, respectively. Each cell was discharged until its voltage reached a cutoff value that was 0.7 times the OCV.

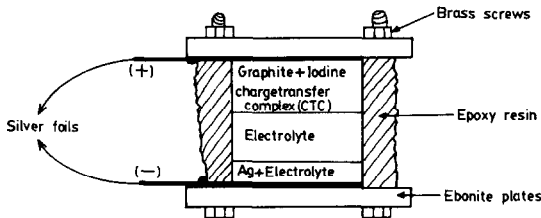


Fig. 1. Cross-sectional view of the fabricated cell.

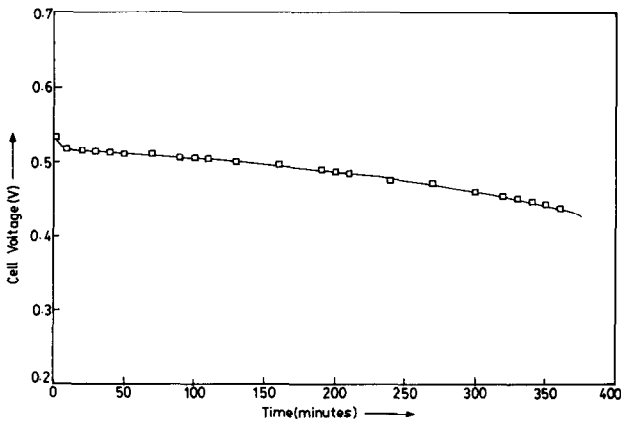


Fig. 2. Discharge curve for cell 1 at constant load 6.4 kΩ.

The patterns of the discharge curves indicate excellent electrochemical stability and compatibility of the electrodes and electrolytes. The patterns also show that during discharge, all the active materials involved in the cell reaction may not exhibit any appreciable change in morphology or crystal structure [12].

The cell voltage as a function of cell capacity is given in Figs. 4 and 5 for cells 1 and 2. A comparison of these curves suggests that both the cells exhibit excellent current capabil-

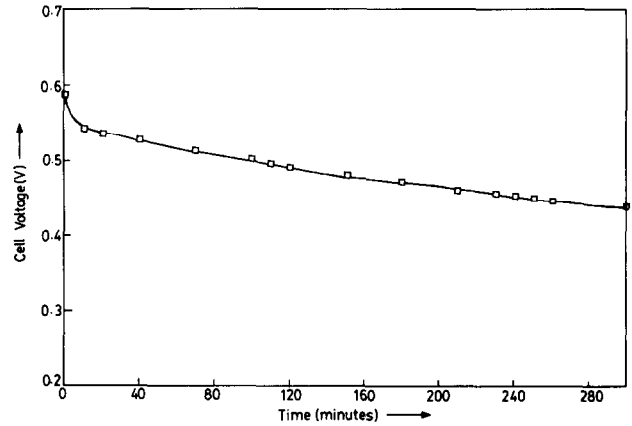


Fig. 3. Discharge curve for cell 2 at constant load 6.4 kΩ.

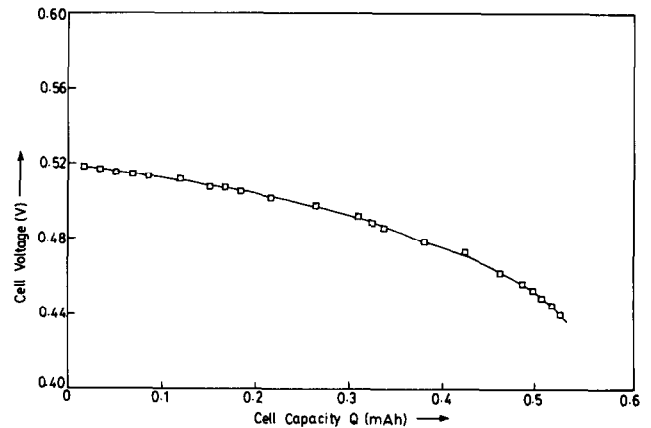


Fig. 4. Polarization curve for cell 1.

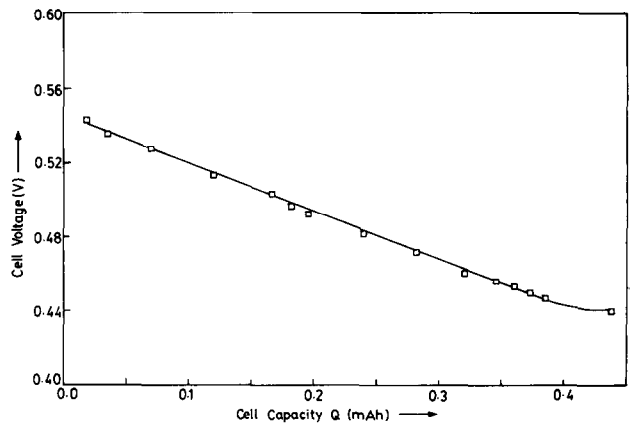


Fig. 5. Polarization curve for cell 2.

Table 1
Cell characteristics

Parameters	Cell 1	Cell 2
Open-circuit voltage (mV)	639	635
Cell diameter (cm)	1	1
Capacity (μAh)	420	350
Operating time (to 70% of OCV) (h)	6	5
Load resistance ($\text{k}\Omega$)	6.4 (medium drain $100 \mu\text{A}$)	6.4 (medium drain $100 \mu\text{A}$)
Cell weight (g)	1	1
Energy density (mWh/kg)	270	220
Short-circuit current density (mA cm^{-2})	1.2	2.0

ities. Cell 1 is characterized by a low continuous discharge current for a long time, without any appreciable polarization loss. This is due to the fact that the observed shape of its performance curve is wider than that of cell 2.

From the above performance curves, it is also interesting to note that the plots are approximately linear, except for a curve at the end. The linear regions may be attributed to the internal resistance, R_i , of the cells. A similar type of voltage loss (known as iR polarization) has already been observed in a number of conventional electrochemical cells. The appearance of a curvature at the end of the performance plots may be attributed to the coupling of the above iR polarization with 'electrode polarization'. Usually, electrode polarization arises due to the depletion of the electroactive materials. In addition, the formation of AgI as the reaction product at the cathode/electrolyte interface would contribute to the observed polarization losses in these cells [13].

Table 1 gives the estimated values of various parameters and other characteristics of the cells 1 and 2. Both cells exhibit interesting behaviour by virtue of the fact that their discharge capacities, energy densities, short-circuit current density and operating time are all appreciable. Typically, cell 1 has a cell capacity of $420 \mu\text{Ah}$, whereas cell 2 has a capacity of

$350 \mu\text{Ah}$. The data given in Table 1 also suggest that cells 1 and 2 have energy densities of 270 and 220 mWh kg^{-1} , respectively.

4. Conclusions

Discharge and polarization studies on solid-state cells with fast ion-conducting phases in two different mixed systems CuI– Ag_3PO_4 and CuI– $\text{Ag}_4\text{P}_2\text{O}_7$ show that high Ag^+ -ion conducting samples, $(\text{CuI})_{0.5}-(\text{Ag}_3\text{PO}_4)_{0.5}$ and $(\text{CuI})_{0.55}-(\text{Ag}_4\text{P}_2\text{O}_7)_{0.45}$ are promising solid electrolytes. This is due to high ionic conductivities and excellent compatibility with electrode materials.

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