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ELECTROCHEMICAL PERFORMANCE OF SILVER/MOLYBDOTUNGSTATE-AMORPHOUS-ELECTROLYTE CELLS WITH CHARGE-TRANSFER-COMPLEX CATHODES

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Summary

For the quaternary fast ion conducting system $AgI-Ag_2O-MoO_3-WO_3$, the highest ionic conductivity, 5.1×10^{-2} $(\Omega\,cm)^{-1}$, was observed when using an amorphous electrolyte composition of $80\%AgI-13.33\%Ag_2O-6.66\%$ $(0.7MoO_3-0.3WO_3)$. This electrolyte was used in the fabrication of solid-state electrochemical cells with the configuration (anode)/(amorphous electrolyte)/(cathode). The anode consisted of silver while a variety of organic charge-transfer-complex materials was employed as cathodes. The latter included phenothiazene, pyrene, and 2-perylene$\cdot 3I_2$. Cell performance was assessed by studying open-circuit voltage (OCV), anodic and cathodic polarisation, current discharge capability, and load discharge characteristics.

It was found that the cell with a 2-perylene$\cdot 3I_2$ cathode yielded the highest OCV (657 mV) without any anodic or cathodic polarisation. The cell exhibited an internal resistance of 32 Ω and a short-circuit current of 10 mA with a rechargeability having marginal coulombic efficiency. The diffusion co-efficients of silver ion were evaluated from the time dependence of cell voltage as a function of current density. The optimum current density (*i.e.*, that giving no polarisation) was fixed and the load curves were recorded to evaluate the applicability of the cells to micropower sources and low-energy-density silver batteries.

Introduction

Recent research activity on the transport and electrochemical properties of the quaternary fast ion conducting systems $AgI-Ag_2O-V_2O_5-P_2O_5$, $AgI-Ag_2O-MoO_3-WO_3$ and $AgI-Ag_2O-B_2O_3-As_2O_3$ has demonstrated the superiority of the quaternary electrolytes over the ternary or pseudobinary systems; $AgI-Ag_2O-V_2O_5$, $AgI-Ag_2O-P_2O_5$, $AgI-Ag_2O-MoO_3$ and $AgI-Ag_2O-B_2O_3$. The former systems have higher ionic conductivities, lower electronic conductivities, relatively high glass-transition temperatures, and

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can therefore be used as electrolytes in solid-state electrochemical cells [1 - 5]. For cells using quaternary fast ion conducting electrolytes, a silver anode and an iodine cathode, reports have highlighted the stability with respect to moisture and iodine diffusion [6, 7]. Although reasonably high capacities have been reported without any significant polarisation effects at low current drains, serious polarisation at the cathode–electrolyte interface has been observed at high current drains. The latter lowers the cell capacity and eventually shortens the shelf-life. In order to reduce these effects and to achieve better cell efficiencies at high current drains, different compositional ratios of cathode, anode, and electrolyte have been investigated for each system. The results, however, have been disappointing. It is considered that this is due to electrode–electrolyte polarisation effects and the formation of compounds with poor ionic conductivity at the cathode–electrolyte interface during the discharge process.

Following Liang's proposal [8] that the electronic conductivity of the solid electrolyte in equilibrium with the electrode system is more important than the intrinsic electronic conductivity, a search has been conducted for new cathode materials among the organic semiconductors commonly known as charge-transfer complexes (CTC) or organo-mineral complexes (OMC). These materials possess several beneficial properties, namely:

- low resistivity for a wide range of halogen compositions;
- ready application as cathodes without having to add dopants to achieve good electronic conductivity;
- reversibility when used as cathodes in solid-state cells.

Through the use of these materials, it is proposed that the electronic and ionic conductivity components of the transport process in the cell system at equilibrium can be engineered so that maximum discharge efficiency at high current drains is attained.

In the present investigation, the $AgI-Ag_2O-MoO_3-WO_3$ system with a composition having the highest conductivity has been used as an electrolyte with each of three organic charge-transfer complexes as the cathode material: phenothiazine (thiodiphenylamine, yellow-green colo red crystals with m.p. = 180 °C); pyrene (benzo-phenanthrene, yellow orange powder with m.p. = 149 °C); perylene (dibenzanthracene, golden yellow colour, crystalline, with m.p. = 280 °C). Silver is used as the anode material, since only this metal is compatible with the electrolyte.

Experimental

Preparation of cell materials
Electrolyte

AnalaR (AR) grade AgI, Ag_2O, MoO_3 and H_2WO_4 chemicals were used to prepare the electrolyte material. Weights of the chemicals corresponding to the required composition, namely, $80\%AgI-13.33\%Ag_2O-6.66\%(0.7MoO_3-0.3WO_3)$, were taken such that an electrolyte of 25 g was

obtained (note, % = mole%). The mixture of the individual components was placed in a quartz crucible and heated in an electric muffle furnace at a temperature of 800 °C for 6 h. The melt was occasionally stirred and finally rapidly quenched in a liquid nitrogen column. The amorphous nature of the electrolyte was confirmed by X-ray diffraction analysis. Further details of the preparation of the electrolyte are given in ref. 6.

Anode

The choice of the anode for a solid-state battery is dependent on the nature of the conducting ion in the electrolyte. In the present investigation, only silver could be used as the anode material. It was prepared by the physical blending of a mixture of silver powder (Loba, 400 mesh, AR grade), electrolyte, and graphite (carbon) powder in the ratio 67:30:3, respectively. The addition of graphite powder appears to improve the cell performance by acting both as a current collector and reducing the anode–electrolyte polarisation.

Cathodes

Three CTC materials were used as cathodes, namely: thiodiphenylamine, benzophenanthrene, and dibenzanthracene (commercially known as phenothiazine, pyrene, and perylene, respectively). The phenothiazine cathode consisted of 28% phenothiazine, 42% iodine, 6% graphite, and 24% electrolyte; while the pyrene cathode comprised 32% pyrene, 38% iodine, 6% graphite and 24% electrolyte.

The compound, 2-perylene·$3I_2$, was synthesized by reacting perylene and iodine granules in a 2:3 molar ratio in a vacuum-sealed quartz tube at 280 °C for 48 h. After cooling, the reaction product was powdered and made into a cathode structure containing 44% 2-perylene·$3I_2$, 26% iodine, 6% graphite and 24% electrolyte.

An iodine cathode was also prepared by mixing iodine, electrolyte, and graphite in the proportions: 45.45:45.45:9.10, using the procedure described earlier [7].

Cell fabrication

A 1.0 g sample of silver powder and a 1.0 g sample of finely-powdered electrolyte were formed into individual disks under a pressure of 2000 kg cm^{-2}. Both disks were then pressed into a single pellet at 6000 kg cm^{-2} in an evacuated die of 1.2 cm dia. to form the anode–electrolyte pellet. A 2.0 g sample of each cathode material was similarly made into pellets of 1.2 cm dia. and stored in an evacuated glass chamber. Cells were constructed by mounting an anode–electrolyte pellet and a cathode pellet between two ebonite plates (Formica, 5 mm thick) that were cut to a diameter of 1.5 cm and had accessible cylindrical ohmic contacts. The cell case was sealed with epoxy resin in order to avoid atmospheric effects on the electrochemical behaviour of the cells. The cells were coded as follows, and further reference is made by the corresponding number:

$$(\text{Anode})/(\text{Amorphous Electrolyte})/(\text{Iodine Cathode}) \qquad (1)$$

$$(\text{Anode})/(\text{Amorphous Electrolyte})/(\text{Phenothiazine Cathode}) \qquad (2)$$

$$(\text{Anode})/(\text{Amorphous Electrolyte})/(\text{Pyrene Cathode}) \qquad (3)$$

$$(\text{Anode})/(\text{Amorphous Electrolyte})/(\text{2-Perylene} \cdot 3I_2 \text{ Cathode}) \qquad (4)$$

Upon fabrication, the open-circuit voltages of each cell were measured with an Agronic high impedance microvoltmeter and then monitored continuously with time. A second cell of each type was discharged at different currents for 120 s and the cell potential was measured with a Keithley 614 digital electrometer. The load–discharge curves were recorded at three current drains and then compared to assess the suitability of the cell for micropower sources and low energy-density silver batteries.

Results and discussion

For the system: $X\text{AgI}-(1-X)[YAg_2O-Z(p.\text{MoO}_3-q.\text{WO}_3)]$ with x fixed at 60% and p/q at 0.5, the glass former to glass modifier ratio (Z/Y) has been varied and the best conducting composition has been found to be: $60\%\text{AgI}-40[2.0\text{Ag}_2O-1.0(\text{MoO}_3-\text{WO}_3)]$, i.e., for $X = 60$, $Z/Y = 0.5$ [3]. Keeping X and Z/Y constant at 60 and 0.5, respectively, the internal ratios of the glass formers (p/q) have been changed from 0.0 to 1.0 to give the best conducting composition at: $60\%\text{AgI}-13.33\%\text{Ag}_2O-6.66\%(0.7\text{MoO}_3-0.3\text{WO}_3)$, i.e., for $X = 60$, $Z/Y = 0.50$ and $p/q = 7/3$ [9]. Finally, on varying the AgI mole%, and fixing the best conducting p/q and Z/Y ratios at 0.7/0.3 and 0.5, respectively, the composition: $80\%\text{AgI}-13.33\%\text{Ag}_2O-6.66\%(0.7\text{MoO}_3-0.3\text{WO}_3)$ yielded the highest ionic conductivity, namely, 5.10×10^{-2} $(\Omega\,\text{cm})^{-1}$, an electronic conductivity of 6.9×10^{-9} $(\Omega\,\text{cm})^{-1}$, and a transport number of 0.9998 at 303 K. These values are higher than those obtained for the $\text{AgI}-\text{Ag}_2O-\text{MoO}_3$ and $\text{AgI}-\text{Ag}_2O-\text{WO}_3$ systems [10 - 12]. This demonstrates the superiority of quaternary amorphous materials as electrolytes for solid-state batteries.

Open-circuit voltage

On activation of the electrochemical cells by pressing anode–electrolyte and cathode pellets together, and after sealing the cell in an ebonite case with epoxy resin, the measured open-circuit voltage (OCV) was 686 mV, 640 mV, 657 mV, and 648 mV for cells (1) - (4), respectively.

Figure 1 gives the variation of cell OCV with temperature. Cell (1) exhibits a large variation in OCV which is due to the high iodine vapour pressure at high temperatures. Thus, liberated iodine diffuses into the electrolyte and reduces the stability of the cells at high temperatures. The same is true for phenothiazine (cell (2)), but to a lesser extent, as the diphenylamine captures the liberated iodine to form a complex in the cathode structure. At higher temperatures, however, thiodiphenylamine liberates
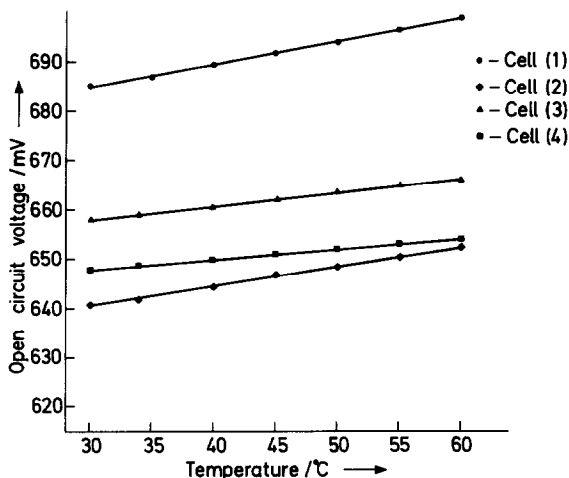
Fig. 1. Temperature dependence of open-circuit voltage for cells of configuration Ag/ electrolyte/cathode with different cathode materials (see text).

iodine due to the break up of the phenylamine and thionyl groups on dehalogenation from the ring structure. For the other two cells (*i.e.*, numbers (3) and (4)) with benzene-derivative complexes in the cathode structure, the variation is less because of the strong trapping nature of the ring-structure, covalently-bonded complexes. The halogenation of complexes to form partial ionic bonds reduces the vapour pressure of free iodine at high temperatures and thus results in stability under such conditions. The variation in OCV is considerably less in the cells using a 2-perylene·$3I_2$ complex cathode. From these studies, it can be concluded that 2-perylene·$3I_2$ cathode cells have the highest stability with the greatest inertness to iodine diffusion into the electrolyte, thus enhancing the shelf-life at ambient temperatures.

Polarisation studies
        The cell potential was continuously monitored for all the cells. It was found that the potential of each cell under no load conditions remained constant for a period of three months. This is partially due to the very low electronic conductivity of the electrolyte and to the lack of iodine diffusion into the electrolyte when the cell is inoperative. On studying the cell potential variation at different current drains ranging from 1.0 μA cm^{-2} to 10.0 mA cm^{-2}, no polarisation effects were noted at low current drains for any of the cells, as shown in Fig. 2.
        The cell potentials were recorded 120 s after connecting the load for various discharge currents. As seen in Fig. 2, cells of type (1) show marked polarisation from 100 μA onwards. Such behaviour was not observed in the cells with CTC cathodes. Hence, discharge current densities in the mA range can be achieved in the case of CTC cathode-material cells. Cell (2) exhibits pronounced polarisation effects at 500 μA, cell (3) at 1.0 mA and cell (4)
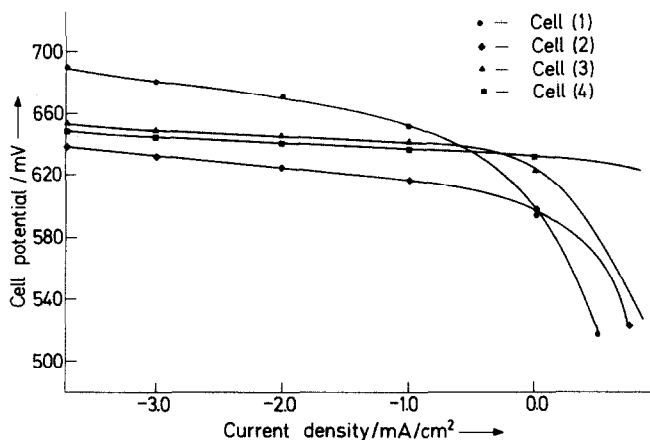
Fig. 2. Current–voltage curves at 32 °C for cells (1) - (4).

at a much higher value of 10.0 mA. Thus, a remarkable increase in the cell efficiency has been observed in cells with 2-perylene·$3I_2$ cathode structures.

To highlight the discharge efficiency of these cells, the discharge profiles were compared with each other at a given current drain of 250 $\mu A\ cm^{-2}$. All the cells exhibit a good discharge efficiency devoid of serious polarisation. As can be seen from Fig. 3, a reduction in the cell potential from 686 mV to 600 mV was observed for cell (1) over a period of 10 h. The reduction was from 648 mV to 635 mV for cell (4) over the same period, which is attributed to the initial polarisation during the discharge process. For cells (2) and (3), the cell potential decreases from 640 mV to 580 mV and from 657 mV to 610 mV, respectively. The observation of negligible initial polarisation effects in cell (4) containing the 2-perylene·$3I_2$ complex suggests the suitability of these cathode cells for both low, and high, discharge current densities. The capacities of cells (1) - (4) were 13.75
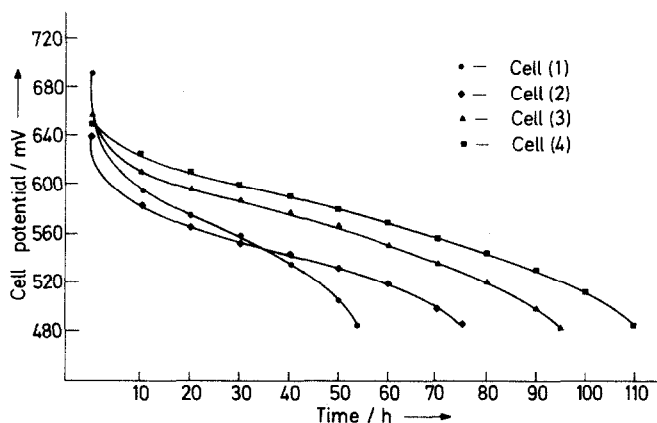

Fig. 3. Cell potential *vs.* time for cells (1) - (4).

mA h, 18.25 mA h, 23.75 mA h, and 27.90 mA h, respectively, as deter-
mined from the discharge patterns to 500 mV (Fig. 3). Thus, on using CTC
materials in the cathode structure, the cell capacity of (silver)/(silver molyb-
dotungstate)/(iodine) increases from 13.75 mA h to 27.90 mA h, which is
considered to be the best result observed to date for silver based systems.

Discharge characteristics

Since 2-perylene·$3I_2$ cells were found to have high cell capacities
without any polarisation effects, the discharge curves were determined at
different current drains (Fig. 4). At low-current drains, high capacities are
achieved and the cells are capable of delivering currents up to 1.0 mA cm^{-2}
without damage. The possibility of rechargeability was also investigated, as
the chemical kinetics of the CTC materials in the cathode structure are
inherently reversible. Discharge/charge cycling tests at a curent density of
0.25 mA cm^{-2} has indicated an excellent discharge efficiency; these results
are very encouraging. High cycle life, however, could not be achieved due to
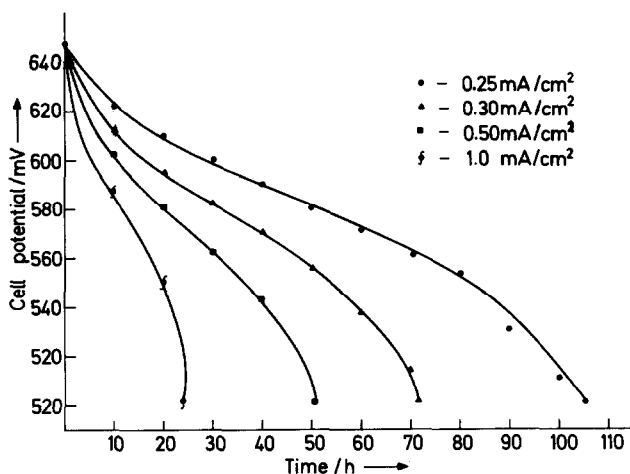the poor reversibility of the amalgamated anode in the cell.

Fig. 4. Constant-current discharge curves at 32 °C for cell (4).

In summary, it is concluded that the cathode material 2-perylene·$3I_2$
fulfils all the requirements of a good cathode devoid of those surface inter-
facial problems that generally exist in solid-electrolyte cells. High cell effi-
ciencies were obtained due to the elimination of electrode polarisation
phenomena that assume real significance in the practical use of solid-state
batteries as micropower sources. Further studies are being directed towards
the development of an all-solid-state battery, with ten cells stacked in series
to obtain a practical voltage of 6.4 V, at a current density of 0.25 mA cm^{-2}.

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