

Short Communication

Performance of 30Li₂SO₄: 70Ag₂SO₄ Solid Electrolyte in Galvanic Cells

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Summary

The performance of electrochemical cells with configurations Ag/30Li₂SO₄: 70Ag₂SO₄/C + I₂ + El and Ag/30Li₂SO₄: 70Ag₂SO₄/MnO₂+ I₂ + El (El = solid electrolyte) has been evaluated at room temperature. The cell with a graphite-containing cathode gives satisfactory results with an open-circuit voltage of 671 mV, a short-circuit current of 380 μA, an internal resistance of 2 kΩ, and an optimum discharge capacity of 0.14 mA h at a current drain of 20 μA.

Introduction

Solid-state batteries have been the subject of intensive investigation because their chemical stability leads to exceptionally long shelf-lives and discharge lifetimes. Most of the reported work has been concerned with silver systems utilizing solid electrolytes derived from silver iodide [1]. Among the existing silver-ion conducting electrolytes, RbAg₄I₅ and Ag₃SI possess a very high ionic conductivity, but the essential requirements for a good solid electrolyte rule out the possibility of using these materials in specific applications because of the thermal instability of RbAg₄I₅ above 300 K [2], and the appreciable electronic conductivity of Ag₃SI. With this background, it is necessary to search for a suitable material based on sulphate compounds that has specific advantages over the other crystalline solid electrolytes. A special advantage is that many mono- and divalent ions are particularly mobile in f.c.c. and b.c.c. sulphate phases and thus could possibly serve as anodes in power sources. As a result of this property, the performance of a number of electrochemical cells using binary and ternary sulphate mixtures at temperatures above ambient has been investigated [3].

Measurements on rapidly quenched specimens of the Li₂SO₄:Ag₂SO₄ binary system reveal an enhancement in conductivity, with a maximum value for a 30Li₂SO₄-70Ag₂SO₄ sample. The improved conductivity has been attributed to the partial trapping of the high-temperature phases at room

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temperature [4]. The aim of the work presented here has been to study the electrolytic properties of the highly conducting $30\text{Li}_2\text{SO}_4:70\text{Ag}_2\text{SO}_4$ system in terms of its application in a galvanic cell operating at room temperature.

Experimental

Electrolyte preparation

The electrolyte was prepared from Ag_2SO_4 (E. Merck, India) and Li_2SO_4 (Fluka A.G., Switzerland), both of AR quality. Appropriate amounts of the previously dried materials were ground thoroughly under acetone and melted in a porcelain crucible, followed by quenching in stainless-steel twin rollers of 5 cm dia. rotating counterclockwise at 2500 r.p.m. A detailed description of sample preparation is given elsewhere [4].

Electrochemical cells

Pellets of a fine silver powder (99.9% pure) to serve as the anode, a previously ground mixture of cathode constituents, and the electrolyte were prepared separately at a pressure of 10 tons cm^{-2} . These pellets were used to assemble the following two cells:

Cell 1: $\text{Ag}/30\text{Li}_2\text{SO}_4:70\text{Ag}_2\text{SO}_4/\text{C} + \text{I}_2 + \text{El}$ (4.5:4.5:1)

Cell 2: $\text{Ag}/30\text{Li}_2\text{SO}_4:70\text{Ag}_2\text{SO}_4/\text{MnO}_2 + \text{I}_2 + \text{El}$ (4.5:4.5:1)

(El = Electrolyte)

The cathode component contained a mixture of electrolyte and graphite (or MnO_2) in addition to I_2 powder, so that both ionic and electronic conductivities corresponded to those reported by Heed *et al.* [3]. The voltage and the current of the cell were measured with a Keithley digital programmable electrometer, Source Model 617.

Results and discussion

Table 1 provides data on the different parameters of cells 1 and 2 at room temperature. It can be seen that the initial value of the open-circuit potential (OCV) for both cells is close to the theoretical value of 687.3 mV [5, 6] for the standard e.m.f. of formation of AgI by the reaction

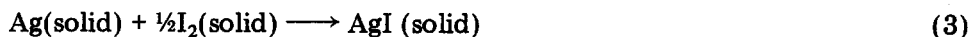
TABLE 1

Comparative performance of $30\text{Li}_2\text{SO}_4:70\text{Ag}_2\text{SO}_4$ with different cathode materials

Cell no.	Maximum OCV (mV)	Maximum SCC (μA)	Time to maximum current (days)
1	671	380	10
2	665	260	13



Electrolyte = Ag^+ produced at anode moves through electrolyte



Cell 1, using graphite, offers higher OCV and short-circuit current (SCC) than cell 2 with MnO_2 .

Figure 1 shows the variation of the SCC with time (days) after assembly of both types of cell. It is observed that the SCC of cell 1 attains a stable, saturated value of $380 \mu\text{A}$ after a period of 10 days, whereas cell 2 fails to provide a stable performance even after 15 days. Thus, work on the latter cell was discontinued.

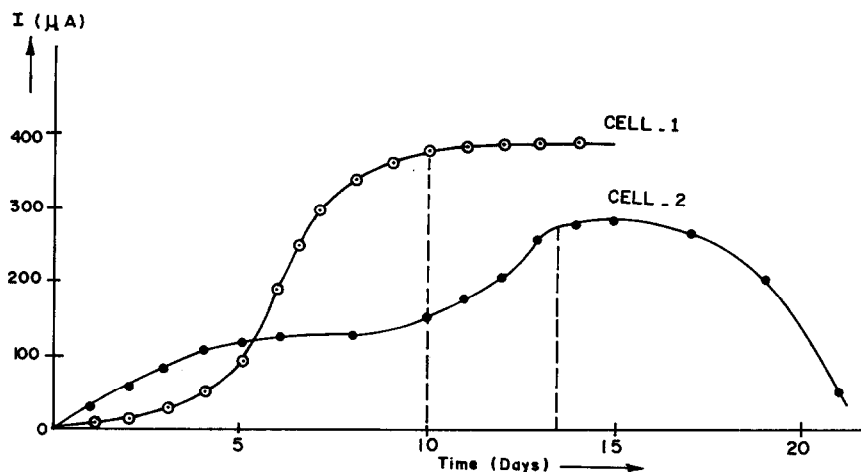


Fig. 1. Variation of short circuit current with time. See test for composition of cells 1 and 2.

Figure 2 presents the voltage-current density relationship for cell 1. The results show that there is a linear relationship up to a current density of $110 \mu\text{A cm}^{-2}$. The deviation from linearity at higher values of the current density can probably be attributed to cathodic and anodic polarization [7]. The latter can be ameliorated by making improvements to the cathode and anode assembly.

The internal resistance (I_R), calculated from the straight line tangent in Fig. 2, up to a current density of $110 \mu\text{A cm}^{-2}$ is $2 \text{ k}\Omega$. The variation of the voltage of cell 1 with time for different load conditions is given in Fig. 3. From these data, it is observed that the voltage initially falls rapidly with time and then attains a steady value. The cell yielded initial current densities of 32.65 , 139.95 and $178.83 \mu\text{A cm}^{-2}$ under $10 \text{ k}\Omega$ load, $1 \text{ k}\Omega$ load and short-circuit conditions, respectively.

The variation of cell voltage with time for different discharge current drains is given in Fig. 4. The inset shows a plot of the calculated discharge

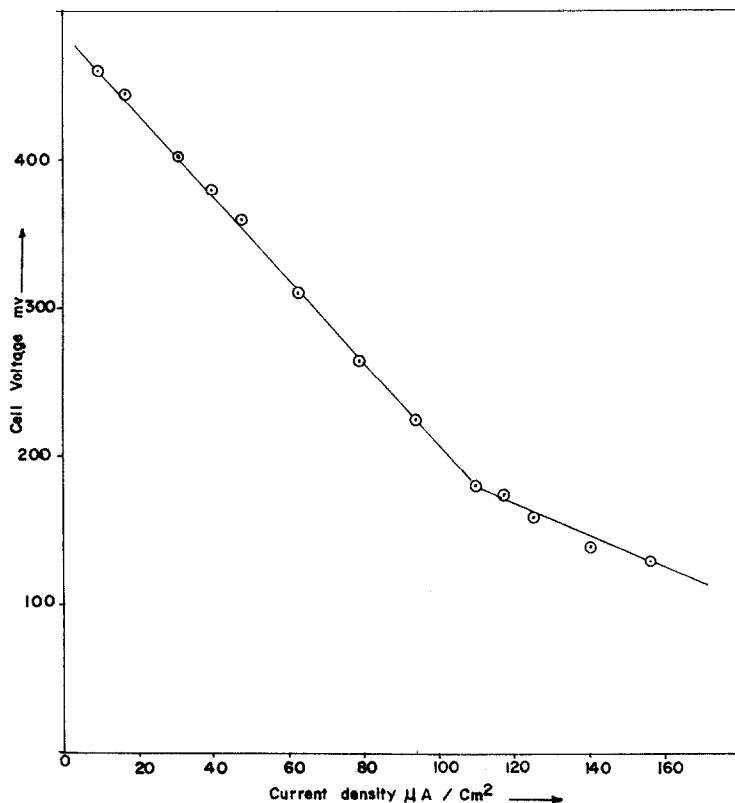


Fig. 2. Voltage-current relationship for cell 1.

capacity as a function of current drain; the discharge parameters are summarized in Table 2. From the inset of Fig. 4, it is clear that the discharge capacity value increases with current drain up to $20 \mu\text{A}$, and then decreases. The maximum discharge capacity values and the corresponding energy density are 0.14 mA h and $23.4 \text{ mW h kg}^{-1}$, respectively, at a current drain of $20 \mu\text{A}$.

TABLE 2

Discharge characteristics of cell 1 under different current drains
(Cell weight, 2.91 g ; electrolyte thickness, 0.15 cm ; electrolyte dia., 1.28 cm .)

	Current drain (μA)			
	10	20	30	40
Discharge capacity (mA h)	0.08	0.14	0.09	0.03
Energy density (mW h kg^{-1})	14.80	23.40	12.52	3.71

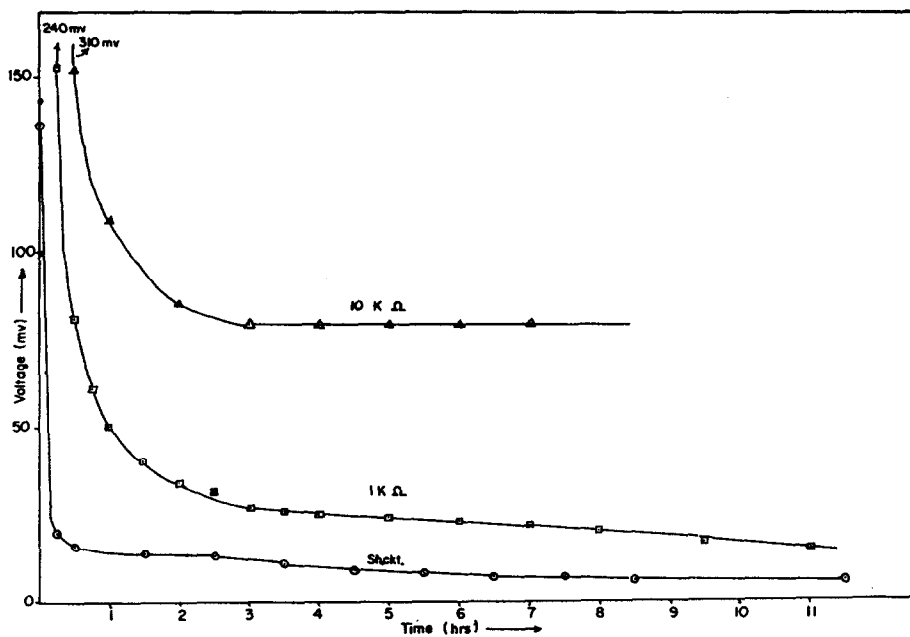


Fig. 3. Time dependence of voltage for cell 1 under different loads.

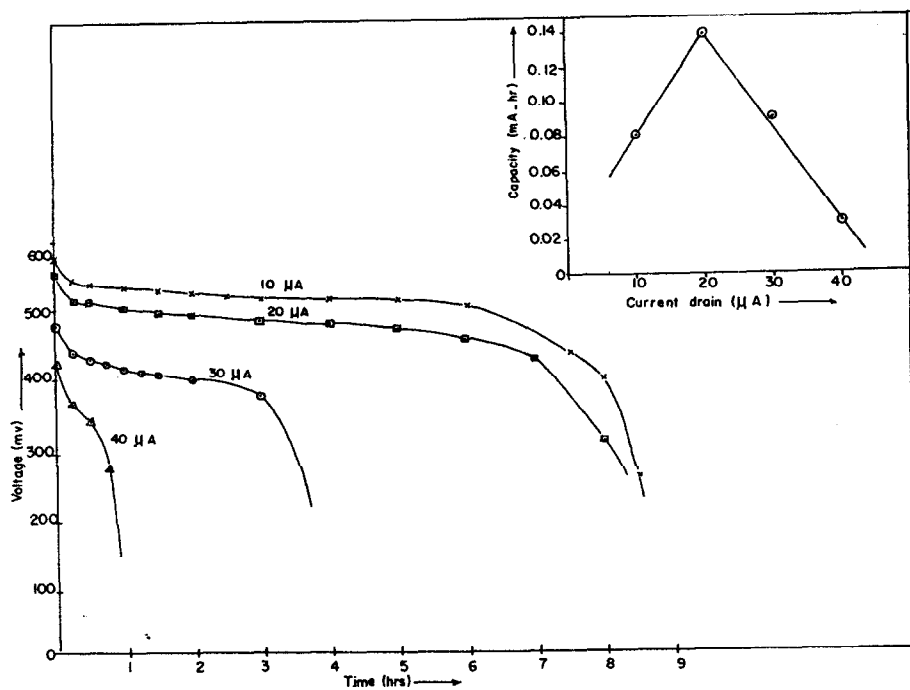


Fig. 4. Time dependence of voltage for cell 1 under different current drains. Inset gives calculated discharge capacity.

Acknowledgement

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