

ELECTROCHEMICAL CHARACTERISATION OF LITHIUM-SILVER CHROMATE COIN CELLS

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The lithium-silver chromate cell, because of its high rate capability, long shelf-life, high reliability and two-stage voltage plateau, is widely used the world over in implantable pacemaker devices. Silver chromate prepared in the laboratory was characterised by X-ray diffraction and particle size analysis. Button type lithium-silver chromate cells of the type 2450 were assembled using two different electrolyte compositions and studied for their cell discharge and current-voltage characteristics. Electrochemical impedance spectra of the cells were obtained at 303 and 278 K and cell parameters were evaluated from the impedance data.

Keywords: Li-Ag chromate cells and pacemaker devices

INTRODUCTION

The development of lightweight, compact power packs having high energy density and long storage life for biomedical applications has been a focus of attention for battery researchers during the past two decades. Lithium-silver chromate cell is one of the early cells that qualified for implantable biomedical devices and it has been in use since 1974 to power cardiac pacemakers [1]. This system is bestowed with a high rate capability, long shelf-life, high reliability and two-stage discharge profile, the second voltage plateau serving as an end-of-life indicator. In this paper, we report the results of a study on the material characterisation of silver chromate as well as studies of current-voltage characteristics, galvanostatic discharge behaviour and impedance analysis of the lithium-silver chromate cell system using two electrolyte solutions at different temperatures.

EXPERIMENTAL

Cathode

The silver chromate powder used in this study was prepared as reported by Gabano and Lehmann [2]. That the product obtained was single phase crystalline silver chromate was confirmed by X-ray diffraction analysis using CuK_α radiation

on a Jeol JDX 8030 X-ray diffractometer. The average particle size and specific surface area of the silver chromate powder were determined using Malvern Instruments EASY particle sizer M 3.0 and were found to be 18.4 μm and 0.08 m^2/cc respectively.

The cathode mix was prepared by intimately mixing silver chromate powder with 10% by weight of colloidal graphite and 10% by weight of Teflon in the form of a colloidal suspension and drying the mixture at 373 K. Cathode pellets of dimensions 20 mm diameter and 2 mm thickness were made by pressing the mix in a die under 200 kg/cm^2 pressure. This pellet was then placed on an expanded nickel mesh spot-welded to the cathode cup [3].

Anode

Pure lithium metal ingots (Cyprus Foote Mineral, USA) was shaped into circular discs of 1.5 mm thickness and 20 mm diameter and swaged on to an expanded nickel mesh welded to the anode can.

Separator

Celgard 2400 was used as the separator.

Electrolyte

Lithium perchlorate (Purum, Fluka) was vacuum-dried at 433 K for 24 hours. Propylene carbonate (PC) (Purum, Fluka) stored over 4Å molecular sieves (Linde, Union Carbide) for several days was dried over calcium oxide for 24 hours and distilled under reduced pressure. 1,3-Dioxolane (DOL) (Purum, Fluka) was refluxed for two hours with lead (IV) oxide, cooled and filtered. Xylene and more lead (IV) oxide were added and the mixture was fractionally distilled. The main fraction collected at 343-344 K was treated with xylene and sodium wire and then distilled. More sodium was added to the product and finally the sample boiling at 347-348 K was collected [4]. 1 M solutions of LiClO_4 in PC and a 1:1 (v/v) mixture of PC and DOL were used as the electrolytes. The water content in the electrolyte solutions was 45 ppm as measured using Photovolt Aquatest [8]. The conductivity of 1 M LiClO_4 solution in the 1:1 PC-DOL mixture was $8.7 \times 10^{-3} \text{ S.cm}^{-1}$.

Cell assembly

Cell assembly was made inside an MBraun (Germany) glove box flooded with argon. 2450 type coin cell hardware in 316 L stainless steel was used. Crimp-sealing of the cells was done using a die mounted on a fly-press.

Electrochemical studies

I-E behaviour and discharge studies were carried out at 303 K with separate cells.

A home-assembled spring-loaded impedance cell with two stainless steel disc electrodes with dimensions matching the 2450 coin cell was used for impedance measurements. The coin cell was held between the stainless steel electrodes, placed in a glass holder and introduced into a Neslab

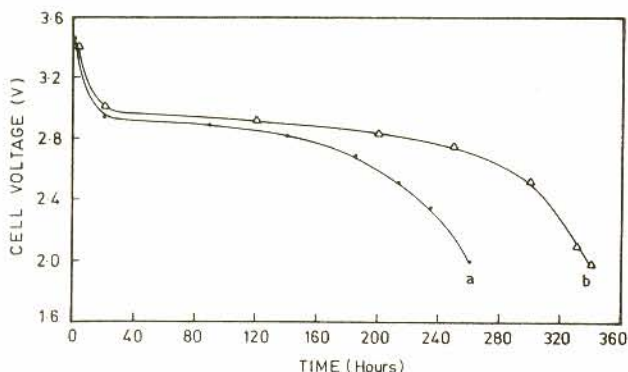


Fig. 1: Discharge curves of $\text{Li}/\text{Ag}_2\text{CrO}_4$ cell at $500 \mu\text{A}$ current drain (a) 1 M LiClO_4 in PC (b) 1 M LiClO_4 in PC and DOL (1:1)

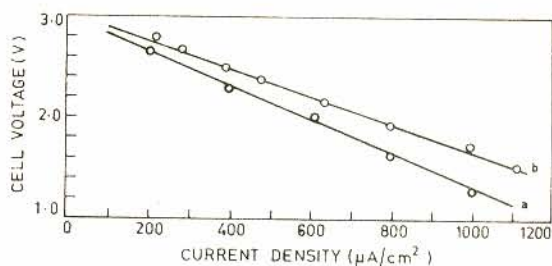


Fig. 2: Polarisation curve of $\text{Li}/\text{Ag}_2\text{CrO}_4$ cell (a) 1 M LiClO_4 in PC; (b) 1 M LiClO_4 in PC and DOL (1:1)

RTE-9DD bath with an ethylene glycol/water medium. A chromel-alumel thermocouple was positioned so that the tip was placed close to the cell environment and the temperature was monitored by a digital temperature controller. The cell was equilibrated at each temperature for at least 15 minutes before impedance measurements were carried out. Cell temperatures were maintained within $\pm 274 \text{ K}$. Impedance measurements were made with a Solartron 1250 frequency response analyser.

RESULTS AND DISCUSSION

For convenience cells employing LiClO_4 in PC and LiClO_4 in 1:1 PC-DOL will hereinafter be designated as cells a and b, respectively. In Fig. 1 typical galvanostatic discharge profiles of cells a and b at a drain rate of $500 \mu\text{A}$ are presented. A plateau at 2.6 V normally observed at low discharge rates is found to be absent in the present discharge profile which is at 500 mA rate, a rate that is about ten times the normal rate of drain. It may be seen that cells based on the PC-DOL mixed electrolyte deliver higher capacity (170 mAh) compared to those using only PC (130 mAh).

The variation of cell voltage with current was followed by varying the load externally. Fig. 2 depicts typical current-voltage curves for cells a and b for different loads. The slope of the curve gives the value for the internal resistance of the cells. Capacity and internal resistance data for cells a and b are presented in Table I.

TABLE I: Effect of electrolyte composition on cell capacity and internal resistance
current drain: $500 \mu\text{A}$; cut off voltage: 2.0 V

Cell No	Electrolyte used	Total cell capacity (mAh)	Internal resistance value from I-E curve (Ohms)
a	1 M LiClO_4 in PC	130	800
b	1 M LiClO_4 in PC + DOL	170	656

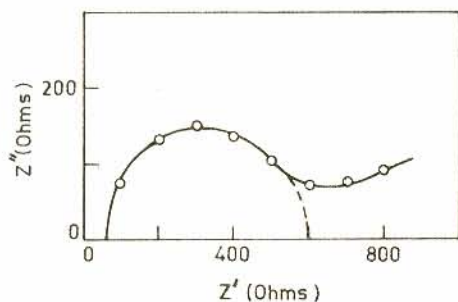


Fig. 3: Impedance diagram of $\text{Li}/\text{Ag}_2\text{CrO}_4$ cell (1 M LiClO_4 in PC) at 303 K

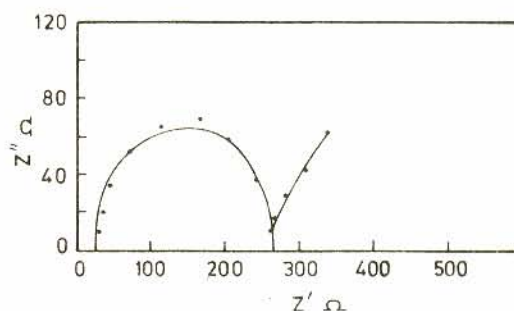


Fig. 5: Impedance diagram of $\text{Li}/\text{Ag}_2\text{CrO}_4$ cell (1 M LiClO_4 in PC and DOL) at 303 K

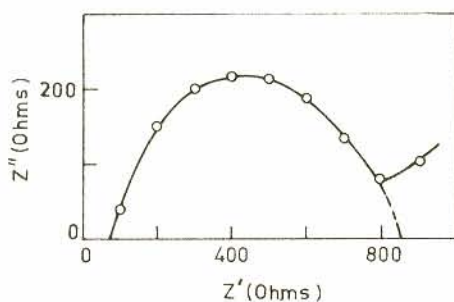


Fig. 4: Impedance diagram of $\text{Li}/\text{Ag}_2\text{CrO}_4$ cell (1 M LiClO_4 in PC) at 278 K

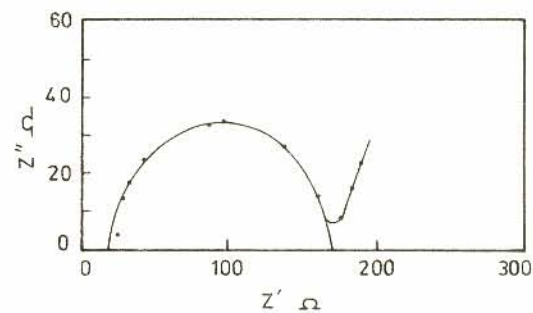


Fig. 6: Impedance diagram of $\text{Li}/\text{Ag}_2\text{CrO}_4$ cell (1 M LiClO_4 in PC and DOL) at 278 K

Cells were fabricated and stored for 10 days before they were subjected to impedance measurements. Figs. 3 to 6 show typical complex plane plots obtained for cells a and b. As may be seen the plots are similar. The semicircular portion appearing at the high frequency end of the plot gives the charge transfer resistance, R_{act} of the anode. The high value of R_{act} implies that there is a passive film on the anode surface. This passive film is the result of interaction of metallic lithium with the components of the electrolyte. The Warburg line appearing at the low frequency end of the semicircular plot is due to diffusion processes taking place through the pores of the cathode. The various parameters obtained from the impedance plots are presented in Tables II and III. At the higher temperature, the value of R_{act} is low. This may be attributed to the lowering of viscosity of the electrolyte which would, therefore, imply that these cells would deliver higher power outputs at higher temperatures.

TABLE II: Variation of impedance parameters of $\text{Li}/\text{Ag}_2\text{CrO}_4$ cell with temperature
Electrolyte: 1 M LiClO_4 in PC

Temp K	R_{soln} (ohm)	R_{act} (ohm)	C_{dl} ($\mu\text{F cm}^{-2}$)	i_0 (mA cm^{-2})
303	60	550	1.45	15×10^{-3}
278	70	780	1.27	9.8×10^{-3}

TABLE IV: Variation of impedance parameters of $\text{Li}/\text{Ag}_2\text{CrO}_4$ cell with temperature
Electrolyte: 1 M LiClO_4 in PC - DOL (1:1)

Temp K	R_{soln} (ohm)	R_{act} (ohm)	C_{dl} ($\mu\text{F cm}^{-1}$)	i_0 (mA cm^{-2})
303	17.5	150	10.6	55×10^{-3}
278	25.0	225	9.4	34×10^{-3}

CONCLUSIONS

It has been shown in this study that 1 M LiClO_4 in 1:1 (v/v) mixture of PC and DOL is a better electrolyte than 1 M LiClO_4 in PC for lithium-silver chromate cells. Cells employing the mixed solvent was found to give more capacity than the cells containing only propylene carbonate.

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