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SHORT COMMUNICATION

A thin layer, solid-state, primary Li|Ag_2CrO_4 polymer battery

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1. Introduction

The majority of lithium polymer batteries under development use intercalation compounds as cathode materials [1]. The lithium-intercalation compound combination benefits from high cyclability, but suffers from sloping charge and discharge voltage profiles. In previous work we have described some new types of lithium polymer batteries based on nonintercalation cathode materials which involved Li|Ag_2WO_4 or Li|$CuWO_4$ couples [2]. The use of these electrochemical systems in combination with a highly-conducting polymer electrolyte membrane, allowed the fabrication of thin-layer, laminated batteries having very interesting features, such as flat, high-voltage discharge curves, high-rate discharge capability and a limited but significant cycling life. Considering these promising results, we have extended the study by considering the Li|Ag_2CrO_4 electrode system, which, although used in liquid electrolyte batteries [3], to our knowledge has never been tested in solid-state, lithium polymer electrolyte batteries. Silver chromate is expected to be more promising cathode material than silver tungstate both in terms of cost and of specific capacity. The results describing the fabrication of this new type of Li|Ag_2CrO_4 polymer battery and its electrochemical evaluation, are illustrated and discussed in this work.

2. Experimental details

The polymer electrolyte was obtained by immobilizing an appropriate solution (e.g., a solution of lithium perchlorate, $LiClO_4$, in a propylene carbonate-ethylene carbonate, PC–EC mixture) in a poly(methylmethacrylate), PMMA matrix. The details of the procedure for the synthesis of these PMMA-$LiClO_4$–PC, EC electrolytes have been reported previously [4].

Silver chromate was prepared by adding an aqueous solution of silver nitrate (0.09 M) to an aqueous solution of sodium chromate (0.0452 M). The precipitate was washed and dried at 180 °C. The purity of the final Ag_2CrO_4 salt was measured by X-ray powder analysis. The cathode membrane was formed by blending a mixture of the salt (i.e., Ag_2CrO_4) and carbon with the polymer electrolyte. The following composition (in weight ratio) was used: salt: 14.9%, carbon 12.3%, PMMA: 15.2%, EC: 35.0%, PC: 18.9%, $LiClO_4$: 3.7%. The silver and the lithium salts, carbon and PMMA were mixed together and dispersed in the PC–EC solvent mixture at a temperature ranging between 40 °C and 50 °C and carefully homogenized. The dispersion was slowly heated to 100 °C to favour gelification and finally cast between glass sheets to obtain free-standing cathode membranes of approximately 300 μm thickness. The active compound in these membranes (i.e., the silver salt) provides the battery capacity, while the carbon and the polymer electrolyte provide the electronic conductivity and the plasticity (together with ionic conductivity), respectively.

The thin-layer Li|Ag_2CrO_4 batteries were fabricated in a laminated structure which included a lithium metal anode strip (Cyprous Foote source, optimized thickness: 50 μm), a polymer electrolyte film (typical thickness: 200 μm) and a cathode membrane (typical thickness: 300 μm). The batteries were assembled and sealed in an argon-filled dry box. For the cyclic voltammetry studies three-electrode cells, having a lithium reference electrode, were used.

The electrochemical characteristics and performance of the batteries were evaluated with standard electrochemical instrumentation.

3. Results and discussion

The battery studied in this work:

$$\text{Li|PMMA, LiClO}_4\text{-PC, EC|Ag}_2\text{WO}_4\text{, C} \qquad (1)$$

has an open circuit voltage (o.c.v.) of 3.35 V at room temperature which may be assumed to be related to the following main discharge process:

$$2Li + Ag_2CrO_4 \Longrightarrow Li_2CrO_4 + 2Ag \qquad (2)$$

This battery has some unique and relevant features. First, it uses a polymer electrolyte which has a very high ionic conductivity (i.e., of the order of $10^{-3}\,S\,cm^{-1}$ at room temperature [4]) and a wide electrochemical stability window (i.e., extending up to 4.5–5.0 V vs Li [4]).

The second important feature of this battery is that the main discharge process is not an intercalation reaction, but rather a displacement reaction which produces Li_2CrO_4 and Ag metal (see [2]). Since this process is based on a two-phase reaction, the voltage is expected to remain flat until completion of the discharge reaction, namely until the consumption of two electrons per Ag_2CrO_4. Furthermore, the continuous production of finely dispersed silver assures a good electronic contact throughout the entire cathode mass and this consistently reduces ohmic polarization during discharge.

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This is confirmed by Fig. 1 which illustrates typical discharge curves run at various rates. The flatness of the curves, which at rates usually required for most microelectronic devices (e.g., 0.01 mA cm^{-2}) remain constant at around 2.9–3.0 V for the entire discharge, is evident. Furthermore, capacity in excess of two faradays per Ag_2CrO_4 mole are obtained. The electrochemical process associated with this excess capacity is not yet clear. The reduction of the chromate anion may be tentatively proposed [3] but, at the present time, there is no evidence to confirm this hypothesis.

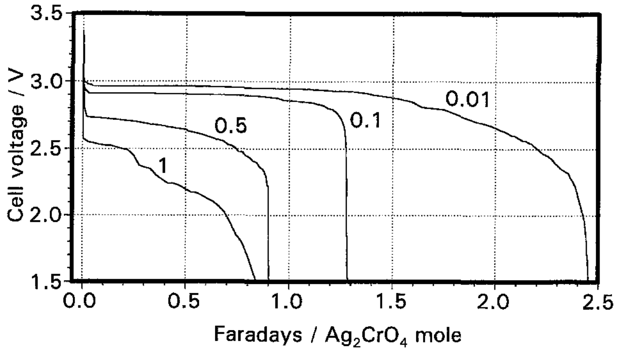

Fig. 1. Typical discharge curves of the Li|Ag_2CrO_4 thin film, polymer battery at room temperature and at various rates. The values of discharge current densities are given in mA cm^{-2}.

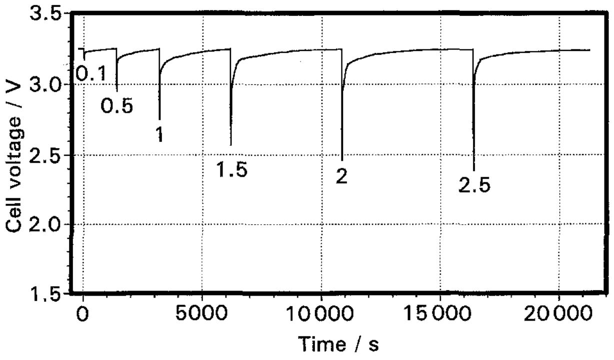

Fig. 2. Pulse (30 s) discharge at various current rates (mA cm^{-2}) of the Li|Ag_2CrO_4 thin film, polymer battery at room temperature.

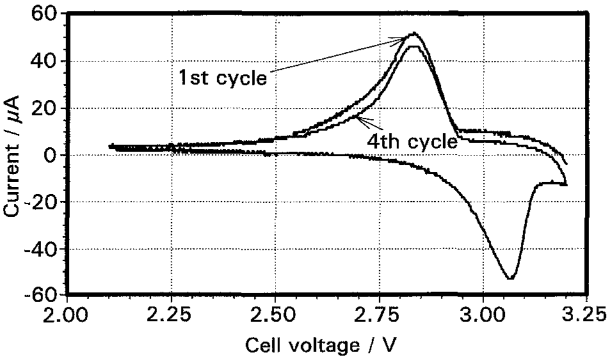

Fig. 3. Cyclic voltammetry of the Ag_2CrO_4 electrode in a PMMA, EC, PC, $LiClO_4$ electrolyte cell. Room temperature. Lithium reference. 0.25 mV s^{-1} scan rate.

The discharge characteristics of the Li|Ag_2CrO_4 polymer battery are similar to those obtained with the parent Li|Ag_2WO_4 battery [1]. These characteristics are very appealing. In fact, a flat, constant voltage discharge is a very important attribute for power sources designed for the electronic market and the availability of extra capacity which can adsorb incidental overdischarge and short circuiting, improves the battery safety and reliability. Furthermore, the control of the ohmic drop, favoured by the continuous production of finely dispersed silver during the discharge process, gives expectations of high rate capabilities. This is confirmed by Fig. 2 which shows the voltage response and the voltage recovery of the battery following short discharge pulses. This figure demonstrates that the battery can sustain high current pulses with a very fast recovery to the initial 3.35 V o.c.v. value.

It is also important to report that, although the Li|Ag_2CrO_4 cell (as the Li|Ag_2WO_4 one) was designed as a primary battery, there are indications that partial rechargeability can also be achieved when the discharge is limited to a fraction of the total capacity. This is demonstrated by Fig. 3 which illustrates a slow-scan voltammetry of the Ag_2CrO_4 electrode cycled around the 3 V range. Another favourable aspect of the Li|Ag_2CrO_4 battery in relation to its Li|Ag_2WO_4 analogue, is the relatively high energy density (670 Wh kg^{-1} theoretical), while a possible drawback is the high cost of the silver cathode. However, the latter is expected to be counterbalanced by the good performance of the battery. We also expect that other metal oxide cathodes having comparable behaviour and improved weight and cost characteristics can also be considered. One possible example is the copper tungstate cathode successfully tested in a previous work [1].

Acknowledgements

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