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Ceramic superconducting materials as intercalation cathodes in secondary non-aqueous lithium batteries

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Abstract

Electrodes formed from PTFE bound $(Ta_{1/2}Cu_{1/2})Sr_2GdCu_2O_{8-d}$ were cycled in 1 M $LiAsF_6$/propylene carbonate electrolyte using cyclic voltammetry. It has been demonstrated that the cyclic voltammograms measured below 2.0 mV s^{-1} exhibit a well defined reversible multi-peaked wave. Prototype cells incorporating both PTFE bound and thin highly porous films of $(Ta_{1/2}Cu_{1/2})Sr_2GdCu_2O_{8-d}$ exhibited an initial discharge with two well defined voltage steps. Subsequent discharge cycles only retain characteristics of the higher voltage step suggesting that the process characterised by the low voltage step is irreversible.

Keywords: Lithium secondary batteries; Ceramic superconductors

1. Introduction

The development of rechargeable lithium batteries has been the subject of intense research activity. Transition metal oxides with layer structures have been reported extensively [1,2]. Recently our attention has been drawn to a class of ceramic materials with a distorted perovskite lattice incorporating a layered structure. This class of materials is of considerable interest as they may exhibit superconductivity at around 100 K. The possibility of utilising ceramic superconductors in batteries and sensors has been discussed by Schauwers [3]. No data have been published on the electrochemical behaviour of this compound.

2. Experimental

The 1,2,1,2 phase of $(Ta_{1/2}Cu_{1/2})Sr_2GdCu_2O_{8-d}$ was synthesised by preparing a stoichiometric mixture of the oxides or carbonates of the required metals followed by milling and firing at 950°C. To achieve the necessary purity, repeated milling/firing cycles were performed until the XRD pattern was satisfactory. The cooled ceramic was then mixed with PTFE binder and biaxially rolled to produce thin mechanically stable sheets.

Thin (10 μm) porous films of $(Ta_{1/2}Cu_{1/2})Sr_2GdCu_2O_{8-d}$ were prepared by painting an ink composed of $(Ta_{1/2}Cu_{1/2})Sr_2GdCu_2O_{8-d}$ suspended in a solution of ethyl cellulose in α-terpineol onto 100 μm nickel foil and firing at 750°C for 12 h.

Electrochemical measurements of these $(Ta_{1/2}Cu_{1/2})$-$Sr_2GdCu_2O_{8-d}$ electrodes were carried out at ambient temperature in a 1 M $LiAsF_6$/propylene carbonate (PC) solution. The working electrode comprised a disc of ceramic material, ink or sheet, in a PTFE holder furnished with a platinum current collector. The counter and reference electrodes were pure lithium foil. All assembly, fabrication and filling procedures were carried out in an argon filled dry box (<25 ppm water content).

Cyclic voltammograms were recorded with a Sycopel Scientific autostat potentiostat and cell discharge profiles obtained with a custom-built battery cycling unit under computer control.

3. Results and discussion

Typical cyclic voltammograms for the ceramic material, shown in Fig. 1, are presented for scan rates between 0.08 and 1.67 mV s^{-1}. Two sets of well defined current peaks were observed on the cathodic sweeps: the largest peak (X) at 2.25 V and peak (Y) at 1.38 V. Two well defined peaks were observed on the anodic sweep: (X') at 2.45 V and peak (Y') at 1.5 V.
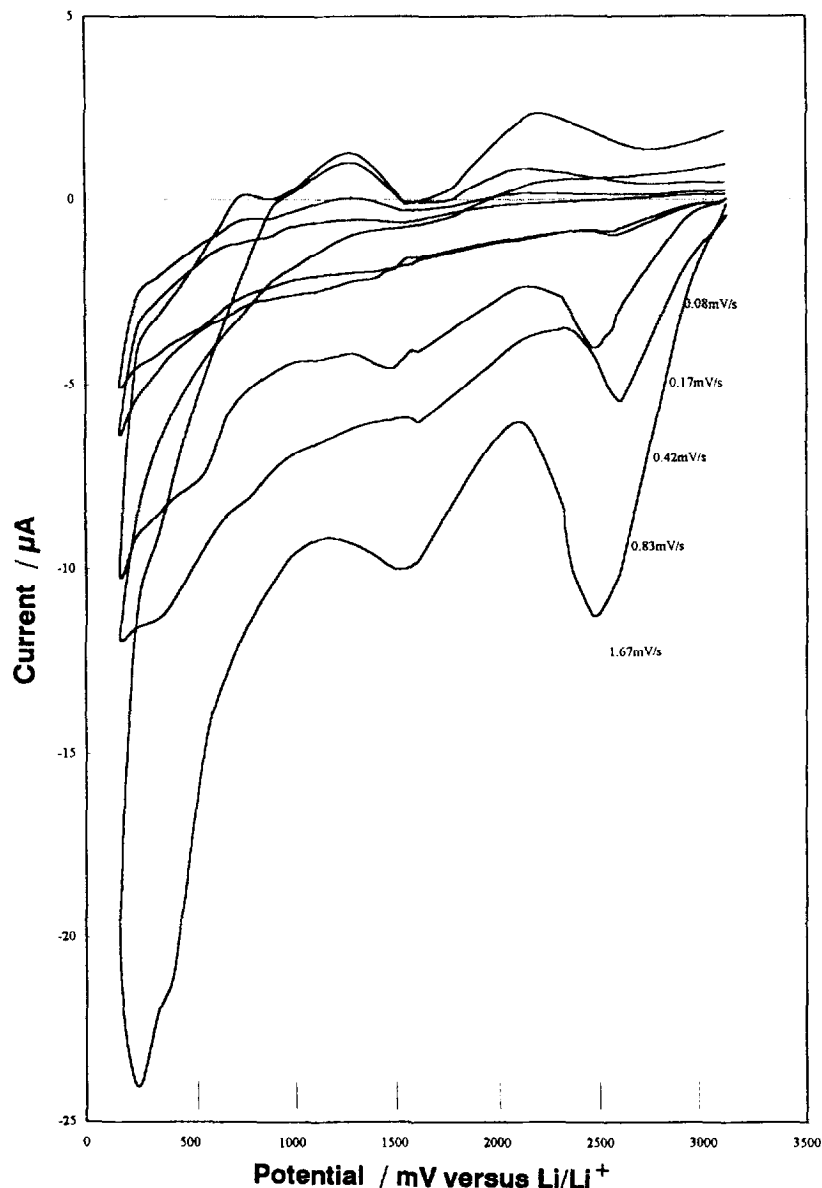
Fig. 1. Scan rate dependence of cyclic voltammograms of $(Ta_{1/2}Cu_{1/2})Sr_2GdCu_2O_{8-d}$ in 1 M $LiAsF_6$/PC.

We propose that the current peak at 2.25 V corresponds to the insertion of Li^+ ions and the corresponding peak at 2.45 V is due to the extraction of Li^+ ions. There is evidence of a large ohmic response below 0.5 V. The rolled electrode is resistive (organic polymer binder), porous and should possess a high surface area. The electrochemical response of such an electrode will be greatly distorted even at the very slow scan speeds employed.

The lower voltage peaks at 1.38 and 1.5 V lose intensity very rapidly, on multiple cycling of the same electrode, being virtually undetectable by the third cycle. This would suggest that the process occurring at the lower voltage is almost completely irreversible under the conditions employed.

Preliminary tests on prototype lithium batteries confirm that repeated cycling is possible between 2.54 V and a cut off

at 1.00 V (shown in Fig. 2). The behaviour of the cell with the rolled cathode incorporating a binder was indistinguishable from the cell utilising a thin cathode formed from the $(Ta_{1/2}Cu_{1/2})Sr_2GdCu_2O_{8-d}$ ink on nickel foil.

Fig. 3 shows the scan rate dependence of the CVs between 0.167 and 16.67 mV s^{-1}. The plot shows a straight line up to 1.5 mV s^{-1} (Fig. 4) for both anodic and cathodic sweeps. The plot deviates from linearity above 1.5 mV s^{-1} which suggests that the process is limited by diffusion of Li^+ into, or out of, the solid.

Based on a linear relationship between the peak current and the square root of the scan rate [4]:

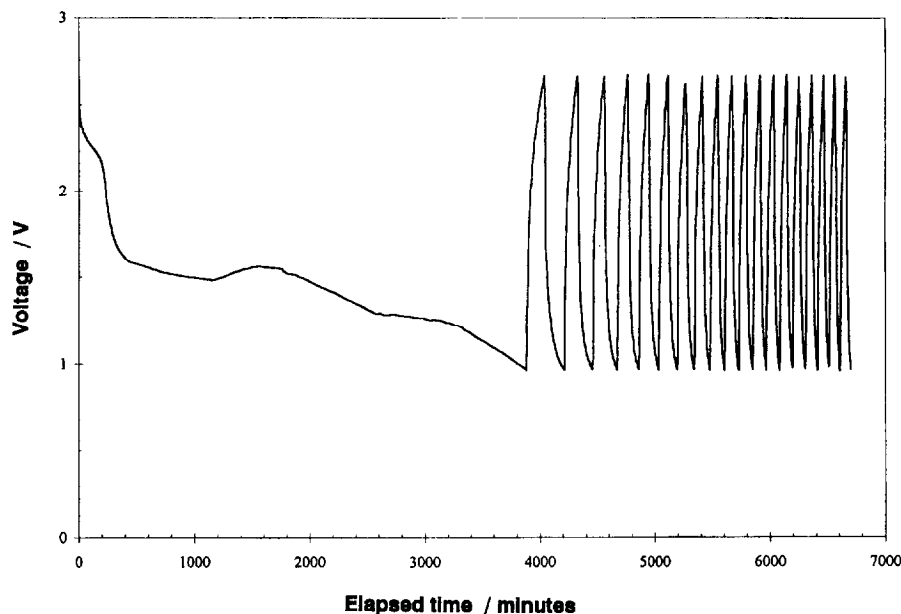$$i_p = (2.69 \times 10^5) n^{3/2} A D_o^{1/2} v^{1/2} C_o$$

Fig. 2. Cycling behaviour of a prototype lithium battery incorporating a cathode comprising $(Ta_{1/2}Cu_{1/2})Sr_2GdCu_2O_{8-d}$ with PTFE binder and 1 M $LiAsF_6$/PC as electrolyte. Cells were discharged at 25 μA cm^{-2} and charged at 12.5 μA cm^{-2} at 20°C.
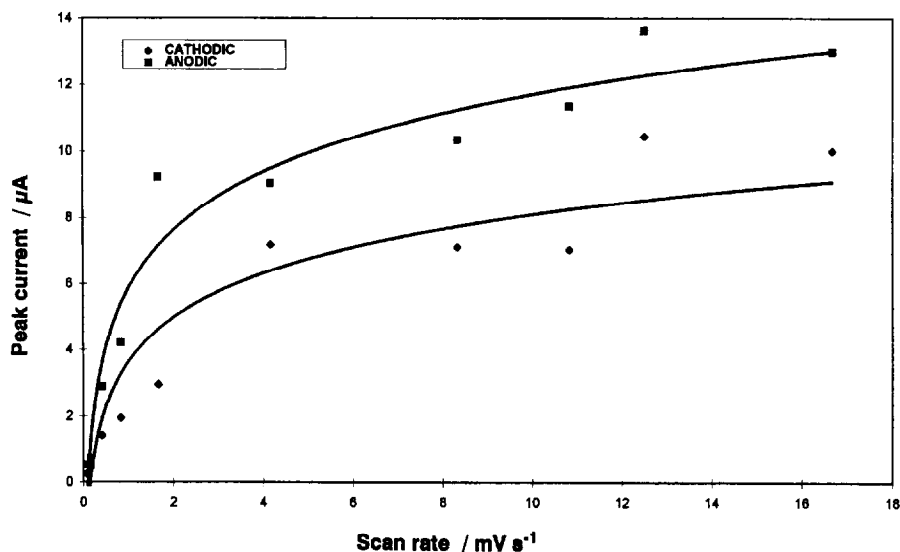

Fig. 3. Scan rate dependence of the main anodic and cathodic peaks for $(Ta_{1/2}Cu_{1/2})Sr_2GdCu_2O_{8-d}$ in 1 M $LiAsF_6$/PC.

with i_p = peak current (A); n = number of electrons associated with the redox process; A = cross sectional area of a porous electrode (m^2); D_o = diffusion coefficient of the species o (m^2 s^{-1}); v = linear potential scan rate (V s^{-1}); C_o = bulk concentration of species o (mol m^{-3}).

This square root of scan rate versus peak current dependence is shown in Fig. 5 for the main anodic (extraction of Li$^+$) peak at 2.45 V and the main cathodic (insertion of Li$^+$) peak at 2.25 V.

The calculated diffusion coefficients for Li$^+$ insertion and extraction relative to the solid phase gave $D_o = 2.2 \times 10^{-15}$ m^2 s^{-1}. This is comparable with the diffusion coefficient of Li$^+$ into the solid phase of $LiCoO_2$ (10^{-16} m^2 s^{-1}), which has been the focus of attention as a battery cathode because of its unique charge/discharge characteristics in PC [5]. $(Ta_{1/2}Cu_{1/2})Sr_2GdCu_2O_{8-d}$ is at least comparable, with respect to Li$^+$ insertion rate, to the more familiar and established $LiCoO_2$.
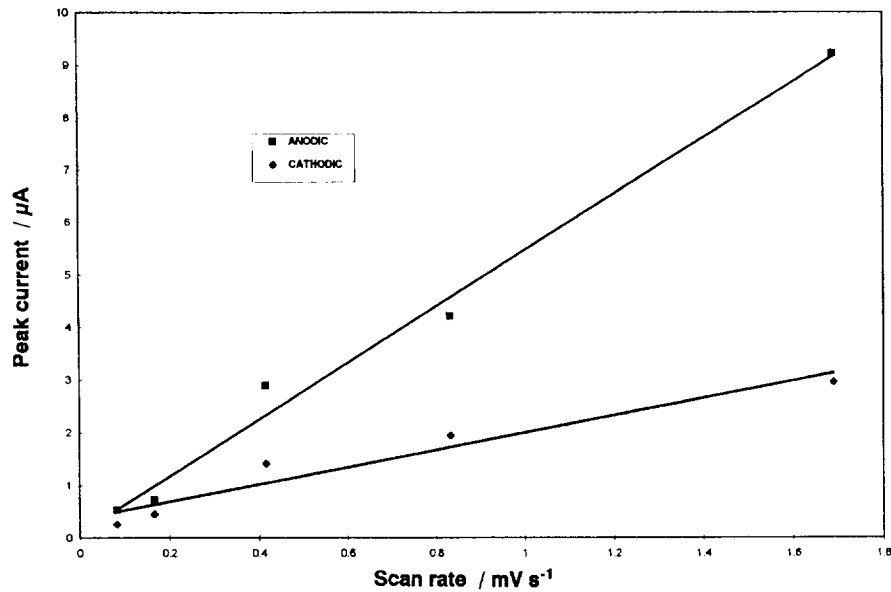
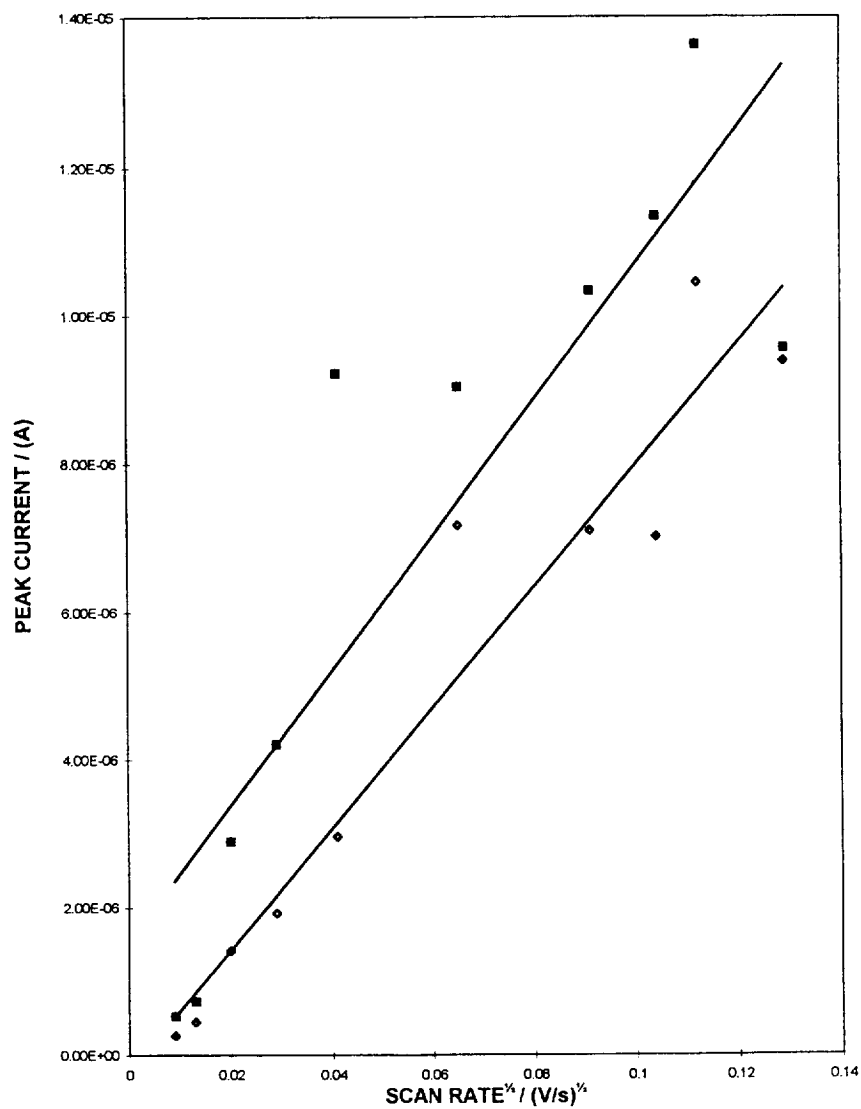Fig. 4. Linear scan rate dependence, below 1.5 mV s^{-1}, of the main anodic and cathodic peaks for $(Ta_{1/2}Cu_{1/2})Sr_2GdCu_2O_{8-d}$ in 1 M LiAsF$_6$/PC.

Fig. 5. Dependence of anodic and cathodic peak currents on the square root of the scan rate for $(Ta_{1/2}Cu_{1/2})Sr_2GdCu_2O_{8-d}$ in 1 M LiAsF$_6$/PC.

It is instantly apparent from Fig. 1 that the cathodic (insertion of Li^+) peak heights are lower than the anodic peak heights (extraction of Li^+) peak heights. This may be attributed to slow mass transfer during insertion of Li^+ ions.

4. Conclusions

The ceramic material $(Ta_{1/2}Cu_{1/2})Sr_2GdCu_2O_{8-d}$ has multi-peaked anodic and cathodic waves due to the extraction and intercalation of Li^+ ions in cyclic voltammograms recorded between 3.0 and 0 V versus Li/Li^+.

References

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