All oxide solid-state lithium-ion cells

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Abstract

Solid-state lithium-ion cells have been prepared using thin film $Li_4Ti_5O_{12}$ as the anode, thin film $LiCoO_2$ as the cathode and $Li_{0.33}La_{0.56}TiO_3$ as the electrolyte. The electrolyte was prepared as a relatively thick ceramic with a thickness close to 1 mm. This type of cell develops a voltage of slightly greater than 2 V and is stable to cycling. Perhaps the most interesting aspect of this cell, is that even with a relatively thick, poor quality ceramic electrolyte, this cell has been able to develop current densities as great as 40 $\mu A/cm^2$. © 1997 Elsevier Science S.A.

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1. Introduction

We have been interested in preparing all solid-state lithium-ion batteries by using simple chemical processes. Although there have been several preparations of thin film solid lithium batteries using physical vapor techniques [1], we have selected more simple chemical techniques to prepare the components of a solid-state lithium battery. By using a simple sol process, we have previously deposited thin film cathodes of $LiCoO_2$ on a variety of substrates [2], and we have also explored the possibility of using similar techniques to prepare the anode material $Li_4Ti_5O_{12}$ [3]. In order to prepare an all oxide solid-state lithium-ion battery it is necessary to choose the correct lithium-ion conductor. Most of our previous efforts have been directed to preparing thin films of LISICON-type materials ($Li_{3.6}Ge_{0.6}V_{0.4}O_4$) [4]. Although we have been successful in preparing this material as a thin film by spray pyrolysis techniques, we have had severe problems with short circuiting between the anode and cathode in total cells. This problem may be due to the rather primitive technique used to apply the films or the large discrepancy in the linear thermal expansion coefficient between the electrolyte and all other components of the cell (the electrolyte

shows a linear expansion coefficient of $72 \times 10^{-6}/K$ whereas the electrodes show values closer to $10 \times 10^{-6}/K$) [5].

Although the LISICON-type materials have good ionic conductivity ($10^{-5}-10^{-6}$ S/cm at room temperature) we have been recently intrigued by the lithiated perovskite $Li_xLa_{0.67-x}TiO_3$. In this work we present results on using the perovskite lithium-ion conductor $Li_{0.33}La_{0.56}TiO_3$ as the electrolyte in an all oxide lithium-ion battery. Literature work had already indicated that this compound had extremely high values of lithium-ion conductivity (of the order of 10^{-4} S/cm at room temperature) [6]; however, no evidence of the usable electrochemical window was available. We have prepared sintered pellets of the material by pressing powders to a pressure of 10 000 kg/cm^2 at room temperature and subsequently annealing. These pellets were then coated with thin film anodes of $Li_4Ti_5O_{12}$ (subsequent lithium intercalation is possible to a composition corresponding to $Li_7Ti_5O_{12}$) and thin film cathodes of $LiCoO_2$ [7] by simple spray pyrolysis in order to prepare solid-state lithium-ion cells. We have studied these cells electrochemically using slow scan cyclic voltametry and have been able to cycle these simple cells in excess of 100 times. The maximum current densities observed for the all solid-state cell are substantially lower than what we have observed in a liquid electrolyte thin film cell (40 versus 800 $\mu A/cm^2$); however, considering the thickness of the electrolyte (approximately 1 mm) and the relatively low density of these initial pellets, we find these results to be quite interesting.

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2. Experimental

We prepared the electrolyte pellets of $Li_{0.33}La_{0.56}TiO_3$ by a two-step procedure. First, we prepared powders with a very small grain size by using a sol process. The powders were prepared by reacting lithium nitrate, lanthanum nitrate and titanium tetrachloride (chloride was subsequently removed by silver nitrate titration and filtration of the silver chloride precipitate) with propylene glycol to prepare a sol. The sol contained the elements in the desired ratio with a concentration of 0.3 M. After reacting at 160–170 °C for 1–3 h the propylene glycol was removed by heating in air. The resulting powder was heated in air at 600 °C. This poorly crystalline material (X-ray diffraction pattern showed broad peaks corresponding to a cubic perovskite) was made into small pellets with 7% vaseline as the binder. The powders were subjected to a pressure of 10 000 kg/cm^2 at room temperature and subsequently annealed at 1275 °C for several hours in vacuum (the pellets were placed on a graphite pedestal for high temperature annealing and vacuum was necessary to prevent reaction of the graphite). The electrolyte was finally annealed at 950–800 °C in air to oxidize all the titanium present in the sample to the (IV) oxidation state. The final pellets had a density varying from 80–94% of the theoretical value, a thickness of slightly less than 1 mm and a diameter of 6 mm. These pellets were then coated with thin film anodes of $Li_4Ti_5O_{12}$ and thin film cathodes of $LiCoO_2$ by simple spray pyrolysis (electrode diameter 4 mm) [7]. The sols used to prepare the electrodes were prepared by reacting the necessary nitrates with propylene glycol or in the case of $Li_4Ti_5O_{12}$ titanium tetrachloride was used as the titanium source and chloride was removed by titration with silver nitrate and subsequent filtration to remove silver chloride. All samples were analyzed for crystallinity by X-ray powder diffraction (Philips XRD 3100) and morphology was examined by scanning electron microscopy (Leica stereoscan 440). Final electrical contacts were applied by evaporating gold onto both anode and cathode. The conductivity on the electrolyte was determined from a.c. impedance measurements from 10 Hz to 1 MHz at constant temperatures between 25 and 175 °C. To ensure uniform contact, the gold electrodes were contacted by soft (lead) contacts in a spring loaded cell. Slow scan cyclic voltamograms were obtained at room temperature using a MacPile battery cycling system (minimum voltage steps of 10 mV) with $Li_4Ti_5O_{12}$ as both the counter and reference electrodes.

3. Results and discussion

Although we were able to observe a broad cubic diffraction diagram on samples of the electrolyte $Li_{0.33}La_{0.56}TiO_3$ prepared at relatively low temperatures by spray pyrolysis (i.e., 600–800 °C) these samples did not show high values of ionic conductivity (conductivity was less than 10^{-7} S/cm). We subsequently prepared several ceramic samples beginning

with powders made by classical solid-state synthesis and progressing to powders with small grain size prepared by a sol approach. The initial ceramics from the relatively large grained powders resulted in pellets with low densities (75–80% of theoretical density). Scanning electron microscopy (see Fig. 1) showed that the pellets had large voids and large grains. By modifying the starting powder, using the small grain size material prepared from our sol, we were able to obtain pellets with substantially fewer voids and with a density at 90% of the theoretical value. In Fig. 2 is shown a electron micrograph of a standard pellet made from this second approach.

Electrical conductivity of the electrolyte was determined by a.c. impedance measurements. These results have shown that there are two very important components in the ionic conductivity (see Fig. 3(a) and (b)). The high frequency component is almost purely resistive and shows a room temperature value of 5×10^{-4} S/cm, whereas the low frequency component shows a substantial capacitive response. At intermediate frequencies the frequency dispersion can be associated with the resistance and capacity across grain boundaries
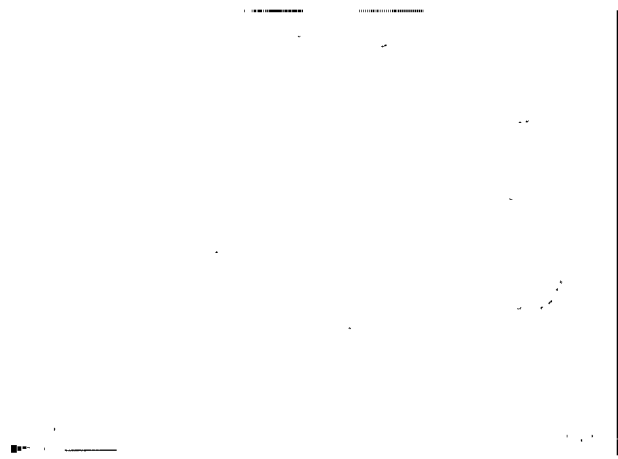

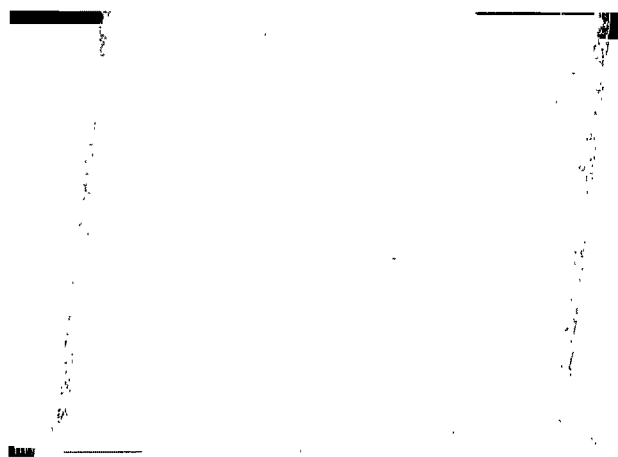Fig. 1 Scanning electron micrograph of an $Li_{0.33}La_{0.56}TiO_3$ pellet prepared from large grain powder

Fig. 2 Scanning electron micrograph of a dense pellet of $Li_{0.33}La_{0.56}TiO_3$ prepared from fine grain powder.

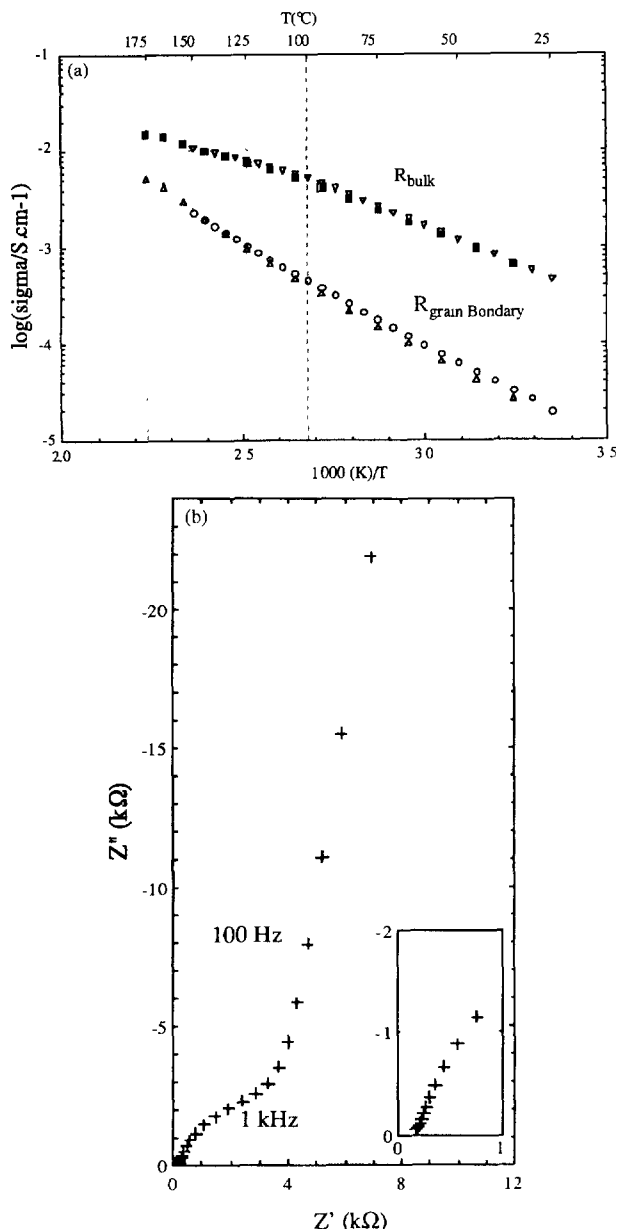Fig. 3. (a) Conductivity as a function of temperature for $Li_3La_{0.67-x}TiO_3$; (b) a.c. impedance response of electrolyte pellet at 45 °C. The insert shows the high frequency part enlarged.

(see Fig. 3(b)). In Fig. 3(a) is shown the two resistive parts of the impedance recalculated as conductivities. The figure contains data measured during the heating sequence of two successive temperature scans. It can be seen that the part of the conductivity due to the bulk component is extremely high, and explains our ongoing efforts in reducing the grain boundary component.

Prior to performing electrochemical studies on a total cell we felt it was necessary to observe our electrodes in a cell using a standard liquid electrolyte. In Fig. 4 is shown slow scan (10 mV/10 s voltage steps) cyclic voltammograms of an $LiCoO_2/1$ M $LiClO_4$ in propylene carbonate/$Li_4Ti_5O_{12}$ cell. Knowing the potentials of these two electrodes in bulk
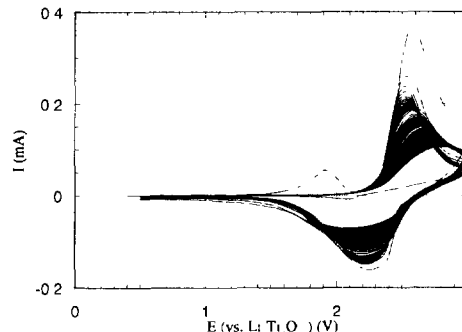

Fig. 4. Cyclic voltammograms of an $LiCoO_2/1$ M $LiClO_4 + PC/Li_4Ti_5O_{12}$ cell.

form versus a lithium reference electrode (1.6 V for $Li_4Ti_5O_{12}$ and 3.8 V for $LiCoO_2$) we expected a potential of the cell of about 2.2 V (cathode reaction $LiCoO_2 \rightarrow Li_{1-x}CoO_2 + Li$ with $0 \leq x \leq 0.6$: anode reaction $Li_4Ti_5O_{12} + Li \rightarrow Li_{4+x}Ti_5O_{12}$ with $0 \leq x \leq 3$). In our liquid cell we observe this expected potential with a gradual degradation in cycling efficiency and broadening of the oxidation/reduction peaks upon cycling.

The solid-state cell was prepared by taking one of our standard electrolyte pellets (approximately 0.9 mm thick and 6 mm in diameter) and subsequently depositing by spray pyrolysis $LiCoO_2$ and $Li_4Ti_5O_{12}$. After each deposition the pellet with the electrode was heated at 600 °C and annealed for 1 h in air. In order to insure contact, gold was evaporated onto each electrode. Since we did not incorporate a third reference electrode into the system, we deposited a thick film of $Li_4Ti_5O_{12}$ (usually 5 μm) and used this electrode as both the reference and counter electrodes relative to our 1–2 μm thick $LiCoO_2$ working electrode. In Fig. 5 is shown a series of slow scan (10 mV/10 s) cyclic voltammograms for a standard cell with an active surface area of 0.12 cm^2. This cell was cycled in an argon-filled dry box (less than 1 ppm water), after being dried at 250 °C. Certain observations should be noted: the oxidation and reduction peaks of the cell are slightly displaced relative to the same cell with a standard liquid electrolyte, the cell shows lower current densities than the liquid electrolyte cell, and the solid-state cell shows less cycling degradation (although there was current loss on the first 3–4 cycles the value stabilized and showed no modifi-
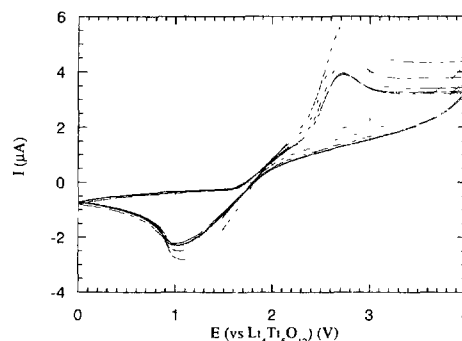

Fig. 5. Cyclic voltammograms of an $LiCoO_2/Li_3La_{0.67-x}TiO_3/Li_4Ti_5O_{12}$ cell.

cation for the next 100 cycles). Two of these three points seem rather straightforward. The superior cycling performance is expected since the solid electrolyte probably has little reaction at the cathode thus leaving no contaminants on the $LiCoO_2$ even at high potentials relative to lithium. The lower current densities were expected, since our electrolyte was very thick (1 mm), and thus has substantial cell impedance. The modifications in the observed voltages are not completely understood at this time but may be due to the added diffusion times due to our thick electrolyte.

4. Conclusions

Although these results are preliminary, it appears that $Li_{0.33}La_{0.56}TiO_3$ can serve as an excellent electrolyte in a solid-state lithium-ion battery using cathodes with a potential as high as 3.8 V versus lithium and anodes with a potential as low as 1.5 V with respect to lithium. It is certain that using metallic lithium as an anode, reduction of the electrolyte occurs and electronic conduction is present. We have been able to cycle an $LiCoO_2$ cathode for over 100 cycles easily and other high voltage cathodes are currently being examined. The cycling of a variety of other cathode materials may also help us to understand the slight voltage shift observed in our $LiCoO_2$ electrodes. Perhaps the most interesting possibility is obtaining relatively high current densities from this solid-state electrolyte. We have obtained current densities as high as 50 $\mu A/cm^2$ from an electrolyte that was almost 1 mm

thick, and had only modest ceramic qualities. We observed by complex impedance that the high frequency conductivity (bulk) was more than 10 times greater than the mid-range frequency (grain boundary) conductivity. By a combination of decreasing the thickness and improving the ceramic quality it seems very possible to decrease the electrolyte impedance by a factor of 10. It will be extremely interesting to see if the current density can also be increased by this factor of 10.

Acknowledgements

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