

Electrochemical investigations of lithium-aluminum alloy anode in Li/polymer cells

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Abstract

A first study demonstrating the electrochemical cyclability of the LiAl alloy anode in the Li/polymer cells reported was carried out using LiAl/PEO₃₀-LiN(CF₃SO₂)₂/V₂O₅ cells in which the cell capacities were limited by LiAl anode. The cells fabricated with LiAl anode exhibited excellent electrochemical performance. The coulombic efficiency throughout the cell cycling was also close to 100% indicating that the lithium dendrite formation in LiAl/PEO₃₀-LiN(CF₃SO₂)₂/V₂O₅ cells is significantly reduced. The reduction in the lithium dendrite formation was attributed to lower lithium activity in the LiAl alloy and its higher open-circuit voltage (370 mV versus Li). The cell voltage was, however, somewhat lower due to the higher open-circuit voltage of LiAl anode. The use of the LiAl alloy allows us to operate the cell at higher temperatures. Higher operating temperature improves the reaction kinetics while reducing the polarization losses associated with ohmic, mass transport, and diffusion. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Li-polymer cells; Coulombic efficiency; LiAl alloy; Electrochemical performance

1. Introduction

The introduction of solid polymer electrolyte possessing significant Li⁺ conductivity [1–4] has resulted in considerable interest in the potential use of these materials in all solid-state Lithium polymer batteries [5–10]. The lithium-polymer batteries based on the cell configuration Li/Li⁺(PEO)/MO_x is a light weight, high-energy system that can operate in a reasonably low temperature range (60–100°C). The transition metal oxide cathode (MO_x) in the polymer cells is based on vanadium oxides [11–15] for intercalating lithium cations. During discharge reaction, the lithium cations intercalate into the host oxide with simultaneous electrochemical reduction of the vanadium oxide. The host oxide structure is highly reversible to both redox and intercalation reactions, thus allowing the lithium cations to exit upon recharge. One of the limitations of the solid-polymer electrolyte is its low ionic conductivity and a low cation transference number, hence limiting the rate capability and the power performance

of the polymer cells. The low ionic conductivity can be offset using thin electrode and electrolyte layers. The lithium-polymer cells, therefore, rely on thin layers and large geometrical areas in order to compensate for the low electrolyte conductivity. One of the key issues related to the performance of the lithium-polymer cells is the dendrite formation, which gives rise to soft-shorts in the cell causing severe self-discharge and thus inefficient cell cycling. These soft-shorts eventually produce a hard short in the cell, which can drive the cell in thermal runaway producing exceedingly high temperatures. Also, under certain conditions such as high rate discharge or power pulse discharge, the large exothermic chemical processes may cause heat to accumulate inside the cell if the heat transfer to the surrounding is not efficient. This in turn may create ‘hot spots’ within the cell with temperatures exceeding the melting point of lithium metal thereby causing lithium meltdown and major safety problems. These problems can be minimized by using solid lithium-metal alloys with lower lithium activity, higher open-circuit voltage, and significantly higher melting point.

In this paper, we describe the first study demonstrating the cyclability of the LiAl alloy anode material in the Li/polymer cells. The use of the alloy anode is expected to provide superior safety features due to its high dis-

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charge capacity, open-circuit voltage, and high melting point.

2. Experimental

Poly(ethylene-oxide) (PEO) with average molecular weight 4×10^6 (Aldrich) was dried at 100°C under vacuum for 24 h prior to use. Vanadium oxide (Aldrich, 99.99%) and acetylene carbon black from Alfa AESAR (<99.9% metals basis) were dried at 100°C under vacuum. Lithium metal foil (Alfa AESAR) was surface cleaned with a soft nylon brush before use. Lithium bis(trifluoromethanesulfonimide), $\text{LiN}(\text{CF}_2\text{SO}_2)_2$, 3 M reagent grade), was dried under vacuum at 120°C for 24 h. High purity acetonitrile (CH_3CN) with 99.5% purity level was purchased from Alfa AESAR and used without further purification. The polymer electrolyte layer consisting of PEO and $\text{LiN}(\text{CF}_2\text{SO}_2)_2$ salt was fabricated by solvent casting method [5,11]. The $\text{LiN}(\text{CF}_2\text{SO}_2)_2$ salt was first dissolved in acetonitrile followed by the addition of PEO. The mixture was then stirred for 24 h. The resulting viscous and homogeneous solution was then cast on a Teflon plate and left at room temperature for 24 h for slow evaporation of the solvent. The casting of polymer electrolytes was carried out in a He-atmosphere glove box.

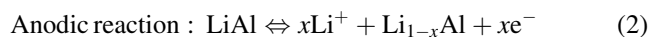
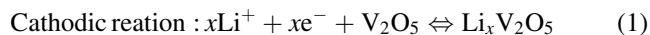
The V_2O_5 cathode layers containing 60.5% V_2O_5 , 34.5% polymer electrolyte, and 5% of acetylene carbon black were prepared by solvent casting method. A mixture of V_2O_5 and acetylene black was suspended in 80 vol.% acetonitrile and 20 vol.% toluene solution containing PEO and Li-imide salt. The resulting mixture was cast on a 20 μm thick aluminum substrate using doctor blade. The choice of aluminum as a current collector for the cathode is due to its passivating properties in nonaqueous electrolytes especially at high voltage (3.5 V versus Li). The remaining solvent was removed by heating in a vacuum oven at 120°C for 48 h. The thickness of the V_2O_5 laminates ranged between 40 and 50 μm . Li-Al powder (46.0 at.% Li) was ground and dried under vacuum at 150°C for 24 h in order to remove moisture and any volatile impurities. Several 1.58 cm diameter pellets of LiAl alloy were fabricated by cold pressing LiAl powder in stainless steel die. The resulting pressed pellets were found to be somewhat brittle especially on the edges. Therefore, special care was taken during cell assembly.

The cells used for the electrochemical measurements were made of V_2O_5 cathode, LiAl anode, and $\text{PEO}_{30}\text{-LiN}(\text{CF}_3\text{SO}_2)_2$ electrolyte sandwiched between cathode and anode. The polymer electrolyte also served as a separator. The cells were fabricated in such a way that LiAl anode had significantly higher capacity than the cathode. Therefore, during charge and discharge reactions there was negligible polarization in the LiAl electrode. Electrochemical measurements were performed using Arbin BT-2043 cyclers in combination with MITS 97 program for data collection. The cell was thermostatically controlled in an environmental chamber to $\pm 1^\circ\text{C}$ during the measurements.

3. Results and discussion

The electrochemical behavior of LiAl alloy anode in high temperature LiAl/FeS₂ batteries has been well investigated [16,17]. According to the phase diagram of LiAl alloy [18], the boundary of α -LiAl phase is about 9.0 at.% lithium. The β -LiAl field has a composition width between 47.0 and 56.0 at.% lithium. The LiAl alloy is typically cycled across the two-phase ($\alpha+\beta$) region between 10.0 and 46.0 at.% lithium, within which the emf of the LiAl electrode remains constant at 292 mV at 450°C relative to elemental lithium. The theoretical capacity of LiAl alloy containing 46.0 at.% lithium, which has a density of 1.75 g/cm^3 , is approximately 0.74 A h/g when the material is discharged at 450°C to 10.0 at.% lithium [19]. Fig. 1 shows the insertion and the extraction of lithium into a LiAl anode in the ($\alpha+\beta$) phase region of LiAl alloy in $\text{Li}/(\text{PEO})_{30}\text{LiN}(\text{CF}_3\text{SO}_2)_2/\text{LiAl}$ cell at 100°C . It can be seen from this figure that the lithium insertion and extraction into LiAl electrode proceed at a constant voltage of 358 and 378 mV, respectively. The capacity of the LiAl anode in the ($\alpha+\beta$) phase region was found to be 550 mA h/g (Fig. 1).

The charge and discharge reactions for a $\text{LiAl}/(\text{PEO})_{30}\text{-LiN}(\text{CF}_3\text{SO}_2)_2/\text{V}_2\text{O}_5$ cell can be written as follows:



where x is degree of lithium intercalation. The first discharge curve of a $\text{LiAl}/(\text{PEO})_{30}\text{LiN}(\text{CF}_3\text{SO}_2)_2/\text{V}_2\text{O}_5$ cell at 100°C is shown in Fig. 2. The capacity of the ($\alpha+\beta$) plateau is large enough ($\sim 550 \text{ mA h/g}$) so that the polymer cells fabricated with V_2O_5 cathode and LiAl alloy anode are essentially cathode limited. Therefore, during the cell discharge reaction, the potential of LiAl does not vary and stays close to 370 mV versus Li. The operating voltage cut-offs are 3.0–1.1 V for the charge and discharge reactions, respectively. The salient features of this material during the first discharge are consistent with the $\text{Li}/\text{Li}^+(\text{PEO})/\text{V}_2\text{O}_5$ cell reported in literature [20–23]. The discharge curve shown in Fig. 2

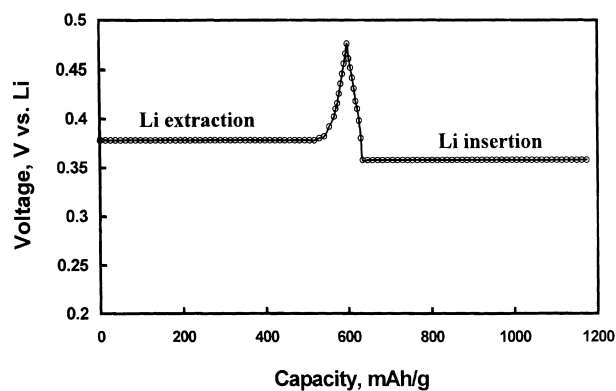


Fig. 1. Insertion and extraction of lithium in the two-phase ($\alpha+\beta$) region of the LiAl alloy. The cell was charged and discharged at a $C/20$ rate at 100°C .

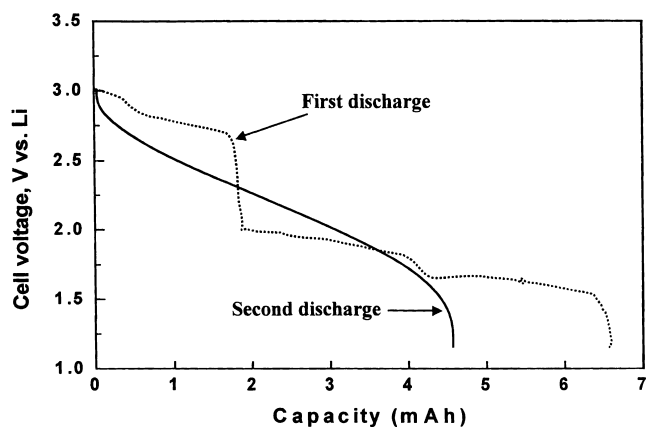


Fig. 2. Electrochemical behavior of the LiAl/PEO₃₀-LiN(CF₃SO₂)₂/V₂O₅ composite cell in the first and second discharge cycles. The cell was charged and discharged at a C/20 rate at 100°C.

shows that the intercalation of lithium from LiAl anode into the V₂O₅ cathode occurs in four steps. The first two plateaus at 3.0 and 2.8 V, respectively, are associated with the formation of Li_xV₂O₅ ($x \sim 1$). This process has been shown to be reversible toward lithium intercalation and extraction involving the V₂O₅ oxide [23]. However, if the discharge continues until 1.1 V, the intercalation process becomes irreversible and involves two additional plateaus. The calculation of the capacity for the overall reaction indicates that a total of 3 mol of lithium are inserted for one mole of V₂O₅ to form ω -Li₃V₂O₅ ($x \sim 3$) [23]. The irreversibility of the overall process can be seen from the fact that the second discharge does not involve any plateau and shows a single sloping voltage. However, the oxide ω -Li₃V₂O₅ was found to be very reversible toward lithium insertion and extraction as shown in Fig. 2. In subsequent charge, only 66% of inserted lithium could be extracted indicating that about 34% of lithium ions were trapped within the oxide lattice.

Fig. 3 is a voltammogram of the V₂O₅ cathode in a LiAl/Polymer/V₂O₅ cell. The positive currents are for reduction (discharge) and the negative currents are for oxidation (charge). A comparison of the voltammetric curves (Fig. 3) and the cell discharge curve (Fig. 2) shows that there is a strong correlation between the voltammetric peaks

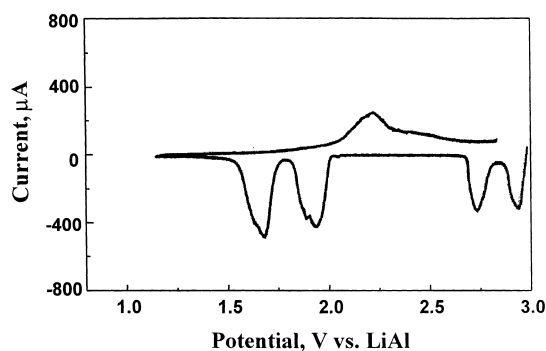


Fig. 3. Cyclic voltammogram of the V₂O₅ cathode in LiAl/Polymer/V₂O₅ cell at a scan rate of 0.02 mV/s at 100°C.

and the discharge plateaus. During the first cyclic voltammetric sweep there are two peaks one at 3.0 V and the other at 2.7 V followed by two major peaks at 1.95 and 1.6 V. The first two peaks at 3.0 and 2.7 V, respectively, are associated with the formation of LiV₂O₅ corresponding to one electron reduction. The two additional peaks in the cyclic voltammogram correspond to further reduction of the cathode. There are also corresponding four plateaus in the discharge curve (Fig. 2). On the second voltage sweep the peaks have disappeared in the voltammogram. Similarly, the plateaus have disappeared during the second discharge of the cell. These results suggest that at the beginning of discharge process vanadium is mostly in +5 oxidation state and is reduced at least partially to Li₃V₂O₅ at the end of discharge. This overall reduction by giving up three electrons take place in four steps in the first discharge.

Fig. 4 shows the electrochemical performance of the LiAl/(PEO)₃₀LiN(CF₃SO₂)₂/V₂O₅ cell at various discharge rates at 100°C. There is no voltage plateau in discharge curves as expected for single-phase Li_xV₂O₅ cathode material. It can be seen from this figure that the capacity decreases steadily with increasing discharge rates. This is similar to Li/polymer cells and is related to the polarization effects, low conductivity of the polymer, and slow lithium diffusion in the oxide lattice. Fig. 5 shows the performance of the cell containing LiAl anode at fast recharge rates. These measurements were taken after charging the cell at C/2, 1C, and 2C rates followed by a C/6 discharge. It can be seen from this figure that the cell produces 55% capacity after a 2 h charge, which is significantly higher than the normal charge rates (C/10) used in Li-polymer cells. The cell was able to produce about 20% of its capacity even at 1C (60 min) charge rate. The coulombic efficiencies during these investigations were also higher than 90%. These results are very encouraging because unlike Li-polymer cells, the cells containing LiAl anode can be recharged at extremely high rates. Fig. 6 shows long-term cycling performance of the Li/polymer cell containing LiAl alloy anode. The cell was fairly stable with some small variations in initial cycles. This cell was sub-

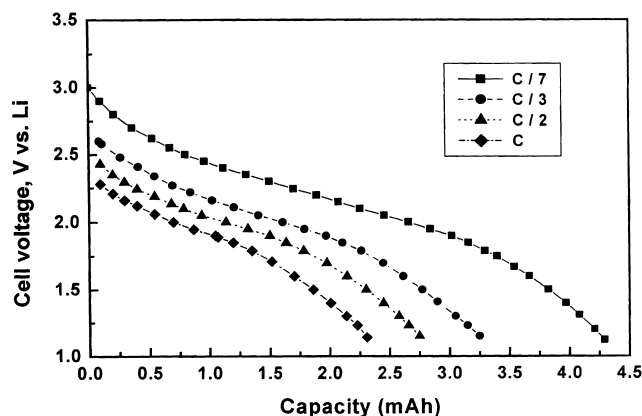


Fig. 4. Electrochemical performance of the LiAl/PEO₃₀-LiN(CF₃SO₂)₂/V₂O₅ cell at various discharge rates at 100°C.

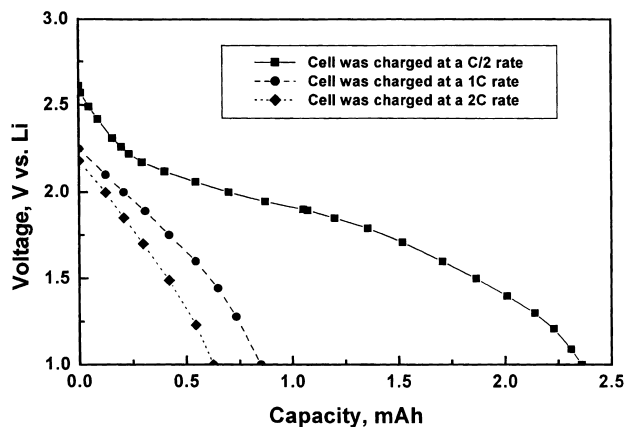


Fig. 5. Discharge behavior of the LiAl/PEO₃₀-LiN(CF₃SO₂)₂/V₂O₅ cell at a C/6 rate following fast recharge.

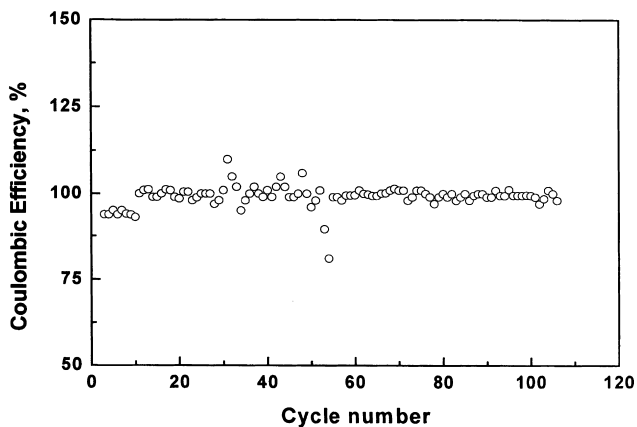


Fig. 6. Coulombic efficiency vs. cycle number for the LiAl/PEO₃₀-LiN(CF₃SO₂)₂/V₂O₅ cell.

jected to 100 cycles with coulombic efficiencies close to 100% before it was terminated suggesting that the lithium dendrite formation is significantly reduced. The reduction in the lithium dendrite formation is due to the lower lithium activity in the LiAl alloy as well as its higher charge voltage of 370 mV versus Li.

These results suggest that LiAl alloy is a promising anode material for the polymer cells. There are, however, some technical concerns related to the use of LiAl anode. These concerns are related to the volume changes of LiAl alloy during cycling and 370 mV loss in the discharge voltage relative to Li anode. We did not investigate the volume changes during charge–discharge cycling in the present study. However, the volume change issue can probably be addressed by optimizing the anode design. For instance, an optimized composite LiAl alloy anode design with mixed-conductor matrix [24] has been shown to minimize volume expansion problems in high temperature batteries. The lower discharge voltage can be compensated by operating the cell

at higher temperatures, thereby providing improved kinetics and reduced polarization losses. The use of the LiAl alloy allows us to operate the cell at higher temperatures. Higher cell operating temperature enhances the reaction kinetics while reducing the polarization losses associated with ohmic, mass transport, and diffusion.

4. Conclusions

This study demonstrates that lithium-aluminum alloy is a promising anode for polymer cells. The LiAl/PEO₃₀-LiN(CF₃SO₂)₂/V₂O₅ cells exhibit overall good electrochemical performance and fast rechargeability. The coulombic efficiency was also found to be close to 100% for over 100 cycles demonstrating excellent cyclability of the LiAl alloy in the polymer cells. The excellent cyclability of the LiAl alloy is attributed to the absence of the lithium dendrite formation in the LiAl/polymer cell.

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