Low-Temperature Sol-Gel LiV_3O_8 Cathodes in Polymer Electrolyte Batteries

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In this work we report the characterization of amorphous LiV_3O_8 in lithium metal anode - polymer electrolyte batteries. The polymer electrolyte is based on high molecular weight PEO and the lithium salt, $LiN(SO_2CF_2CF_3)_2$ (LiBETI). A comparative characterization in liquid electrolytes is reported as well.

Amorphous $Li_{1+x}V_3O_8$ was prepared by a sol-gel process in which V_2O_5 powder was reacted in water with a stoichiometric amount of LiOH. To a solution containing 2 moles of LiOH, 3 moles of V_2O_5 were slowly added while stirring and with a moderate heating (80°C) if shorter reaction times were desired. The heterogeneous reaction proceeds through the following steps

$$2\ LiOH + 1/3\ V_2O_5 \ \text{-->}\ 2/3\ Li_3VO_4 + H_2O$$
$$2/3\ Li_3VO_4 + 2/3\ V_2O_5 \ \text{-->}\ 2\ LiVO_3$$
$$2\ LiVO_3 + 2\ V_2O_5 \ \text{-->}\ 2\ LiV_3O_8$$

The dissolution of V_2O_5 is slow in the final stages of the reaction that is completed in 24-36 h, as indicated by the color change of the yellow V_2O_5 to the red brown color of the bronze. The procedure yields a gel material that is dried under vacuum and finally ground by ball-milling to obtain a very fine powder, which showed a completely amorphous pattern with X-ray analysis [1, 2].

Electrodes for liquid electrolyte cells were prepared by mixing the active material (70wt%), carbon (20wt%, Ketjen black, AKZO) and teflon binder (10 wt%) in methanol. The slurry was dried in a vacuum oven at 80°C. The dry powder was roll-milled to form sheets about 0.1 mm thick from which pellets of 10 mm diameter were cut. After a 5-minute treatment at 160°C, the pellets were assembled in sealed, two-electrode cells in which the anode was a disc of lithium and the electrolyte was 1M $LiPF_6$ in EC:DMC (1:1 w) with a glass felt separator.

Electrodes for polymer electrolyte cells were prepared by milling the active material (60wt%), carbon (10wt%, SuperP, MMM Carbon), PEO (3wt%; WSR N301, DOW) and PEG (27wt%; Carbowax 1500, DOW) in trichloroethane (10 ml per gram of dry mixture). The slurry was coated on aluminum foil (12 μm thick), and dried in air, calendered and vacuum dried at 50°C. Electrodes were cut from the foil and assembled in coffee-bag cells with a lithium anode and a $P(EO)_{20}LiBETI$ polymer electrolyte as described earlier [3].

Figures 1 and 2 illustrate the cycling behavior of amorphous LiV_3O_8 electrodes in liquid and polymer electrolytes, respectively. The long-term cycling tests were performed at various discharge currents while the charge was always driven at a C/10 rate.

The theoretical capacity of LiV_3O_8 is 280 mAh g^{-1} corresponding to the insertion of 3 equivalents of lithium per mole assuming the vanadium reduction from +5 to +4. From Figure 1 it is seen that the material is able to deliver 380 mAh g^{-1}, for low-rate discharges (C/10) in liquid electrolytes, corresponding to the reduction of about 35% of vanadium to the trivalent state. However, the performance decreases on increasing discharge current densities. In polymer electrolytes, the cathodes perform well although a decrease in delivered capacity is observed.

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References

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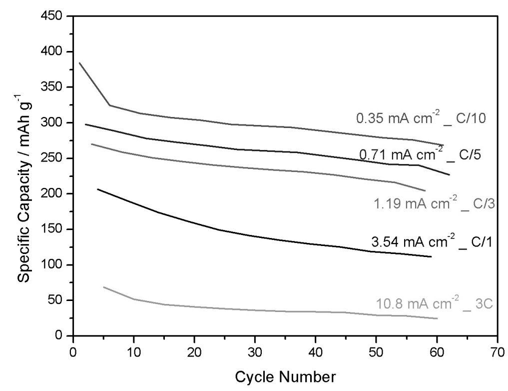

Figure 1. Cycling behavior of a LiV_3O_8-based cathode in a liquid electrolyte (1M $LiPF_6$ in EC:DMC (1:1 w)) at various discharge rates. Voltage range: 1.8 V - 3.5 V. Electrode (active material) mass loading: 15 mg cm^{-2}. Temperature: 20°C.

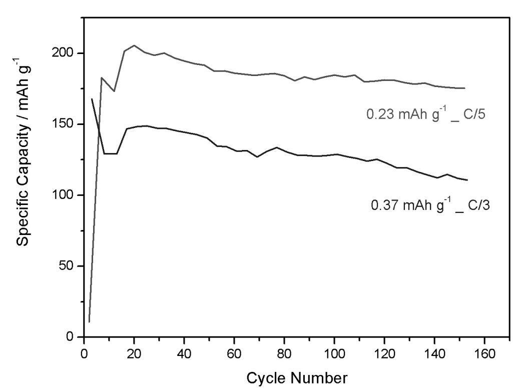

Figure 2. Cycling behavior of a LiV_3O_8-based cathode in a polymer electrolyte ($P(EO)_{20}LiBETI$) at various discharge rates. Voltage range: 1.8 V - 3.5 V. Electrode (active material) mass loading: 5 mg cm^{-2}. Temperature: 90°C