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The two-phase battery concept: a new strategy for high performance lithium polymer batteries

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Abstract

A new concept is proposed to realize high performance lithium polymer batteries. The two-phase battery concept is based on the use of two polyethers of different molecular weight. A low molecular weight polyether is used in the composite cathode to assure high ionic conductivity while a high molecular weight polyether is used in the electrolyte formulation. In this work, a composite cathode based on a solid, low molecular weight poly(ethyleneglycol) dimethyl ether (PEG-DME, M.W. 2000), was coupled with a solid polymer electrolyte (SPE) based on poly(ethylenoxide) (PEO, M.W. 4×10^6). The electrochemical stability window, evaluated by a slow sweep voltammetry, showed that the system has an anodic breakdown voltage higher than 4.0 V versus Li. The feasibility of two-phase batteries was evaluated by cycling tests. The results indicate that two-phase batteries have enhanced performance with respect to PEO based batteries. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: PEG; Composite cathode; Polymer electrolyte; Lithium battery

1. Introduction

Electric vehicle (EV) application requires batteries with high energy density, high pulse power and extremely long life at deep depth of discharge. Lithium metal, with a theoretical capacity exceeding 3.8 Ah/g, represents the ultimate frontier in the realization of high energy density storage devices. Chemical and electrochemical stabilities of SPE in contact with lithium metal were shown to be superior to those of liquid electrolytes [1]. However, although under development for over than 20 years, SPE technology has yet to demonstrate to be able to achieve the critical performance issues requested for EV applications.

The failure of the SPE technology to deliver the above mentioned performance is related to

- Inadequate ionic transport properties
- Insufficient chemical and electrochemical stabilities.

PEO based electrolytes have received great attention as SPE's. Due to their particular structure, the conductivity of PEO-based SPE's becomes appreciable at temperatures above the ambient. The operative temperature of the system

is of fundamental importance and it must be carefully controlled. If the temperature is kept too low, the electrolyte transport properties and the kinetics at the electrode/electrolyte interface diminish. On the other hand, if the temperature is raised above a critical value, the electrolyte tends to decompose.

At high discharge rate, current can flow through the electrolyte at values higher than the limiting diffusion current. This situation cannot be sustained forever. Eventually, the over-voltage related to the establishment of a concentration gradient would suddenly increase, as predicted by the Sand equation [2]. The concentration polarization affects first the composite cathode, where the cross-section of the polymer electrolyte is lower than in the separator [3].

In this paper, we propose a new approach to realize high energy density, high power lithium polymer batteries. The approach is based on the two-phase battery concept [4]. It is well known that the conductivity of polyether-based electrolytes decreases by increasing the molecular weight of the polymer [5]. Low molecular weight poly(ethyleneglycol)'s (PEG's) show high ion conductivity, even at ambient temperature, but their mechanical properties are not quite good. On the other hand, solid polymer electrolyte batteries suffer of low conductivity especially in the cathode compartment where strong mechanical stability is not requested.

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For such a reason we propose the use of two different polymers:

- A low molecular weight PEG in the cathode, to assure high ionic mobility.
- A high molecular weight PEO in the separator, to impart mechanical integrity.

In this work a solid, low molecular weight (average MW = 2,000) PEG-DME, was used as lithium conductive matrix in the cathode compartment. The composite cathode was coupled with a separator based on high molecular weight PEO. The electrochemical stability window was evaluated by slow sweep voltammetry and the feasibility of the two-phase batteries was evaluated by cycle tests.

2. Experimental

The composite cathode and the polymeric membrane were prepared by following a dry, solvent-free procedure. Samples preparation and handling were performed in a dry-room (R.H. < 0.2% at 20°C).

The polymer electrolyte was prepared following the procedure described earlier [3]. LiClO₄ was used as received. PEO (Union carbide, MW = 4,000,000) and γ -LiAlO₂ (Cyprus Foote Mineral Co., HSA10) were dried in dry argon atmosphere (H₂O < 5 ppm), respectively, at 55 and 300°C for 24 h.

The powders were carefully sieved through 200 and 400 mesh sieves and gently mixed by ball milling. The mixture was placed in an aluminum dye and hot-pressed at about 1000 N/cm² and 120°C for 30 min. During the hot-pressing the mixture melted and after cooling, a one millimeter thick ribbon was obtained. The ribbon was reduced to a thinner tape by cold-calendering. The electrolyte tape was heated at 110°C under pressure to relax the stress induced by the cold-calendering. A mechanically stable membrane with an average thickness of 150 μ m was produced. The weight fraction of the polymer electrolyte was 70.6% of PEO, 12.8% of lithium salt and 16.6% of γ -LiAlO₂. The EO/Li (EO: ethylene oxide unit) ratio in the polymer electrolyte was 20.

The composite cathode was prepared by a modification of the procedure described to prepare the polymer electrolyte. PEG-DME (Aldrich, average MW = 2000) and LiClO₄ (Fluka, 99%), were used as received. The two components were weighted to give an EO/Li ratio of 20 and mixed in a mortar. The active material (LiMn₃O₆, Seimi Ltd.) and the carbon (Super-P, MMM Carbon) were dried at 100°C. The active material and carbon were gently mixed in the proportion of 11:1. The blend of powders was added to the polymer-salt mixture and homogenized in the mortar. The weight fraction of the composite cathode was 55% of active material, 10% of carbon, 5% of lithium salt and 30% of PEG-DME.

The electrodes were obtained by screen printing the composite cathode on an aluminum foil heated at 80°C. Disks of 0.8 cm of diameter were cut from the foil. The weight of the cathode was about 2.7–3.0 mg corresponding to a mass loading of about 3.0–3.3 mg/cm² of active material. To evaluate the electrochemical stability window a composite electrode was prepared adding the carbon to the polymer-salt complex in the same ratio as in the composite cathode. A cell was built sandwiching the polymer electrolyte between the composite electrode and a lithium foil. The electrochemical stability window was evaluated by a slow sweep voltammetry performed by means of an AMEL voltammetric set-up.

Batteries were assembled by sandwiching a polymer electrolyte disc between a lithium foil and a composite cathode disc. The electrochemical systems were contained in Teflon cells using stainless steel current collectors. The cells were heated at 60–65°C in an oven and galvanostatically cycled between fixed voltage values. The working temperature was selected based on the ionic conductivity and the active material/polymer electrolyte interfacial characteristics.

Galvanostatic charge and discharge cycles were performed by using a Maccor battery cyler (S 4000).

3. Results and discussion

3.1. Electrochemical stability window

The stability of the PEG-DME was evaluated by using a composite electrode containing the polymer, the salt and the carbon but without the active material. We used this special electrode to take into account the catalytic activity of the fine carbon particles that are used to supply the electronic conductivity in the composite cathode.

Fig. 1 shows the current-voltage profile for a carbon containing electrode/SPE/lithium cell. The stability limit,

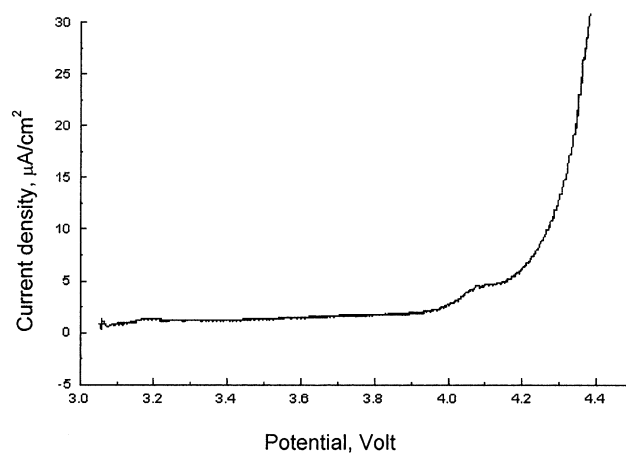


Fig. 1. Voltage sweep for a PEO-LiClO₄ + 20% γ -LiAlO₂ electrolyte sandwiched between a lithium disc and a PEG-DME composite carbon electrode. Temperature: 90°C. Scan rate: 0.05 mV/s.

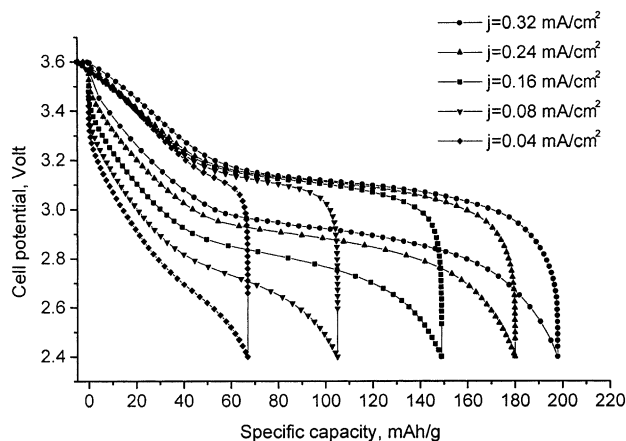


Fig. 2. Voltage profiles vs. capacity for a Li/PEO-LiClO₄ + 20% γ -LiAlO₂/PEG-DME-LiClO₄-LiMn₃O₆ cell. Charge current: 0.04 mA/cm². Discharge currents are indicated in the figure. Temperature: 60°C.

individuated by the onset of the current, can be roughly evaluated at about 4.0 V.

The stability of the carbon-containing electrode based on PEG-DME is higher than that of the corresponding PEO based electrode [3]. Since PEO and PEG have the same chemical bonds, the increase of the anodic stability could be related with the reduction of the molecular weight. Due to the higher number of ethyleneoxide units, the PEO chain is undergone to stronger mechanical constrictions. The stress produced from the chains entanglement can lower the energy needed for the bonds to break, reducing the electrochemical stability.

3.2. 3V LiMn₃O₆ based batteries

The discharge behavior of a LiMn₃O₆ lithium polymer cell is shown in Fig. 2. The voltage profiles were recorded cycling the cell at different current densities. The cell was always recharged using the lower current density (0.04 mA/cm²).

As expected, the utilization of the active material decreased by increasing the current density. From the comparison with the active material behavior in liquid electrolyte (data not shown), the rate-determining step could be related with the concentration polarization of the polymer electrolyte into the cathode rather than with the slow diffusion of the lithium ions into the active material. A limited contact area due to a poor wettability of the active material aside the polymer electrolyte could be responsible of the cell polarization. At the lowest discharge current density used (0.04 mA/cm²) the cell was completely discharged in about 15.5 h. An energy density of about 600 Wh/kg was achieved, a reasonable value that approached the theoretical one. At the highest current density (0.32 mA/cm²) the cell was completely discharged in about 0.6 h delivering a specific power of about 300 W/kg while the active material utilization was about 33%.

The cycling behavior of the battery is shown in Fig. 3. A reasonable capacity fading affects the battery. The fading

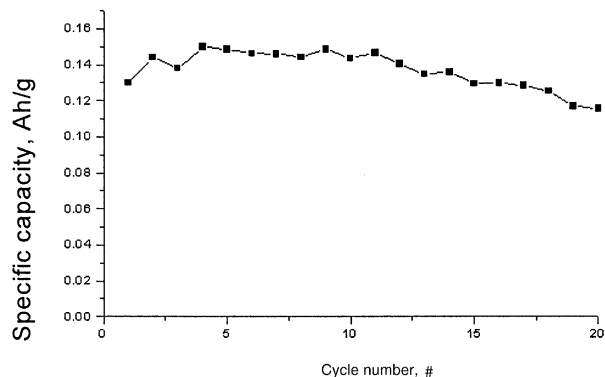


Fig. 3. Specific capacity upon galvanostatic cycles for a Li/PEO-LiClO₄ + 20% γ -LiAlO₂/PEG-DME-LiClO₄-LiMn₃O₆ battery. Current density was 0.2 mA/cm² for charge and discharge. Temperature: 65°C.

can be related to a not completely reversible lithium intercalation process into the active material. It has to be considered that the active material is not optimized to operate at temperature of 65°C.

4. Conclusion

A new approach to realize high performance lithium polymer battery based on the two-phase battery concept was proposed. A low molecular weight PEG-DME was used in the cathode, to assure high ionic mobility while a high molecular weight PEO was used in the separator to impart mechanical integrity.

Several advantages can be obtained by using two different polymers for the composite cathode and the polymer electrolyte. First it allows to reduce the working temperature with respect to PEO based batteries. The possibility to work at lower temperature reduces the degradation reactions enhancing the battery cycle life. Second, the possibility to screen printing the cathode enables to realize thinner electrodes. The reduction of the electrode mass loading enables to fully discharge the electrode in short time, thus increasing the power density of the battery.

The electrochemical stability window, evaluated by a slow sweep voltammetry, showed that a parasitic reaction starts at about 4.0 V. The performance of cells working at 60–65°C was evaluated using a 3 V lithium manganese oxide as cathode active material. Two lithium equivalents were cycled in about 15.5 h at a current density of 0.04 mA/cm². An energy density of about 600 Wh/kg was achieved, a reasonable value that approached the theoretical one. The utilization of the active material decreased by increasing the current density. About 67 mAh/g (corresponding to an active material utilization of about 33%) were delivered in 0.6 h at 0.32 mA/cm². At this current density a power density of about 300 W/kg and an energy density larger than 180 Wh/kg were attained.

Work is in progress to further investigate the properties of this system and to evaluate the possibility to realize larger area batteries.

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