In situ SEM study for intercalation compounds

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Introduction

Insertion compounds still constitute the most attractive positive electrode materials when associated with lithium and carbon as negative electrode in secondary batteries. However, structural and morphological change on the cathode material occurs during operation of such cells resulting in gradual capacity loss.
Ionic conductive polymers appear as electrolytes of choice since their electrometric proprieties limit. The problems caused by the volume expansion and encountered with other solid electrolyte. Therefore, it has possible to build solid rechargeable lithium batteries with in a thin film technology. In contrast to liquid electrolyte, the extremely low vapor pressure of polymeric electrolyte allows for the use of vacuum technique experiments. Following this observation, the purpose of this paper have observe in situ scanning electron microscope (SEM) the morphological of selected cathode materials during discharge of lithium batteries. In the composite electrode (i.e. the mixture of electroactive material and the electrolyte), the interface is located at the surface of every particle. Thus those easily observed with SEM. Located on the father side of negative electrode are still in contact with electrolyte. In this paper we will present and over view from particles and interface of different cathode and anode materials (TiS_2, V_6O_{13}, Lithium, graphite, $Li_4Ti_5O_{12}$, Al Exmet). The original of this work is applied an in situ for all gel Li-ion based on LiFePO4/GEL/Natural graphite by the variation of the temperature and the pressure in side the SEM chamber

Experimental

Special design was use to cycle the fall or half cell by using special designed controlled atmosphere holder and set it in the SEM chamber (figure 1). In situ SEM can ether made on a plane view or in cross section (figure 2), tungsten carbide (WC) probes with tip diameter 1 micron are used to probe cell assembly. Temperature range between –20 to 125 °C is controlled by Pelletier device witch is used to heat (cold) cell in the SEM chamber.
Different chemistries were observed by in situ SEM:
Li/SPE/FES, Li/SPE/TIS_2, LI/SPE/VO_X, LI/SPE/$Li_4Ti_5O_{12}$.
Li/SPE/Al Exmet and NG/GeL/$LiFePO_4$

Results and discussion

FE/S (1)

The stage on discharge curve is located at 1,35 V Vs Li.
The cathodic reaction is Li+FeS ----> Li2S + Fe
During discharge, a considerable swelling of the electrode appears (morphology 1)

TiS_2 and $Li_4Ti_5O_{12}$

TiS_2 is the typical case of bidimensional intercalation. $Li_4Ti_5O_{12}$ is spinel structural. We have noticed any crack or change between the charge and discharge of the both materials (morphology 2). The phenomena related to TiS_2 seems due to the preferential orientation of the laminar particles ad the $Li_4Ti_5O_{12}$ (2) seems due to the zero-strain structural

V_6O_{13}

The volume expansion is below 7% up to $Li_6V_6O_{13}$ but increase to nearly 15 % beyond this composition. Cracks occur and get wider on the second discharge, moreover. particulation occurs (morphology 3). Macroscopically, the electrode has swelled during the discharge; his might explain a decrease in capacity observed with cycling cells

LiFeO4/Gel/NG

The cell was cycled at 0 °C between 2,5 V and 4 V, the impedance was taking in situ before and after the vacuum was applied. The impedance spectra show no difference (before and after vacuum). In particularly the resistance of electrolyte was stable in the vacuum condition. At this stage, we are at the preliminary study of this technology. During our presentation, we will show the new development based on the morphology change and the interface phenomena

Reference

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2. K. Zaghib, *et al*, J. Electrochem. Soc., **145**, (1998), 3135

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Time Laps Video

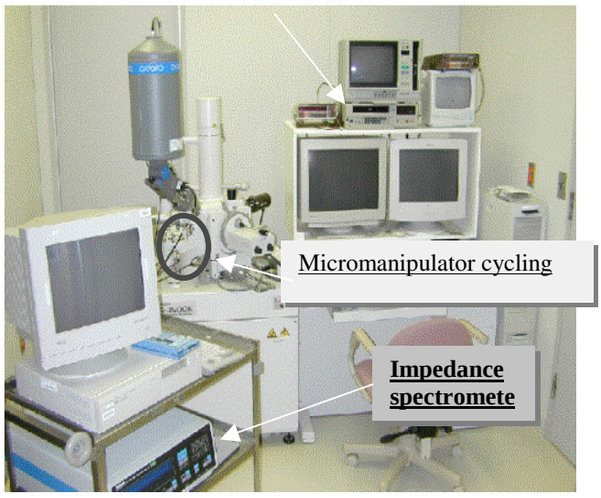

Fig. 1 SEM, cycler, impedance Measurements apparatuses for the in situ experiment

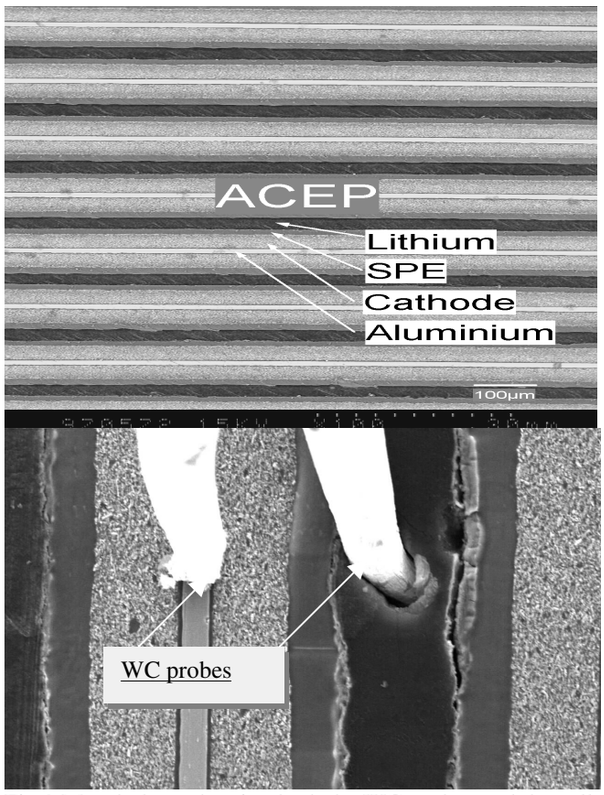

Fig.2 Morphology showing both the WC probes and the cell under in situ Cycling