

In situ SEM study of the interfaces in plastic lithium cells

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Abstract

The interfaces of lithium cells were studied upon cycling within a scanning electron microscope (SEM). The LiMn_2O_4 -cathode and the electrolyte consisted of a polymer matrix embedding a solution of LiPF_6 , while three types of anodes, Li, Cu and graphite, were tested and compared. For each configuration the morphology of the lithium deposit was correlated to the current density. Mossy lithium, at low current, and Li-dendrites, at high current, were observed at the Cu/electrolyte and Li/electrolyte interfaces, while no special morphology was noted at the graphite/electrolyte interface. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Rechargeable Li^0 -batteries present safety problems because of the growth of dendrites at the anode/electrolyte interface. To alleviate this problem, lithium metal was replaced by an insertion electrode, such as graphite or coke [1]. However the energy density of these Li-ion batteries is lower than for the Li^0 -cells which theoretically stay the most promising rechargeable batteries. In order to solve this dendrite issue, we decided to study the way by which lithium deposition occurs by means of electron microscopy techniques. More specifically, we observed the lithium deposit on Li, Cu and graphite at different cycling rates, in order to correlate the morphology to the current density.

Although lithium deposits have been already observed by Scanning Electron Microscopy (SEM) [2], these experiments were performed with samples which were exposed to air during the transfer to the microscope, so that reactions between air and lithiated compounds could mask the reality. In this proceeding, we report cross-section micrographs from plastic cells of various configurations obtained by means of a specific transfer system, designed by Philips, preventing any air exposure during the transfer of the cell from a glove box into the SEM. Besides, the

sample was cooled down to limit the solvent evaporation due to the vacuum in the antechamber during the observation.

2. Experimental

The plastic laminates of the cells were based on the Bellcore plastic technology [3]. The separator film consisted of a copolymer matrix (polyvinylidene fluoride hexafluoropropylene PVdF-HFP) mixed with SiO_2 as filter, and dibutyl phthalate (DBP) as plasticizer. The plastic cathode film was composed of LiMn_2O_4 , PVdF-HFP, DBP, and carbon black. These cathode and separator films were laminated with an aluminum collector to form the positive electrode used for the three kinds of cells studied. This laminate was then associated with lithium, copper or graphite anode to obtain the *lithium batteries*, *copper cells* and *lithium ion batteries*, respectively (Fig. 1). Just before cycling, the cells were swollen in a 1 M LiPF_6 liquid electrolyte (EC/DMC 2/1 in weight ratio).

The electrochemical experiments were performed by means of a Mac Pile system (Biologic, Claix, France). The cells were galvanostatically cycled between 3.5 and 4.5 V, while the current values depended on the wished cycling rate.

The cross-sectional morphologies were observed in a SEM (Philips XL30 FEG) equipped with a special transfer

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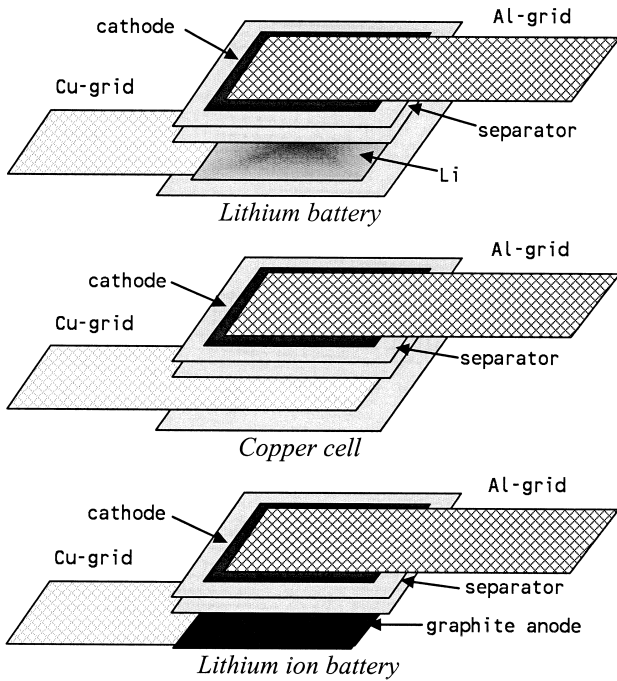


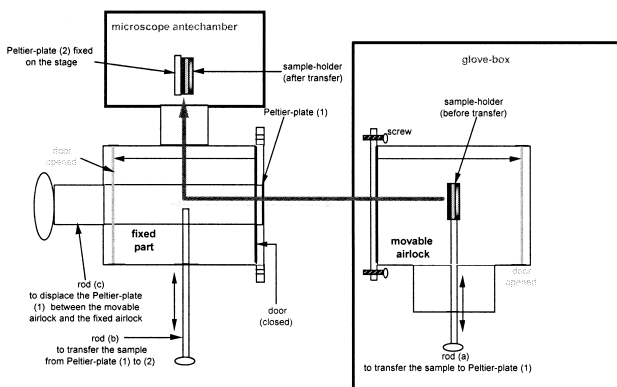
Fig. 1. Cell configurations.

system that was conceived and built by Philips (Scheme 1). A *fixed part*, directly attached to the microscope, and a *movable airlock*, that can be put into the glove box, allow the transfer of the sample from the glove box to the antechamber without air exposure. Details of the transferring procedure are reported in Ref. [4]. This equipment allowed us to directly observe the cross-sections after cutting the cell with a razor blade.

3. Results

3.1. Lithium batteries

The influence of the current densities on the capacity retention is shown in Fig. 2. As expected, the larger the



Scheme 1. Top view of the transfer system designed by Philips.

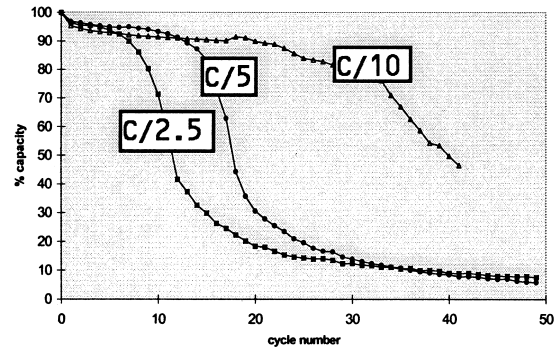


Fig. 2. Capacity vs. cycle number for lithium batteries at different cycling rates.

current density, the quicker the capacity fades upon cycling. For instance, the *C/5* cycling rate is characterized by a dramatic capacity loss after 15 cycles. This phenomenon will be explained by the following SEM micrographs depicting the state of the interfaces.

Cross-section images of a not cycled battery are shown in Fig. 3. The cathode is identified by the LiMn_2O_4 particles embedded in the polymer matrix, while the *Li/separator* boundary is pristine.

After a cycling at *C/5* (0.45 mA/cm^2), the micrographs revealed that the *Li/separator* interface rapidly deteriorated: a moss has formed at the *Li/separator* interface, and induced the separator disconnection from the lithium (Fig. 4b). This deterioration of the interface explained thereby the rapid capacity decrease shown in Fig. 2.

To observe the growth of true dendrites, similar experiments were carried out on lithium batteries charged at higher currents. After one charge at *C* rate (2.2 mA/cm^2) Fig. 5a shows a general view of the cell section, which presents a deteriorated *Li/separator* interface, due to the

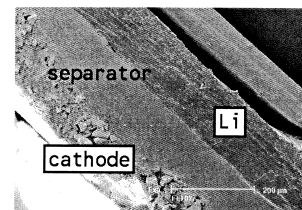


Fig. 3. Cross-section of a not-cycled lithium battery.

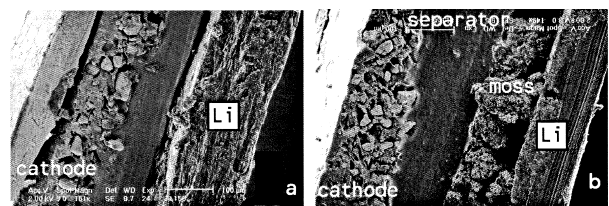


Fig. 4. Lithium battery section after 1 charge (a) and 14 charges (b) (*C/5*, 0.45 mA/cm^2).

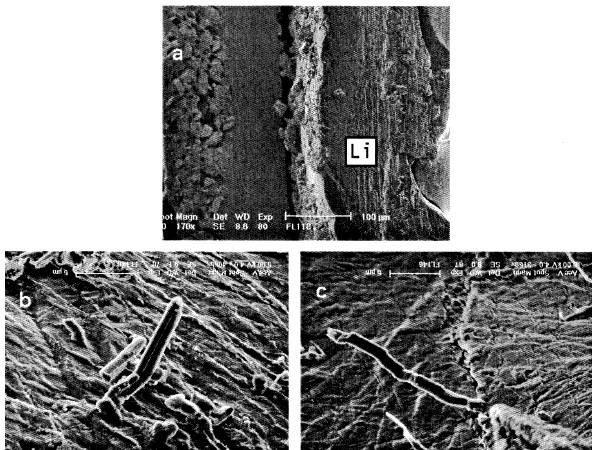


Fig. 5. Section (a) of a lithium battery after 1 charge at C (2.2 mA/cm²) and dendrites (b,c) after 1/2 charge.

growth of tangled and ramified dendrites at the lithium–polymer interface [4]. To obtain single crystallized dendrites (Fig. 5b,c), the cell must be stopped before the end of charge, otherwise only ramified dendrites were observed.

3.2. Copper cells

Similar experiments were carried out with the copper cells to study Li-plating on Cu instead of Li. Before cycling, the Cu grid was embedded in the electrolyte polymer and the copper/separator interface was homogeneous (Fig. 6).

The cells were cycled at C/10 to obtain a current density (0.45 mA/cm² of Cu) comparable to a lithium battery cycled at C/5. After one charge (Fig. 7), a moss

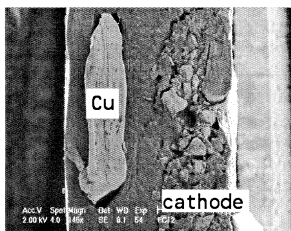


Fig. 6. Cross-section and Cu/electrolyte interface of a not-cycled copper cell.

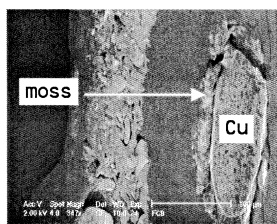


Fig. 7. Copper cell section after 1 charge at C/10 (0.45 mA/cm²).

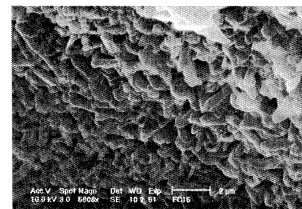


Fig. 8. Cu-surface of a copper cell after 1 charge at C/1.7 (2.6 mA/cm²).

has formed on the copper surface, like in the case of the lithium batteries.

The influence of the lithium-plating rate on the copper surface was also studied. Fig. 8 shows the interface after a plating performed at a current density of 2.6 mA/cm², value at which dendrites were observed with the lithium batteries. In the present case, the shape of the lithium deposit was more dendritic than the previous moss but no true dendrite was observed.

The current was then increased again to reach a value of 4.4 mA/cm². In this case, dendritic lithium wires have grown on Cu (Fig. 9). Nevertheless this kind of dendrites was more regular and thinner than the ramified ones observed in the lithium batteries.

3.3. Lithium ion battery

In order to induce Li-plating on graphite particles, a lithium ion battery, presenting an excess of LiMn₂O₄ towards graphite, was charged at a C rate. The general view of the cross-section is shown in Fig. 10a. No particular Li-deposit morphology was observed. The graphite particles (Fig. 10b) only presented a roughness which was also noted for a non-cycled cell. Since the specific surface of the graphite particles was high, the actual current den-

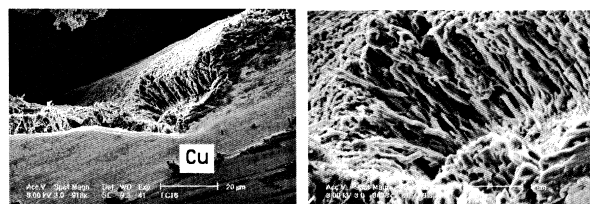


Fig. 9. Cu-surface of a copper cell after 1 charge at C (4.4 mA/cm²).

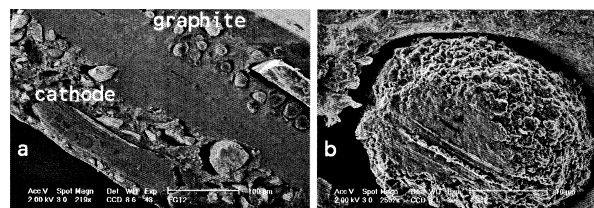


Fig. 10. Cross-section of a lithium ion battery and overlithiated graphite particle after 1 charge at C.

Table 1
Li-deposit morphologies after the first charge

Cell kind	Rate	Current density	Morphology
Lithium battery	$C/5$	0.45 mA/cm ²	moss
	C	2.2 mA/cm ²	dendrites
Copper cell	$C/10$	0.45 mA/cm ²	moss
	$C/1.7$	2.6 mA/cm ²	dendritic moss
	C	4.4 mA/cm ²	dendritic wires
Lithium ion battery	$C, 2C$	< 0.1 mA/cm ²	roughness

sity was very low in comparison with the lithium batteries and copper cells. This difference probably explains the smooth lithium deposition observed with the lithium ion batteries.

The morphologies of the lithium deposits on Li, Cu and graphite are summarized in Table 1. Considering the copper and the lithium as substrates, a low current density induced a mossy lithium deposition, while more dendritic shapes were obtained at higher current densities. Finally, the lower values of the current density involved in the lithium ion batteries led to a smooth lithium deposition.

4. Discussion

SEM micrographs of lithium cells were obtained by means of a new technique which presents the following advantage: the batteries were never exposed to air during the transfer from the glove box to the microscope. Moreover, they are cooled down to limit the evaporation of the volatile electrolyte compounds during the observation under vacuum. Other hermetic transfer techniques have been previously used to study lithium surfaces in many electrolytes [5]. However the cells were dismantled, and the lithium-sheet washed and dried. These treatments could induce morphological and chemical changes of the samples, while our transfer method does not require any special conditioning of the battery which is directly examined.

Concerning our lithium batteries, the rapid decrease in the capacity upon cycling is due to the cell configuration which was specifically dedicated for the observation of dendrites. Indeed, if the interfaces are maintained by means of a physical pressure, the separator stays in contact with the lithium and the cycle-life becomes longer (for instance, more than 70 cycles could be achieved at $C/5$), which was not the aim of this work. Thus, since an external pressure was not desired for this study, we used a specific laminated Li⁰-battery leading to free lithium deposition. Besides, this special configurations allowed a direct SEM-examinations of the cross-sections, without dismantling or additional steps which could change the initial state of the cell.

In this way, it was possible to determine the influence of the current density on the lithium deposit morphology. At sufficiently high current, Li⁰ and Cu induced dendritic morphologies, while the composite graphite anode still led to a uniform lithium deposit. The trend of these results is consistent with the literature.

5. Conclusion

We have shown a direct correlation between current density and dendrite formation, with more dendritic deposits formed at high currents. Further investigations are in progress to determine a solution to suppress the dendrites by conceiving high surface area Li-anodes, leading thereby to low current densities.

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