ON THE PROCESSES RESPONSIBLE FOR THE DEGRADATION OF THE ALUMINIUM–LITHIUM ELECTRODE USED AS ANODE MATERIAL IN LITHIUM APROTIC ELECTROLYTE BATTERIES

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Summary

A study has been carried out of the different processes --- chemical corrosion, solid state diffusion and mechanical disintegration — affecting aluminium–lithium electrodes formed either by an electrochemical or a pyrometallurgical process. Cycling operations present similar limitations with aprotic electrolytes using dioxolane and propylene carbonate as solvents, and $LiClO_4$ and $LiAsF_6$ as solutes. Preliminary tests conducted with compressed LiAl powder electrodes show the existence of other processes responsible for the degradation of these electrodes during cycling.

Introduction

It is well known that the main performance limitations in the development of high energy density lithium secondary batteries are predominantly due to the chemical attack on lithium by all the usual electrolytes. For example, a satisfactory number of cycles ($n > 100$) can be achieved with a dense lithium anode and propylene carbonate or dioxolane-based electrolytes only when the charge capacity and current density used are reduced to values inferior to those likely to be useful in practical batteries [1]. In order to overcome this obstacle, various attempts have been made which take into account the advantages offered by the reduced vulnerability of the lithium when it is incorporated in metallic lattices. This paper summarizes a study conducted to determine the relative importance of the different processes which limit the performances of such a type of electrode consisting of aluminium–lithium substrates formed either by an electrochemical or a pyrometallurgical method.

Experimental

The study was carried out at 25 °C with two solvents, propylene carbonate (PC) and dioxolane (DX), (MERCK for synthesis) used without

further purification, and dried over molecular sieves, and two solutes ($LiClO_4$ and $LiAsF_6$) dehydrated by heating under vacuum. The residual water content was less than 10 ppm with the $LiClO_4$-based electrolytes (1M $LiClO_4$/PC; 1M $LiClO_4$/DX) and was of the order of 100 ppm with the $LiAsF_6$-based electrolytes (0.5M $LiAsF_6$/PC; 0.5M $LiAsF_6$/PC (80%)–DX (20%)).

The useful part of the Li–Al electrode consisted of discs 0.5 cm in diameter and 1 mm thick. The pyrometallurgical aluminium–lithium electrodes were prepared by compressing LiAl powder (Lithium Corporation of America) inside a glove box ($[H_2O] < 5$ ppm); the electrochemical aluminium–lithium electrodes were formed with pure aluminium (Johnson Matthey) using a preliminary cathodic charge.

Results and discussion

(i) Electrochemically formed LiAl

(a) Morphological and kinetic characteristics

The cathodic reduction of Li^+ ions on an aluminium substrate leads to the formation of the intermetallic compound LiAl — identified by X-ray diffraction analysis — which avoids any detrimental dendritic formation as long as the charge density is less than a threshold value which depends on the current density used (e.g., $Q \sim 100$ C cm^{-2} for $J = 1$ mA cm^{-2}; $Q \sim 50$ C cm^{-2} for $J = 10$ mA cm^{-2}). Scanning electron microscopy (S.E.M.) observations of electrode cross-sections have shown that the depth of penetration, δ, of the lithium does not exceed about 3×10^{-4} cm/C cm^{-2}. The Li concentration obtained by X-ray spectroscopy presented a sharp discontinuity for $x = \delta$, a value for which the LiAl lattice would be separated from the Al lattice by a very narrow two-phase zone. X-ray photoelectron spectroscopy (ESCA) studies have shown that the passivating layers were thinner on the aluminium–lithium electrode than on the lithium surface. The analysis of the superficial layer by means of electron microdiffraction has revealed the presence of decomposition products of both solvent and solute [2].

Kinetic studies have shown that the superficial layers are ionic conductor films able to permit the passage of satisfactory cycling current densities as long as no dendritic formation occurs at the electrode surfaces. In other respects, although the exchange current densities determined from either polarization curves or impedance analysis are high (3 mA $cm^{-2} < J < 18$ mA cm^{-2}) the electrode kinetics are principally determined by the solid state diffusion of lithium into the alloy.

(b) Chemical corrosion of the lithium and cycling

The study of the chemical attack on the lithium by the electrolyte was conducted by determining the progressive decrease in the amount of lithium remaining in aluminium–lithium electrodes after long contact periods — up to 100 h — of electrode and electrolyte. The measurements were made by dissolving the electrode in an hydrochloric acid solution and then analysing the solution so obtained by flame emission spectroscopy. The quantities lost

by the electrode are high enough to permit the determination of average current densities equivalent to the chemical corrosion: $-I_{cor} \sim 36$ μA cm^{-2} with the electrolyte LiClO$_4$/DX, $-I_{cor} \sim 4$ μA cm^{-2} with the electrolytes LiClO$_4$/PC and LiAsF$_6$/PC (80%)–DX (20%).

The number of cycles achievable has been estimated taking into account the values obtained for the corrosion current densities. Under smooth cycling conditions (Q_c = 2.5 C cm^{-2}, J_c = 2 mA cm^{-2}) the chemical attack can roughly account for the actual number of cycles obtained with the LiClO$_4$/DX electrolyte. By contrast, it clearly appears that with the electrolyte containing PC as the solvent this chemical attack is a secondary limiting factor for the cycle life of the electrode (*e.g.*, n (obtained) $\simeq$ 250 instead of n (estimated) $\simeq$ 1700, for the same conditions as above).

Various formation procedures were tested in order to obtain, tentatively, a porous host material structure more favorable for cycling. To date, the best results appear to have been obtained by removing most (85%) of the lithium initially incorporated into the electrode either by anodic dissolution at low current densities or by chemical attack of the alloy by anhydrous ethanol under low vapor pressure. After such treatment, cycling has been performed with both a higher depth of discharge (Δ = 60%) and a higher cycling efficiency ($E \sim$ 98%).

(c) Diffusion of lithium into the aluminium–lithium alloy

A study of the electrode impedance diagrams has enabled the diffusion properties of lithium into the aluminium–lithium electrode to be defined. These diagrams did not significantly change during cycling except when the failure of the electrode was imminent. In this instance, the frequency dispersion showed a radical modification of the diffusion characteristics of the electrode.

The analysis of the diagrams was carried out starting from the application of the Nernst diffusion layer model, using results on the diffusion overpotentials deduced from the analysis of the polarization measurements, and assuming that the quasi-invariability of the chemical diffusion coefficient $\tilde{D}$ of Li into Li$_{(1+x)}$Al (near stoichiometry) established for high temperature conditions [3] was transposable to experiments performed at normal temperature. This model has led to a value of about 10^{-10} cm^2 s^{-1} for $\tilde{D}$ [4], a value which is in good agreement with what was expected from the extrapolation of the high temperature measurements.

(d) Mechanical disintegration of the electrode

S.E.M. examinations have shown that the thickness, δ, of the active zone of the electrode progressively decreased during the course of cycling, from its initial value δ_0 corresponding to the formation period (initial charge Q_0) to a value δ_m which roughly corresponds to the cycled charge Q_c ($\delta_m/\delta_0 \sim Q_c/Q_0$). On the other hand flame emission spectroscopy analysis showed that the powder that escaped from the electrode was formed entirely from the stoichiometric intermetallic LiAl compound, in contrast with data reported in the literature. This lack of mechanical cohesion of the electrochemically formed LiAl thus appears to be the main factor responsible for

cycling breakdown. However, with the electrolytes under study cycling performances were more satisfactory with this electrode than with the dense lithium electrode when low depths of discharge are used ($\Delta = Q_c/Q_0 < 20\%$). For example, $E \sim 95\%$ with the $LiClO_4/PC$ electrolyte for current and charge densities lower or equal to 5 mA/cm² and 5 C/cm², respectively, and $\Delta \sim 10\%$. It is worth noting that, with the aluminium–lithium electrode, the substitution of the usual $LiClO_4$ for $LiAsF_6$ as the solute did not provoke any significant modification of the cycling performances. This may be taken into account when seeking to avoid the safety problems often raised about the use of perchlorates in commercial devices.

(ii) Powdered electrode (pyrometallurgical LiAl)

In an attempt to reduce the detrimental effect of mechanical disintegration of electrochemically formed LiAl and actually to achieve high energy densities, electrodes were prepared by compressing pyrometallurgical LiAl grains of small size (30 μm $< 1 < 250$ μm). The electrode presents a satisfactory mechanical cohesion only when its average density exceeds about 1 g cm^{-3}.

Polarization measurements have shown difficulties in the cathodic restoration of the LiAl compound after anodic dissolution. This fact has provoked rapid failures in the cycling experiments. For example, with $LiAsF_6/PC$ and $LiAsF_6/PC$-DX electrolytes, only 7 cycles have been achieved under the following conditions: $\Delta \simeq 10\%$, $J = 2$ mA cm^{-2}, $Q_c = 30$ C cm^{-2}, using an anodic cut-off potential of 1 V/Li, and starting anodically from stoichiometry.

All other attempts carried out to cycle relatively high charge densities with this powdered substrate have led to similar disappointing results, in spite of what could be expected from results obtained earlier with a dense, pyrometallurgical LiAl substrate ($n > 500$ for $Q_c = 2.5$ C cm^{-2} and $J_c = 2$ mA/cm²). The exact origin of the obstacles encountered in this approach towards a type of electrode more promising than those formed by dense substrates is under study.

Conclusion

Study of the processes responsible for the degradation of the aluminium–lithium electrode, e.g., chemical corrosion, solid state diffusion and mechanical disintegration has made possible an evaluation of the cycling possibilities of such a type of electrode in various classical electrolytes.

References

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