A COMPARATIVE STUDY OF THE ELECTROCHEMISTRY OF
THE LiAl ANODE IN MOLTEN SALT AND ORGANIC MEDIA

Y.S. Fung,
Department of Chemistry,
University of Hong Kong,
Hong Kong

ABSTRACT

The electrochemistry of the LiAl anode in molten salt and organic media was investigated using cyclic voltammetry, chronopotentiometry and chronoamperometry. Electrochemical formation of the β-LiAl phase was shown highly dependent on the nucleation polarisation in both media and the difference observed is attributed to the difference in the operation temperature. Development of the anode as indicated by lowering polarisation potential and expanding electrode structure was observed upon cycling. The impurities was shown to have a greater effect on the cycling efficiency using the organic solvent. Moreover, an unstable passive film was formed at the electrode surface as a result of the interaction with the organic solvent, which occurred continuously over a wide span of the cathodic potential. On the other hand, the anode/solvent interaction under the molten salt medium was affected by the liberation of potassium as a vapour, which only occurred at a highly cathodic potential.

INTRODUCTION

Due to the high electronegativity and low atomic weight, lithium and its alloys provide promising anode materials for various advanced battery systems (1,2). The alloying of lithium with aluminium in the form of LiAl anode is at present the most promising anode due to the good retention of the corrosive lithium metal and a moderate lowering of the voltage of the cell (3-5). The LiAl anode has thus been used in the molten salt batteries and in the organic lithium cells. The use of an organic medium has the advantage of operating the cell under ambient temperature, whereas the use of the molten salt medium provides a cell with high current drain. It could be interesting to compare the electrochemical behaviour of LiAl in these two media so as to identify the limiting areas in each system and to provide a direction for searching new media to be used in the secondary lithium battery. In the present study, LiCl.KCl eutectic system was chosen as the molten salt medium and methyl acetate as the organic medium.
Three electrochemical techniques, the cyclic voltammetry, chronopotentiometry and chronoamperometry, were employed for the investigation of the electrochemical kinetics for the formation of the LiAl anode in the two selected media.

EXPERIMENTAL

The LiCl.KCl eutectic mixture was prepared by mixing appropriate amounts of LiCl and KCl and purified by fusion under vacuum, preelectrolysis and filtration. Methyl acetate was purified by first shaking with anhydrous potassium carbonate to remove acidic impurities, then refluxed with acetic anhydride (85 mL/L) for 6 hours before fractional distillation to remove methanol, finally refluxed and distilled with phosphorus pentoxide under argon atmosphere to reduce the moisture content and only the middle 60% was collected after distillation. The purified solvent was kept in the dry box with dehydrated molecular sieve. All the lithium salts used were finely ground and dried under vacuum at 160°C for 48 hours before use. The experiments were performed inside the dry box.

Aluminium wire or aluminium rod encased in tygon tubing was used as the working electrode for the molten salt and the organic system. The electrode was first degreased with acetone, then mechanically polished to a mirror shine surface with alumina powder, followed by cleaning in an ultrasonic bath with methyl acetate. Electrochemically formed LiAl (50 a/o) electrode was used as the reference electrode for the molten salt study, whereas 0.1 M Ag+/Ag electrode in acetonitrile was used as reference electrode for the organic medium. Lithium metal or thermally preformed LiAl alloy was used as the counter electrode to provide a source of lithium for the electrochemical experiment.

A Princeton Applied Research (PAR) 175 Universal Programmer, a PAR 173 Potentiostat/Galvanostat and a PAR 179 Digital Coulometer/Current-to-Voltage Converter was used for cyclic voltammetric studies and chronoamperometric studies, while a PAR 363 Potentiostat/Galvanostat was used to provide constant currents for chronopotentiometric studies. For fast transient signal, Datalab DL 501 transient recorder with a Tektronix 564 oscilloscope attachment was used for recording, whereas Houston Instrument Omniscrite Y-t recorder or Esterline Angus (Model 575) X-Y recorder was used for recording slow signal. In the cyclic chronopotentiometric studies, a self-constructed electronic automatic switching unit was used to limit the coulomb of charges plated onto the electrode surface, as well as to reverse the current direction at the end of the deposition process. The adjustable timing trigger was supplied by the Chemical Electronic Model 01 Waveform Generator.
RESULTS AND DISCUSSION

Electrochemical formation of the Li/Al intermetallic phases

The appearance of a critical potential (6) for the electrochemical formation of the β-LiAl phase indicates the occurrence of nucleation polarisation, which is clearly shown to occur in freshly prepared aluminium electrode. The occurrence of a potential spike and large polarisation potential during charging and discharging were attributed to the nucleation polarisation, as both of them are markedly decreased in the use of nonalloying substrate such as nickel metal (7). The nucleation of the β-LiAl on aluminium substrate was studied using chronoamperometry and the results are shown in fig. 1. The normal i-t curves were obtained upon small potential step. However, a current minimum, followed by a current growth curve was found to occur after the potentials were stepped above a critical value in both the molten salt and the organic media.

The growth in the current growth region for the β-LiAl formation was shown (8) to follow a three-dimensional growth of the lithium in the direction from surface to the bulk of the aluminium. As the charge transfer rate for metal deposition is generally high, the current observed will be limited by mass diffusion. Under such conditions, the current density for a fixed number of crystallites, \( N_0 \), growing by hemispherical diffusive flux, is given by the following equation (9):

\[
I(t) = \frac{nF}{5\pi^2} \left( \frac{2}{D} \right) \left( \frac{N_0^2}{M} \right)^{1/2} t^{-3/2}
\]

where \( I(t) \) = current at time \( t \) in Ampere;
\( n \) = number of electron transferred;
\( F \) = Faraday constant in Coul. equiv. \( \cdot \)
\( D \) = the diffusion coefficient of the electroactive species in \( \text{cm}^2 \cdot \text{s} \)
\( C \) = the concentration of the electroactive species in \( \text{mol cm}^{-3} \)
\( M \) = the molecular weight of the electroactive species in gram;
and \( d \) = the density of the deposited species in \( \text{g cm}^{-3} \).

The \( 1/t^{3/2} \) as indicated to be constant by the above equation was verified (10) in the LiAl system. The constancy of \( i/t^{3/2} \) was further shown to be dependent on potential and a change in the nucleation growth mechanism was shown to occur during the electrochemical deposition of lithium at aluminium at intermediate potential (10).

The difference in the nucleation behaviour under molten salt and organic media is mainly due to the difference in temperature (fig. 1).
Both systems exhibit the existence of a critical potential and the change in the nucleation growth mechanism at a given stepping potential. The chronoamperograms differ in the response time and the charge density. Under molten salt media, the nucleation rate is more affected by potential and it is in general much faster than the use of the organic solvent.

Cycling studies

The cyclability of the LiAl anode is shown in fig. 2. The polarisation potential between charging and discharging is shown to be much less in the molten salt medium. Moreover, well defined plateaus for other lithium rich intermetallic phases are clearly shown using the molten salt system and only one plateau was observed under the organic medium. This is due to the occurrence of numerous lithium rich intermetallic phases and the chemical reactivities of the anode towards the organic solvent at ambient temperature.

The LiAl anode is shown to develop upon cycling under both high and low temperature systems. The polarisation potential was shown (10,11) to decrease upon cycling and the morphology of the electrode was expanded and developed into a well characterised structure under cycling with suitable c.d. The nucleation polarisation was also decreased upon cycling. However, impurities like H,O or oxide was shown (10) to have a more marked influence on the cycling efficiency for the organic than the molten salt system.

Anode/solvent interaction

The interaction between the anode and the solvent was studied using the cyclic voltammetric technique, as the system can be temporarily exposed to high activity lithium alloys during the cathodic scan. The results are shown in fig. 3. Cyclic voltammograms for the high lithium activity alloys are well characterised in the molten salt study and scanning into very cathodic potential leads to the appearance of oscillating current in the stripping voltammogram due to the liberation of potassium as a vapour from the LiCl.KCl eutectic. More interesting interaction was observed for the organic system. Three cross-over points are observed in the cyclic voltammogram upon successive cathodic scan. The first cross-over is due to the activation of the electrode surface by the deposition of the 8-LiCl. Thus, the electrode can accept more lithium at the reverse scan. The second cross-over is due to the formation of a passive film at the electrode surface, leading to a reduction in current. Further cathodic scan leads to a breakdown of the passive film with subsequent increase in current and the appearance of a wavy voltammogram. Based on the evidence from the identification of the reaction products by the i.r. and N.M.R. techniques (10), the following reaction mechanism is proposed with a two step reaction initiated by the abstraction of an acidic α hydrogen from methyl acetate.
CONCLUSION

The formation of the $\beta$-LiAl is shown to be strongly affected by the nucleation of the $\beta$ phase, which grows rapidly three-dimensionally after the potential was stepped above a critical value. The difference in the nucleation polarisation under molten salt and organic media is mainly due to the difference in temperature, which affects the nucleation rates and the current density. The LiAl anode is shown to develop upon cycling under both high and low temperature system. The polarisation potential was found to decrease while the electrode structure was developed upon cycling. However, only one plateau was observed under the organic solvent while other lithium rich alloy phases were suppressed due to their activities with the solvent. For the same reason, impurities in the solvent affect the cycling efficiency more under the organic solvent. The anode/solvent interaction as studied by cyclic voltammetry indicates a continued interaction of the solvent with the anode over a wide potential span in the organic medium, whereas the molten salt medium only deteriorates at highly cathodic potential with the liberation of potassium vapour. The formation of an unstable passivated film in the organic medium leads to further interaction of the anode and the solvent. Although a better passive film can be made by the use of LiAsF$_6$ (12, 13), the reactivity between the anode and the organic solvent is a major problem facing the use of the organic solvent. The recent development of the room temperature molten salt system may provide a medium with suitable conductivity and inertness towards lithium and its alloys. Initial promising results were obtained in the preliminary work (14,15) and the compatibility of various room temperature molten salt systems towards lithium and its alloys is at present investigated in our laboratory.
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Fig. 1. Chronoamperometric study of the nucleation of β-LiAl

A) Organic Solvent

B) Molten Salt Medium
Fig. 2. Chronopotentiometric study of the LiAl anode

A) Organic Solvent

\[
\begin{align*}
\text{Potential, volt vs Li}^+/	ext{Li}^+ & \\
0 & \quad 0.1 \quad 0.2 \quad 0.3 \quad 0.4 \quad 0.5 \quad 0.6 \quad 0.7 \quad 0.8 \quad 0.9 \quad 1.0 \\
\text{Time, min} & \\
\end{align*}
\]

\[c.d. = 5 \text{ mA cm}^{-2}\]
\[A = 0.13 \text{ cm}^2\]

charging

discharging

B) Molten Salt Medium

\[0.1 \text{ V vs Li}^+/	ext{Li}\]

charging

discharging

\[\rightarrow 1 \text{ MINUTE} \leftarrow\]

\[c.d. = 0.21 \text{ A/cm}^2\]
\[A = 0.2 \text{ cm}^2\]
Fig. 3. Cyclic Voltammetric Study of the Li/Al anode

A) Organic Solvent

R.E. = Ag⁺/Ag

Switching potential

1) -3.80 V

2) -4.00 V

3) -4.50 V

Switching potential

4) -5.00 V

5) -6.70 V
Fig. 3 (Continued)

B) Molten Salt Medium

Switching potential

1) -2.70 V

2) -2.80 V

3) -2.90 V

4) -3.05 V

R.E. = 0.2 m/o Ag⁺/Ag