LINEAR SWEEP VOLTAMMETRIC STUDIES OF THE LITHIUM/ALUMINUM ELECTRODE IN MOLTEN LiCl-KCl
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The deposition of lithium on aluminum leads to extensive alloy formation. Several fundamental phenomena, such as monolayer formation and nucleation polarisation, affect the kinetics of the deposition process. In the present investigation these phenomena were studied by (fast) cyclic voltammetry. The latter is a very useful technique for understanding qualitatively the deposition process and in its scanning coulometric modification, which is also utilised in this investigation, it can provide useful semi-quantitative information.

Voltammetric profiles corresponding to the formation of the α-phase (a solid solution of Li and Al), the β-phase (Li-Al) and the γ-phase (Li₃Al) amongst others, were identified and their characteristics investigated. The results are discussed against the background of the possible vitiating effects of impurities in the present paper.

1. Introduction.

The well tested lithium/aluminum electrode has so far proved to be the most promising anode for use in the high-temperature molten salt lithium/iron sulfide battery (1,2). The retention of lithium is good and the potential is stable throughout the α/β phase transformation from 9 a/o to 50 a/o lithium (3). However, only very few fundamental studies of the kinetics of the electrode have been carried out and these have concentrated for the most part on the β-phase (4-7).

The deposition of lithium on aluminum occurs with extensive alloy formation. Several fundamental phenomena seem to affect the kinetics of the deposition process, viz. undervoltage deposition, monolayer formation, nucleation polarisation and the formation of successive alloys with increasing lithium contents.

The present study is concerned with the light that linear sweep voltammetry throws on these phenomena, particularly in the case of the deposition (i.e. charging) process. The aim has been to complement those studies which have already been carried out using different electrochemical as well as structural techniques. Attention has been paid to the processes which occur during overcharge and overdischarge conditions, that is well away from the usual range of operation of the cell but nevertheless conditions which could

(* ** current addresses) The work was conducted at Imperial College.
Although the rapid linear sweep voltammetric technique, as has been increasingly realised in recent years, is a very powerful one for unravelling the complexities of multistep electrode processes (8-12), it does have some disadvantages in the present case because of the changes of electrode geometry which occur during charging and discharging. Because of this, linear sweep voltammetry can best be regarded as a semi-quantitative tool in the present context. Nevertheless its usefulness lies in its ability to scan the whole potential range and to provide in effect an "electrochemical spectrum". The useful potential range extends from +1.2V to -0.7V vs. a &-phase Li/Al reference electrode (see below). AlCl₃ is evolved at the anodic limit and alkali metals are deposited in massive quantities at the cathodic limit. Two types of peak are present in the "electrochemical spectrum": intrinsic peaks which arise from the deposition and stripping of alkali metals from various solid solutions and alloys and extrinsic peaks which, in spite of rigorous purification, can arise from the oxidation and reduction of various oxides, hydroxides and water.

2. Experimental.

The purification of the LiCl-KCl eutectic used as the solvent and the procedure for the assembly of the reaction cells have been described elsewhere (13). In any event, molten salt methodology is now becoming increasingly well known and several general texts describing it are available or will shortly become available (14). Ag/AgCl (0.2 m/o) was used as the reference electrode, along with Li/Al alloyed in the &-phase, particularly in later experiments. The Li/Al electrode potential is -2.27V vs. the Ag/AgCl (0.2 m/o) reference electrode. In early experiments, a graphite electrode was used as the counter electrode but as the chlorine liberated was found to be detrimental to the other cell components, a preformed Li/Al electrode was used as the counter electrode in later experiments. The working electrode was an aluminum wire, diameter 0.74 mm, supplied by BDH. Electrode potentials were controlled using a Wenking Potentiostat Control Amplifier 72L. The current output was recorded using a Bryans 26000 X-Y recorder. In the case of very fast signals, they were recorded by a Datlab DL 501 transient recorder with a Tektronix 564 oscilloscope attachment for temporary viewing. They were later reproduced at a slower rate on the Bryans X-Y recorder. Four methods were used to measure the charge passed to the electrode in the scanning coulometry experiment. The initial two manual methods were quickly superseded by two electronic methods. (a) That in which a Bentham Hi-Tek integrator was used to measure the charge directly. This is a very convenient method to measure the charge passed between the rest potential and the switching potential, as the instrument can be operated either on the total charge passed or on the positive charge alone. However, it cannot be used to measure the charge passed at intermediate potentials. (b) That in which an electronic integrator, built in this laboratory, was used.
to measure the charge passed from the rest potential to the switching potential. The integration can be initiated, held or terminated by an external TTL trigger or manually and the initial potential can be set to a potential other than zero. The design is such that if the initial potential is set to a potential other than zero, the charges in the anodic as well as the cathodic sweep can be measured.

3. Results and discussion.

3.1 General aspects.

As a framework for discussing the voltammetric behaviour of the electrode, the plot of electrode potential vs. composition from the paper by Selman, DelTuccio, Sy and Steunenberg, (3), (Figure 1), is very useful. This shows clearly the intervals of stability of the various solid solutions and intermetallic compounds for the Li/Al system at equilibrium. The battery is usually operated in the 9 a/o to 50 a/o Li region. In practice, the aluminum working electrode was always held at a potential of about +0.7v (vs. the LiAl reference electrode) to protect it cathodically before applying the voltammetric sweeps.

3.2 Cathodic to anodic switching potential in the α-phase (solid solution) region.

Figure 2 shows a typical cyclic voltammogram corresponding to the region where the deposited lithium forms a solid solution (the α-phase)(15,16,17) with the substrate aluminum. Lithium begins to deposit in fact at +0.4V vs. the Li-Al reference electrode but it is noteworthy that there is no corresponding anodic stripping peak. (It should be noted of course that there is no cathodic peak anyway.) Coulombic efficiency is low and, especially at the cathodic end, the current is much smaller at the same potential during the reverse scan than during the forward scan. Since the sizes of the lithium and aluminum atoms are similar (1.55Å and 1.38Å respectively) transportation of the lithium within the aluminum will probably be by a vacancy mechanism. The voltammetric behaviour is typical of that for the formation of a solid solution, i.e. the final equilibrium sites of the lithium atoms have a range of energies and therefore the solid solution does not form at a discrete (sharply defined) electrode potential. Also, it is difficult to remove the lithium atoms because of their low rates of diffusion in the solid solution (18,19).

3.3 Switching potential in the β-phase formation region.

Figure 3 shows what happens when the switching potential is shifted in the cathodic direction and beyond what is obviously a critical value. The much larger currents which flow at the cathodic end are marked by sharp anodic stripping peaks. This phenomenon can be related to the formation and stripping of the β-phase (the compound Li-Al) which has a much more open structure than the α-phase (bcc, a = 6.37 Å compared with the fcc structure, a = 4.05 Å of the α-phase, which is in effect an expanded Al lattice (15,16,17,20), which occurs
over a narrow range of electrode potentials.

3.4 The effect of repetitive cycling.

This is exemplified in figure 4 which shows the increases of current which occur in both the cathodic and anodic modes during repetitive cycling. This phenomenon is known as the development of the electrode and arises from two factors (a) an increase of the surface area of the electrode due to a roughening effect and (b) the creation of new frozen vacancy sites for the accommodation of deposited lithium atoms by the selective dissolution of lithium during the anodic cycles.

3.5 The behavior of newly-immersed aluminum electrodes.

The importance of surface properties is also exemplified by the cyclic voltammetric behavior of a newly-immersed aluminum electrode, shown in figure 5. New, very sharp, cathodic and anodic waves can be seen at +0.63v and +0.75v respectively, vs. the Li/Al reference electrode. The sharpness of the peaks indicates that they may originate from adsorption phenomena. As the charge under one of these peaks is roughly 40 μC and that for the formation of a monolayer (21,22) of lithium about 50 μC, it is tempting to speculate that they arise from the formation and stripping of the latter. However, as indicated by figure 6, the repeated deposition and dissolution of lithium over the α-phase region does not seem to affect these peaks although they do disappear after the electrode is exposed to repeated cycling of the β-phase. There is, of course, the possibility that these peaks may be due to electrode processes involving hydroxides and oxides of aluminum. In this regard it is perhaps worth noting that OH⁻ ions are cathodically electroactive on platinum at +0.47v vs. the Li/Al reference electrode (23).

Two more pre-peaks, which only appear with newly-immersed aluminum electrodes, are revealed (figure 7) if switching is carried out at more cathodic potentials in the β-phase formation region. These occur at +20 and +100mv respectively, vs the Li/Al reference electrode and are very sharp. The charge under one of them is about 15 μC. They gradually disappear with cycling in the β-phase region or after the aluminum electrode is immersed in the melt for a few hours. It is tempting to speculate that they are due to the redeposition of lithium atoms (to form the β-phase with the underlying aluminum) on energetically favorable sites and that these sites are annealed out during either operation or prolonged immersion on open-circuit.

3.6 Scanning coulometry.

The phenomena taking place on the aluminum substrate following the predeposition of lithium are further exemplified by the results of scanning coulometry experiments shown in figure (8) and (9). Figure 8 is a plot of total charge vs. electrode potential, whereas figure 9 shows the same data but this time plotted as the average charge...
to take account of the variation of time elapsed during a sweep when different switching potentials are utilised. Undervoltage deposition is clearly exemplified as well as the absence of a well defined threshold potential for the formation of the solid solution (α-phase) and the very marked increase of charge passed during the formation of the β-phase.

The ratios of the anodic to the cathodic charges are shown in figures 10 and 11. In the α-phase formation region, the anodic charge is always less than the cathodic charge at the same switching potential. However, as the switching potential moves into the β-phase formation region, the ratio moves closer to unity. The most obvious (and intrinsic) explanation for this reversibility of the charging process is that in this phase the lithium atoms are present in easily accessible sites. An alternative explanation is that the effects of impurities are less marked as the charging and discharging currents increase.

3.7 Dependence of the formation potential of the β-phase on the sweep rate.

Figure 12 shows clearly that the slower the sweep rate, the sharper is the β-phase formation peak because the behavior corresponds more closely to that at equilibrium. At the slowest sweep rate it is noteworthy that the cathodic and anodic peaks are identical. However, the most important factor which emerges from the variation of sweep rate is that the formation potential for the β-phase shifts in the cathodic direction with increase of sweep rate. (In the present study, it is seen that the switching potential has to be shifted in the cathodic direction in order to observe the β-phase formation peak with increasing sweep rate.) On these grounds it is reasonable to speculate that this behavior results from nucleation polarisation which it is necessary to overcome to germinate the β-phase.

3.8 The effects of more cathodic switching.

The effects of sweep rate when the switching potential is made even more cathodic (>0.2v negative to the β-phase potential) are shown in figure 13. Switching is now being carried out after the appearance of a conventional linear sweep voltammetric maximum. This indicates that the current is limited by the rate of diffusion of lithium through the β-phase. The most noteworthy feature is that, for post-peak switching at the same electrode potential, the current during the reverse sweep is smaller than during the forward sweep. The steepness of the slopes of the deposition and stripping waves indicates that the electrode is well poised and that the current is limited mainly by the uncompensated resistance of the cell. Current oscillations appear at low sweep rates, presumably as a result of changes in the (active) surface area of the electrode.
3.9 Effects of holding the electrode potential in the β-phase formation region.

It can be seen (figure 14) that two stripping (anodic) peaks manifest themselves following the 'hold' whereas, if the reverse sweep is carried out immediately following the forward (cathodic) sweep, only one stripping peak appears. The height of the second (more anodic) peak increases with 'hold' time whereas the height of the first peak only increases slightly.

It is probable that this phenomenon arises because the lithium atoms have time (with increasing 'hold' time) to diffuse from their initial sites to more (energetically) stable sites. Needless to say an extrinsic explanation based on impurity effects could also be invoked here.

3.10 Switching at extreme cathodic potentials.

Figure 15 shows that two pairs (anodic/cathodic) of peaks appear in this region. The potentials indicate that the larger pair probably results from the formation (cathodic) and dissolution (anodic) of liquid alloy and that the smaller pair results from the formation and dissolution of the γ-phase. The electrode potentials for both sets however are slightly more cathodic than their equilibrium potentials which perhaps indicates that their formation is attended by nucelation polarisation. Large currents are finally manifested at the most cathodic potentials, the cathodic limit (Fig. 15 C and D). The appearance of current oscillations in the region of the anodic peaks is accompanied by the evolution of gases from the electrode surface and the disappearance of the peaks due to lithium dissolution. Thus the formation of potassium (which is a vapor at 400°C) by the displacement reaction

\[ \text{Li} + \text{KCl} \rightarrow \text{K} + \text{LiCl} \]

is likely to take place, even though the equilibrium state would be expected to lie to the left, because the reaction is driven by the loss of potassium from the system. To confirm this hypothesis, lithium metal was added to the melt and a voltammogram recorded. The melt turned a reddish-brown and a red deposit appeared on the cool surfaces above the melt. Figure 16 shows that a stripping peak for potassium then appeared.

4. Conclusions.

These are as follows.

1. Undervoltage deposition of lithium on aluminum takes place mainly by the formation of a solid solution (the α-phase) and the β-phase.

2. There is no clear cut threshold potential for the formation of the α-phase.
3. There is a critical potential for the formation of the β-phase which seems to be accompanied by a nucleation polarisation.

4. Once the β-phase is formed, the electrode is well poised (as evidenced by the linear sweep voltammograms) and can sustain a high current with minimum polarisation.

5. The phenomena occurring at the electrode and their kinetics are very much influenced by the surface states of the electrode. Deposited metal monolayers may be involved but oxide/hydroxide arising from impurities can also play a part.

6. Fast cycling of the electrodes leads to their "development", that is both the anodic and cathodic currents flowing increase.

7. If too cathodic potential excursions occur, potassium can form. This would have a deleterious effect by leading to electronic conduction.

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Fig. 1. KMK composition diagram of lithium-aluminum alloy at 700 K (3).

Fig. 2. The formation of the α-phase on the aluminum electrode.
- Sweep rate: 100 mV/sec.
- Rest potential: +0.009 V vs LiAl
- Electrode area: 0.2 cm$^2$.

Fig. 3. The formation of the β-phase on the aluminum electrode.
- Switching potential: A -0.96V, B - 0.93V, C -0.90V.
- Rest potential: -1.376V vs Ag/AgCl reference electrode (0.2 m/o)
- Sweep rate: 100 mV/sec
- Electrode area: 0.2 cm$^2$.

Fig. 4. The effect of cycling on the deposition and stripping of lithium from aluminum.
- Rest potential: +0.8 V vs LiAl
- Sweep rate: 100 mV/sec
- Electrode area: 0.2 cm$^2$
Fig. 5 The voltammetric behavior of a newly immersed aluminum electrode.
Sweep rate: 0.1 V/sec
Rest potential: -1.411V vs Ag/AgCl (0.2 m/o)
Electrode area: 0.2 cm²

Fig. 6 The effects of lithium deposition and dissolution on the behavior of a newly immersed aluminum electrode.
Rest potential: -1.41V vs Ag/AgCl (0.2 m/o)
Sweep rate: 100 mV/sec
Electrode area: 0.2 cm²

Fig. 7 The behavior of a newly-immersed aluminum electrode in the β-phase formation region.
Sweep rate: 100 mV/sec
Electrode area: 0.2 cm²
Rest potential: -1.409V vs Ag/AgCl (0.2 m/o)
Fig. 8  Switching potential vs total charge delivered to the aluminum electrode.

Fig. 9  Switching potential vs average charge delivered to the aluminum electrode.

Fig. 10  Switching potential vs anodic and cathodic charges delivered to the aluminum electrode.

Fig. 11  Switching potential vs average anodic and cathodic charges delivered to the aluminum electrode.

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**Fig. 12** The effect of the sweep rate on the formation of the \( \beta \)-phase.

Sweep rate (mV/sec): A - 100, B - 10, C - 1

Switching potential (V): A - 0.9225, B - 0.915, C - 0.90

Rest potential: -1.375 V vs Ag/AgCl reference electrode (0.2 M)

Electrode area: 0.2 cm\(^2\)

**Fig. 13** The effect of scan rate on the deposition of lithium on aluminum.

Sweep rate: A - 100 mV/sec, B - 50 mV/sec, C - 20 mV/sec, D - 2 mV/sec, E - 5 mV/sec

Rest potential: -1.2 V

Switching potential: -2.5 V

Electrode area: 0.2 cm\(^2\)

All potentials are measured wrt Ag/AgCl (0.2 M)

**Fig. 14** The effect of different hold times on the stripping voltammogram.

Hold time: A - 5 mins., B - 15 mins., C - 55 mins.

Hold potential: +0.5 V vs LiAl reference electrode

Reverse sweep rate: 100 mV/sec

Electrode area: 0.2 cm\(^2\)

Rest potential: +0.8 V vs LiAl reference electrode.
Fig. 15 The effect of switching potential on the deposition of γ-phase and liquid lithium-aluminum alloy
Switching potential: A -2.70V, B -2.80V, C -2.90V, D -3.05V
Rest potential: -1.2V vs Ag/AgCl reference electrode (0.2 m/o)
Sweep rate 100 mV/sec
Electrode area 0.2 cm²

Fig. 16 The effect of the switching potential on the stripping of lithium and potassium in the presence of dissolved lithium metal.
Switching potential: A -0.40 V, B -0.41V, C -0.42V
Rest potential: +0.6V vs LiAl reference electrode
Sweep rate: 100 mV/sec
Electrode area: 0.2 cm²