

THE SECONDARY LITHIUM-ALUMINIUM ELECTRODE AT ROOM TEMPERATURE

I. CYCLING IN LiClO_4 -PROPYLENE CARBONATE SOLUTIONS

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Summary

The cyclability of Li-Al electrodes in 1M LiClO_4 -propylene electrolyte solutions has been studied at current densities up to 8 mA/cm^2 , charge densities up to 4 C/cm^2 and with up to 100 C/cm^2 of initially deposited lithium. It was shown that the cyclability was affected more by increasing the charge density from 2 to 3 C/cm^2 than by increasing the current density from 3 to 6 mA/cm^2 . The major factor limiting the cyclability is believed to be the utilization of lithium in the lithium-aluminium alloy.

1. Introduction

The major drawbacks of using (pure) lithium negative electrodes in room temperature secondary cells are low utilization at current densities exceeding 1 mA/cm^2 , dendrite formation, and the formation of passivating films during storage [1, 2]. Recent papers [3] suggest that these drawbacks can largely be overcome by replacing the pure metal with a lithium/aluminium alloy. The principle disadvantage of the alloy electrode is that the voltage is reduced by about 0.4 V. This could, however, be overlooked if better cyclability and better utilization were to be achieved at practical current levels up to $5 - 10 \text{ mA/cm}^2$.

The cyclability of the lithium/aluminium electrode in propylene carbonate (PC) electrolytes, together with some of its electrochemical and thermodynamic properties, have been studied recently by Garreau *et al.* [4] and by Baranski and Fawcett [5]. The data on the cyclability of these electrodes under various loads and depths of discharge are not complete and the results presented in ref. 4, for example, are obtained on Al substrates with practically unlimited thickness. Real cells operate with much thinner substrate material and it is under these conditions that the cyclability of the Li-Al electrode is of practical interest.

The present study is aimed at giving a more detailed picture of the behaviour of the Li-Al electrode in aprotic electrolytes at ambient temperature during continuous cycling as a function of current density, charge density, and the depth of discharge (DOD).

2. Experimental

The all-glass cell cases were tightly closed so that the measurements could be carried out outside the glove box. The substrate used was pure aluminium foil (99.99%). The electrodes were 0.5 mm thick with an exposed geometric surface area of 0.5 cm² and were etched in 5% KOH for 3 - 4 min. The oxide film on the Al surface was removed with 4/o's emery paper inside a glove box flushed with argon until its potential against a Li/Li⁺ reference electrode in the test solution - 1M LiClO₄/PC - was greater than 2.3 V. The counter electrodes were two Li foils (2 cm² each) pressed to Ni grids and the Li wire reference electrode was held within a glass tube. The salt and solvent were dried under vacuum to reduce the water content in the 1M LiClO₄/PC test solution to less than 50 ppm. Cycling was automatically timed.

3. Results and discussion

Since the lithium utilization (η) is equal to $(Q_a/Q_t) \times 100$ (where Q_a is the charge used for lithium dissolution and Q_t is the theoretical electric charge corresponding to the dissolved lithium), and is always less than 100%, it is necessary to preform a layer of the Li-Al alloy before cycling. This is done by cathodic deposition of lithium onto the aluminium substrate with a charge, Q_0 . It is this alloy layer which is the active part of the electrode and which takes part in the subsequent cycling process.

In these studies we have defined the cyclability of the reversible electrode as the number of usable cycles, n (*i.e.*, the number of balanced cycles with equal electric charge during deposition and dissolution, $Q_c = Q_a$), in which the overvoltage at the end of the discharge does not exceed by 100 mV the overvoltage at the end of the second discharge. This criterion was first given by Garreau [4] and is illustrated in Fig. 1 which shows the increase of polarization at the end of discharge with the number of cycles at three different current densities.

The effect Q_0 has on the cyclability of a lithium-aluminium electrode during cycling at $Q_a = Q_c = 3.6 \text{ C/cm}^2$ and $i_c = i_a = 4 \text{ mA/cm}^2$ is presented in Fig. 2. The cyclability, n , increases with Q_0 and reaches saturation at $Q_0 = 100 \text{ C/cm}^2$. This is approximately equal to 43% of the theoretical electric charge necessary to completely transform the Al substrate into lithium (50%)-aluminium (50%) alloy. Further increase of Q_0 leads to irreproducible results associated with mechanical cleavage of the alloy from the Al substrate.

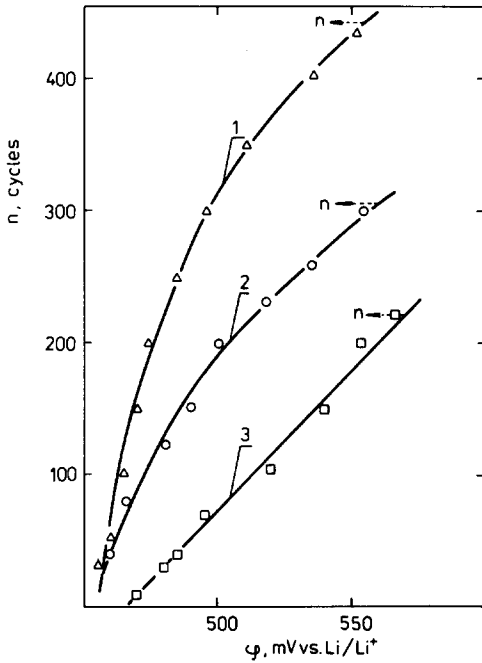


Fig. 1. The increase of Li-Al electrode polarization at the end of the discharge with cycling at different current densities: 1, 3 mA/cm²; 2, 4 mA/cm²; 3, 7 mA/cm².

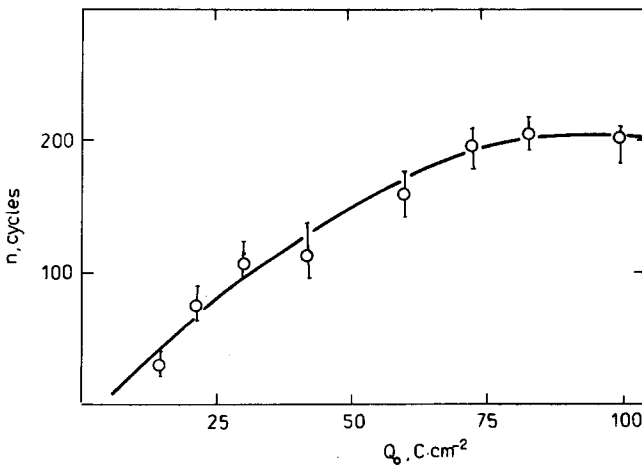


Fig. 2. The effect of the initially deposited quantity of Li (Q_0) on the cyclability (n) of Li-Al electrodes at $i_c = 4$ mA/cm² and $Q_c = 3.6$ C/cm².

The depth of discharge (DOD) has a strong effect on the cyclability, as shown in Fig. 3, curve 1. The cycling efficiency (E) defined recently by Garreau [4] as:

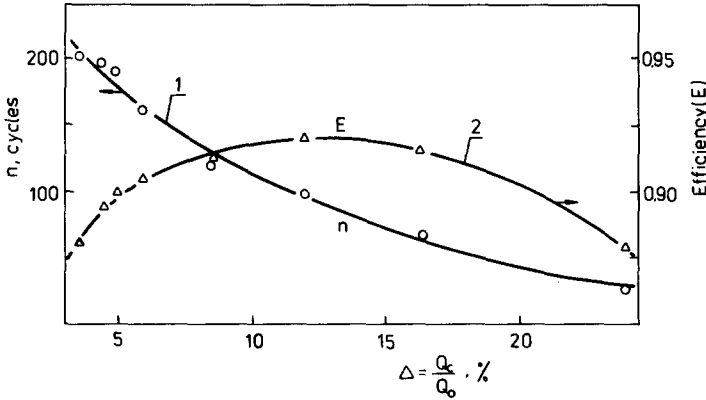


Fig. 3. The influence of the depth of discharge (Δ) on the cyclability (n) and efficiency (E) at $i_c = 4 \text{ mA/cm}^2$ and $Q_c = 3.6 \text{ C/cm}^2$.

$$E = \frac{nQ_c}{nQ_c + Q_0} \quad (1)$$

is also a function of the DOD (curve 2 in Fig. 3) and has a maximum value of $E = 0.92$ at a DOD of 13% in this particular case. This maximum, however, is a function of the cycling conditions (current density and Q_c).

With $Q_c = 3.6 \text{ C/cm}^2$ and $i_c = 4 \text{ mA/cm}^2$ the cyclability at maximum efficiency is 95 and this can only be increased by reducing the efficiency (E).

The effect the current density (i_c) has on the cyclability (n) and on the efficiency (E) at two constant charge densities (Q_c) — equivalent to DOD values of 4.2% and 8.4% — and at constant $Q_0 (= 43 \text{ C/cm}^2)$ is illustrated in Fig. 4(a) and (b), respectively. It can be seen that increasing i_c from 3 to 6 mA/cm² at $Q_c = 1.8 \text{ C/cm}^2$ (curves 1) has no significant effect on either the cyclability or the cycling efficiency of the alloy electrode, which remains between 0.91 and 0.94. At $Q_c = 3.6 \text{ C/cm}^2$ (curves 2), the same increase of i_c , however, brings about a sharp decline in the cyclability and the efficiency.

Figure 5 shows the effect charge density (Q_c) has on the cyclability (n) (curve 1) and on the efficiency (E) (curve 2) at constant forming charge (Q_0) and current density (i_c) equal to 6 mA/cm². Increasing Q_c by only 22% approximately halves the usable number of cycles (n).

It was observed that there is an optimum charge density (Q_c) for each current density, and if the latter is exceeded the efficiency drops very sharply. A decrease of i_c from 6 to 4 mA/cm² does not increase the cyclability in the range $Q_c = 1.8 - 2.2 \text{ C/cm}^2$. The same decrease of i_c has a significant effect at values of Q_c higher than 2.6 C/cm².

These results cannot be fully explained by assuming that the low cyclability of the alloy electrode is caused by mechanical degradation during cycling, as has been proposed in the literature [3, 4]. For example, it cannot explain the steep decay of the cyclability shown in Fig. 5. On the other hand, it was recently established [6] that the corrosion rate of the Li-Al

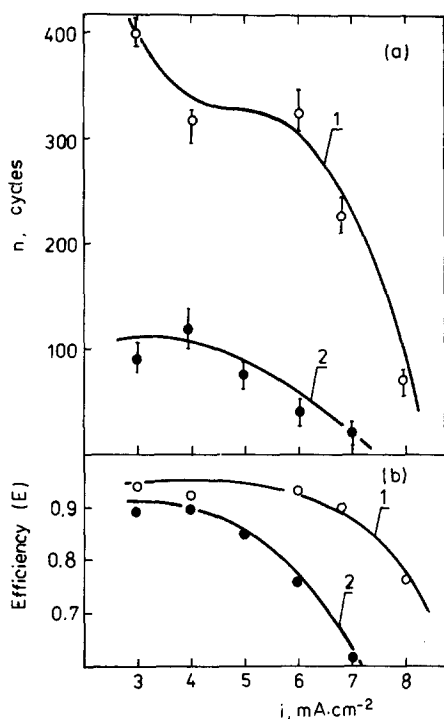


Fig. 4. The effect of current density at two different constant charge densities, Q_c and a constant $Q_0 = 43 \text{ C/cm}^2$, on: (a) cyclability (n); (b) efficiency of Li-Al electrodes: 1, $Q_c = 1.8 \text{ C/cm}^2$; 2, $Q_c = 3.6 \text{ C/cm}^2$.

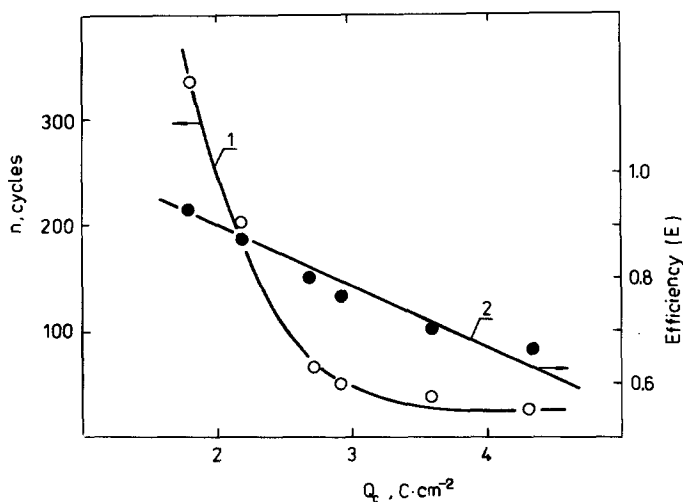


Fig. 5. The effect of the charge density (Q_c) on the cyclability (n) and efficiency (E) of Li-Al electrodes at a constant current density $i_c = 6 \text{ mA/cm}^2$ and constant $Q_0 = 43 \text{ C/cm}^2$.

electrode is very low and cannot be responsible for the unexpectedly low cyclability of this electrode.

In a recent paper Baranski and Fawcett [5] showed that, in PC using solutions of LiBr and LiI, the lithium utilization ($\eta_{\text{Li}} = Q_{\text{a}}/Q_{\text{c}}$) was not significantly affected by variations of the charge density (Q_{c}) in the range from 0.03 to 3 C/cm² and at current densities up to 2.5 mA/cm². It was therefore of interest to study the influence of Q_{c} and i_{c} on lithium under the cycling conditions used to generate the curves in Figs. 4 and 5. This was done by removing all the lithium from the lithium-aluminium electrodes prior to each charging cycle. In this way the macrostructure of the electrode was similar to that of the Li-Al alloy electrodes, but the determination of Q_{c} was not influenced by any residual lithium in the electrode.

These conditions were met by forming the lithium-aluminium alloy as described in Section 2: cycling it 40 - 50 times with $Q_{\text{c}} = 1.8$ C/cm² and $Q_{\text{a}} = 0.8 \times Q_{\text{c}}$ at $i_{\text{c}} = 2$ mA/cm² and finally discharging to a cut off voltage of 2.5 V against Li/Li⁺. This procedure gave a "lithium-free electrode" with a suitable structure for cycling. We studied the effects which Q_{c} had on η_{Li} at constant i_{c} and which i_{c} had at constant Q_{c} . The data shown in Table 1 are averaged over at least 5 cycles with the end of the discharge time (τ_{a}) determined from the steepest part of the $\varphi-t$ plots. This procedure was repeated under the same conditions (Q_{c} and i_{c}) until the reproducibility of the lithium utilization (η_{Li}) was better than 2 - 3%. Finally, the electrode was discharged at 2 mA/cm² to a cut-off voltage of 2.5 V (Li/Li⁺).

TABLE 1

No.	i_{c}	Q_{c}	η_{Li}
1	6.0	1.8	0.932
2	6.0	2.54	0.885
3	6.0	3.24	0.858
4	6.0	3.94	0.795
5	3.0	1.8	0.950
6	4.0	1.8	0.943
7	6.7	1.8	0.920
8	8.0	1.8	0.885

Figure 6 presents the theoretical cyclability (n_{t}) as a function of the charge density (Q_{c}). n_{t} was calculated using the data shown in Table 1 and is given by:

$$n_{\text{t}} = \frac{Q_0}{Q_{\text{c}}(1 - \eta_{\text{Li}})} \quad (2)$$

The assumption implicit in the determination of n_{t} is that the deficit in the discharge density (Q_{a}) is compensated on each cycle by the excess lithium initially introduced into the electrode (Q_0) (see Figs. 2, 4, 5). This excess does not vary during cycling. Also in Fig. 6, the experimentally found

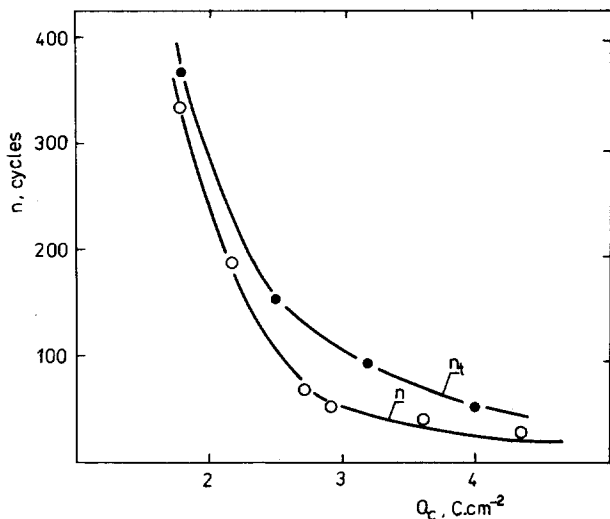


Fig. 6. The theoretically estimated cyclability (n_t) and experimentally achieved cyclability (n) as a function of charge density at $Q_0 = 43 \text{ C/cm}^2$ and $i_c = 6 \text{ mA/cm}^2$.

relationship of Q_c vs. n at $Q_0 = 43 \text{ C/cm}^2$ (given in Fig. 5) is plotted for comparison. It can be seen that there is very good agreement between the theoretical and experimental curves.

The data in Table 1 make it clear that increasing the current density up to 6 mA/cm^2 at constant Q_c results in only insignificant changes in the lithium utilization. This may explain the small variations of cyclability with the relatively large increase of the current density from 4 to 6 mA/cm^2 shown in Fig. 4.

Scanning electron microscope pictures of Li-Al electrodes cycled at constant charge density ($= 1.8 \text{ C/cm}^2$) and at two current densities, 3 mA/cm^2 at the 420th cycle and 6.7 mA/cm^2 at the 220th cycle, are shown in Figs. 7 and 8. Figure 7 demonstrates, in agreement with the data in Table 1, that the high cyclability obtained under these conditions is associated with the presence of a well developed surface exhibiting only few shallow cracks. Increasing the current density by about a factor of 2, however, results in extensive cracking of the electrodes, as shown in Fig. 8. Nevertheless, even in the latter case, the theoretical cyclability ($n = 290$) was still close to that found experimentally ($n = 220 - 250$) — see Figs. 1 and 4. This finding, therefore, refutes the assertion that changes in the macrostructure, and the degradation in the mechanical bonding between the alloy and the aluminium substrate, are the major factors limiting cyclability [3, 4].

A microscopic study of electrodes cycled at $i = 6 \text{ mA/cm}^2$ but at a higher Q_c (2.7 C/cm^2) revealed a structure virtually identical with that shown in Fig. 8 (i.e., at $Q_c = 1.8 \text{ C/cm}^2$) although they were cycled 4 times less. Again, it appears that the major factor limiting the electrode cyclability is low lithium utilization at the higher charge density (see Table 1). This

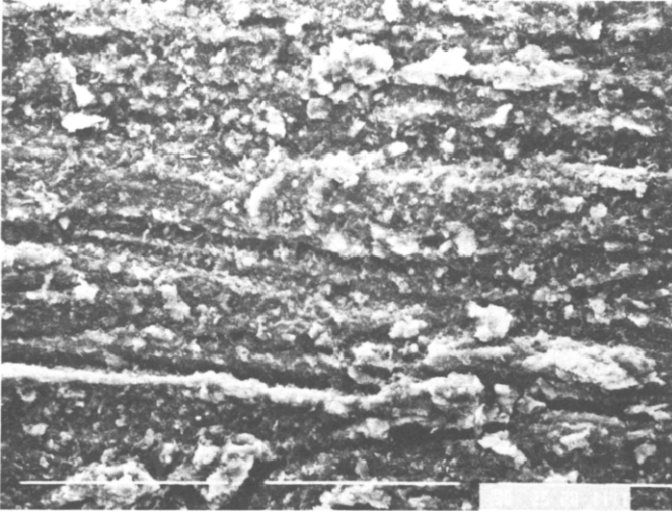


Fig. 7. Scanning electron micrograph of a Li-Al electrode after 420 cycles at $Q_0 = 43 \text{ C/cm}^2$, $Q_c = 1.8 \text{ C/cm}^2$ and $i_c = 3 \text{ mA/cm}^2$. ($\times 350$.)

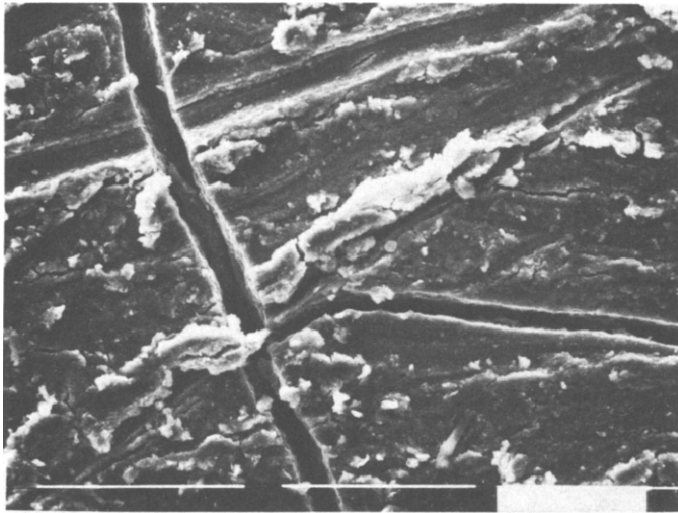


Fig. 8. Scanning electron micrograph of a Li-Al electrode after 225 cycles at $Q_0 = 43 \text{ C/cm}^2$, $Q_c = 1.8 \text{ C/cm}^2$ and $i = 6.7 \text{ mA/cm}^2$. ($\times 350$.)

could, in turn, lead to degradation in the macrostructure of the Li-Al alloy due to the continuous increase of non-utilized lithium during cycling and hence, to the development of excess stresses in the structure. Thus, under heavy duty conditions ($i_c > 6 \text{ mA/cm}^2$ and $Q_c > 2 \text{ C/cm}^2$), where lithium utilization is significantly reduced, degradation of the mechanical bond between the Li-Al alloy and the aluminium substrate could occur. In these cases the relative deviations between the experimental and theoretical (eqn. (2)) cyclability are more pronounced (see Fig. 6 at $Q_c > 2.7 \text{ C/cm}^2$).

4. Conclusions

The Li-Al electrode can be cycled continuously with a high utilization at charge/discharge densities up to 2 C/cm² and current densities up to 6 mA/cm². The good cyclability is achieved by the preliminary electrochemical formation of a layer of Li-Al alloy on the aluminium substrate. Increasing the depth of discharge, however, deteriorates the cyclability of the electrode as a result of the decrease in the lithium utilization and the consequent fast depletion of the Li reserves.

List of symbols

Q_0	Charge used to preform a layer of β -Li-Al alloy (C cm ⁻²)
Q_t	Theoretical electric charge corresponding to the dissolved Li (C cm ⁻²)
Q_a	Charge used for Li dissolution (C cm ⁻²)
Q_c	Charge used for Li deposition (C cm ⁻²)
η_{Li}	= $(Q_a/Q_t) \times 100$ lithium utilization (%)
Δ	= $(Q_a/Q_0) \times 100$ depth of discharge (%)
E	Cycling efficiency — see eqn. (1)
n_t	Theoretically expected electrode cyclability (cycles) — see eqn. (2)
n	Electrode cyclability (cycles)
i_c	Cathodic current density (mA cm ⁻²)
i_a	Anodic current density (mA cm ⁻²)
φ	Electrode potential (mV) vs. Li/Li reference electrode

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