

Lithium electrodes with and without CO₂ treatment: electrochemical behavior and effect on high rate lithium battery performance

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Abstract

The ionic resistivity and integrity of a solid-electrolyte interphase (SEI) film on a lithium electrode surface was investigated. The preformed lithium carbonate film on the surface of the lithium electrode was found to improve the electrode behavior by maintaining a low ionic resistance. In lithium/silver vanadium oxide batteries, voltage delay can be eliminated with the use of a lithium anode pretreated with CO₂. An SEI consisting of lithium carbonate appears to be responsible. Unlike the surface film formed from lithium-electrolyte reactions, the lithium carbonate film is relatively strong and can withstand high current density pulses (~20 mA/cm²) without significant damage. An ion exchange mechanism involving the carbonate anion is proposed.

Keywords: Lithium carbonate; Voltage delay; Solid-electrolyte interphase; Lithium batteries

1. Introduction

Since all nonaqueous organic electrolytes are thermodynamically unstable toward lithium metal, the successful development of lithium battery technology using organic electrolytes is largely based on the formation of a lithium anode–solid electrolyte interphase (SEI) passivation layer. In reality, the anode SEI surface film always exists in lithium batteries. The composition and properties of the SEI surface film play a critical role in determining a lithium battery's electrochemical performance. In some cases, the SEI film increases the internal cell resistance due to its high ionic resistivity which can lead to poor performance characteristics. Therefore, the characterization and modification of SEI surface films have been areas of intensive investigation during the last decade [1–13]. Understanding the properties of the SEI is not only interesting fundamentally, but also important for practical applications.

One way to modify the SEI is to use electrolyte additives [12–23]. Among those studies, one important finding is that CO₂ saturation of nonaqueous organic electrolytes leads to significant improvement in the performance of lithium batteries (both primary and secondary) [12,13,18–23]. The improvement has been attributed to the formation of Li₂CO₃ as a dominant component on the lithium anode surface due to the following reaction



This lithium carbonate modified surface film provides better protection of lithium or lithium ion intercalated carbon anodes from further reactions with the electrolyte.

Although many reports have demonstrated the beneficial effect of Li₂CO₃ derived from the above reaction, the chemical and physical properties of the Li₂CO₃ film are not well defined due to the complexity of the surface film composition which also contains electrolyte decomposition products. The composition of the surface film depends on the competing reactivity of lithium metal with solvents, electrolyte salts and CO₂ [23].

In the present paper we report an investigation in which the lithium electrode is precoated with Li₂CO₃ by exposing a fresh lithium surface to CO₂ atmosphere. The effects of this surface film on the performance of lithium/silver vanadium oxide (SVO) batteries [24–27] under high current density discharge are evaluated. Furthermore, the kinetics of lithium ion transfer across this Li₂CO₃ SEI are studied by linear polarization experiments. Based on the results of the above experiments, a mechanism for lithium ion transfer across the SEI is proposed.

2. Experimental

All the electrochemical kinetic studies were carried out in a glove box under an argon atmosphere. A five-electrode cell

(with two working electrodes, two counter electrodes and one reference electrode) was used in which the reference electrode (placed above the center of the working and reference electrodes) was made from lithium ribbon. The working lithium electrodes and counter electrodes (placed face-to-face) were prepared by pressing a lithium rod (99.9% from Aldrich) into a hole in the electrode holders. The lithium rod was then cut with a razor blade to obtain a mirror-like flat surface with approximately 0.1 cm^2 surface area. One working electrode thus prepared was transferred into the glove box port which was pumped to remove argon and filled with CO_2 (99.99% from Air Products). The electrode was kept under CO_2 for 65 h. The second working electrode was used without any treatment. Some small variations between different electrodes exist due to the difficulty in getting a perfectly flat lithium surface. However, these variations do not affect the conclusions obtained from the present study.

The electrolyte used in this study was 1.0 M LiAsF_6 in 1:1 by volume ratio of propylene carbonate (PC) and 1,2-dimethoxyethane (DME). LiAsF_6 (electrolyte grade) was obtained from FMC Corporation and used as received. PC was dried with 4A molecular sieves and filtered through an alumina column. DME was purified by distillation over sodium and benzophenone. The electrolyte was also used in building the SVO batteries as described below.

Linear polarization measurements with a scan rate of 0.15 mV/s and scan range of 0 to 15 mV versus Li/Li^+ were conducted with an EG&G Princeton Applied Research potentiostat/galvanostat Model 273 and Model 352 Soft CorrTM II corrosion measurement and analysis software. The galvanostatic measurements (high current discharge: 2 mA for 20 s; $\sim 20 \text{ mA}/\text{cm}^2$) were also conducted with the same instrumentation and software. The electrochemical test cell assembled with the above lithium electrodes was kept in the glove box under argon throughout the entire experiment. The potential-current linear relationship was monitored periodically at room temperature (22–23 °C). The effect of electrode/electrolyte contact time (or storage time) on the exchange current was analyzed.

SVO batteries were fabricated using anodes with and without CO_2 treatment. Lithium anodes were prepared by pressing lithium ribbon onto nickel current collector screens under dry air. For test cells (group 1), the surface of the anodes was brushed to expose fresh lithium in the glove box under argon. The anodes were then treated with CO_2 in the same manner as described above for 17.5 h before moving them out of the glove box. SVO cathode material was pressed onto titanium current collector screens. Prismatic cell stack assemblies with two layers of microporous membrane polypropylene separator sandwiched between the anode and cathode were prepared. The electrode assemblies were placed into stainless-steel casings and activated with electrolyte. The final package was hermetically sealed. The comparative cells (group 2) were prepared in the same manner except that the anodes were not brushed when treated with CO_2 . The control cells (group 3) were assembled in the same way as group 2

cells except that the anodes were not treated with CO_2 . Electrochemical tests were conducted by discharging the batteries under various conditions. High current pulses with a current density of $18.4 \text{ mA}/\text{cm}^2$ were applied at various depths-of-discharge. The results from batteries with CO_2 treated anodes (with brushing, group 1) and batteries with standard anodes (without brushing, group 2 and group 3) were compared and analyzed.

3. Results and discussion

3.1. Effect of lithium anode CO_2 treatment on Li/SVO battery electrochemical behavior

In 1988, Ebner and Lin [18] reported the beneficial effect of CO_2 saturated electrolyte on the electrochemical performance of lithium batteries. Since then, many studies have been carried out to further confirm this conclusion [12,13,18–23]. The formation of lithium carbonate as one of the components in the anode surface passivation layer is believed to be responsible for the observed improvements. In our studies, SVO batteries with lithium carbonate coated lithium anodes were constructed. In contrast to others, the anodes were pretreated with CO_2 to generate the desired lithium carbonate surface film prior to cell assembly. Standard electrolyte (1.0 M LiAsF_6 in 1:1 volume ratio PC/DME) without CO_2 was used.

One phenomenon observed in lithium/SVO battery discharge is voltage delay under high current pulses ($\sim 20 \text{ mA}/\text{cm}^2$). Voltage delay is defined by the positive value of pulse end potential minus pulse minimum potential. As shown in Fig. 1 (control cells), in a typical pulse train (current density = $18.4 \text{ mA}/\text{cm}^2$; four 10 s pulses with 15 s rest between the pulses), voltage delay exists in the first pulse. For batteries assembled with the CO_2 pretreated anode (group 1 cells), voltage delay was found to be completely suppressed (Fig. 2).

Since voltage delay is known to be caused primarily by the high ionic resistance of the lithium anode surface film, the



Fig. 1. Li/SVO battery with standard lithium anode discharged at 37 °C under $18.4 \text{ mA}/\text{cm}^2$.

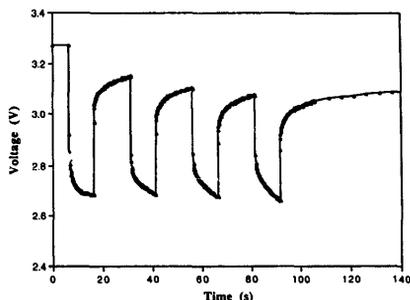


Fig. 2. Li/SVO battery with CO_2 treated lithium anode discharged at 37°C under 18.4 mA/cm^2 .

chemical composition and properties of the film can have a significant effect on battery pulse behavior. In the above examples, cells were pulse discharged at the beginning of life. Since the lithium anodes were exposed to air before the cell assembly, the naturally present lithium oxide layer on the lithium anode surface in the control cells is believed to be responsible for the observed voltage delay. For the cells with CO_2 pretreated anodes, the original Li_2O film was replaced by a Li_2CO_3 film by exposing the fresh lithium surface [1]. In addition, this lithium carbonate film present on the anode surface prevents or slows further reaction of lithium with the oxygen in the air. The film may also prevent the reaction of lithium with the electrolyte after battery assembly. Thus, no voltage delay was observed.

The necessity of brushing the anode surface to generate the desired lithium carbonate surface layer by CO_2 treatment is also demonstrated in the present study. If the anode surface was not brushed to remove the lithium oxide film before CO_2 treatment (group 2), the test results show that this group of cells behaved very similar to the cells of control group (group 3). Large voltage delay was observed (see Table 1).

It is also interesting to point out that the voltage delay exists only in the first pulse (Fig. 1). This suggests that the surface film (lithium oxide + electrolyte decomposition

products) which causes voltage delay can be broken up under high current pulses. For control cells, the ionically high resistance lithium oxide layer was broken during the first pulse. Therefore, in the second to fourth pulses, no voltage delay can be detected. The exposed fresh lithium surface, however, can react with electrolyte to generate a new surface passivation layer. After significant storage time, a new surface layer may introduce voltage delay under high current pulses if it has high ionic resistance. It may also be again disrupted under the pulses as demonstrated in the following experiments.

Based on the above pulse train results, we cannot distinguish whether or not the lithium carbonate film on the anode surface was also disrupted during the first pulse train, since there was no voltage delay in any of the four pulses (Fig. 2). However, if the surface film was broken, the pulse behavior of these cells would be similar to that of the control cells in the subsequent tests. An additional consideration is that the lithium anode is consumed under discharge. Dissolution of lithium will definitely affect the anode surface conditions, and the initial surface film could be disrupted and then replaced by a new surface film generated from reactions between lithium metal and electrolyte components. To clarify these questions, we further discharge the SVO batteries discussed above under $200\ \Omega$ constant resistors to remove about 50% of their capacity. The cells were then stored at 37°C at open-circuit potential for eight weeks before applying another pulse train (pulse train 2, see Table 1). As expected, significant voltage delay was present in the control cells (group 2 and group 3). Whereas, the test cells (group 1) with CO_2 treated anodes showed very small voltage delay. Similar results were obtained when the above cells were further discharged under $17.4\text{ k}\Omega$ loads at 37°C and pulsed every eight weeks (Table 1, trains 3 and 4).

The results indicate that the lithium carbonate film on the anode surface in the treated cells was not broken under either high current density pulses or under constant load discharge. Even the dissolution of the lithium metal (up to about 50%) under discharge did not completely remove the lithium carbonate surface layer. Voltage delay was still substantially smaller in the treated cells than in the control cells even when

Table 1
Effect of anode surface treatment on voltage delay

Pulse train	% Discharge	Anode pretreatment	Prepulse potential (V)	Voltage delay (V)
1	0	CO_2 (brushed)	3.276	0.000
1	0	CO_2 (not brushed)	3.273	0.130
1	0	None	3.274	0.159
2	54	CO_2 (brushed)	2.608	0.011
2	54	CO_2 (not brushed)	2.606	0.170
2	54	None	2.604	0.144
3	66	CO_2 (brushed)	2.497	0.071
3	66	CO_2 (not brushed)	2.497	0.138
3	66	None	2.494	0.140
4	78	CO_2 (brushed)	2.383	0.027
4	78	CO_2 (not brushed)	2.379	0.030
4	78	None	2.372	0.047

the cells had been pulsed 12 times (three pulse trains) and were discharged to about 80% of their capacity (pulse train 4). This improvement was achieved without the presence of CO_2 in the electrolyte, as in previously reported examples, where the CO_2 in the electrolyte can act as a lithium carbonate film repairing agent. This unexpected finding provides further insight into the nature of the lithium carbonate film and sheds some light on the mechanism of lithium ion transfer across the SEI.

3.2. Kinetics of lithium ion transport across the SEI surface film: exchange current study

Due to the high reactivity of lithium metal, it is very difficult, if not impossible, to get the true exchange current for a film-free lithium surface. The exchange current densities for lithium electrodes reported in the literature are widely scattered, ranging from 0.30 to 10.2 mA/cm^2 , depending on the experimental conditions and method used in preparing the working electrode [28–31]. The disagreement among these reports can be best explained by the specific state of surface film formation of the lithium electrode. It can be viewed as a process of Li^+ moving across the SEI. The kinetics of this lithium ion transfer process are strongly affected by the composition, thickness and properties of the SEI surface film. Therefore, exchange current density measurements can be a good method to study the kinetics of lithium ion transfer across the SEI under controlled conditions which, in conjunction with other studies, may provide insight into the physical and chemical properties of lithium electrode SEI film.

Fig. 3 shows the correlation of exchange current density (i_0) with storage time. The measured i_0 decreases as storage time increases for both fresh cut and CO_2 treated lithium electrodes. This trend can be explained by the lithium electrode passivation. In the case of the freshly cut lithium electrode, a sharp decrease in i_0 was observed within the first 48 h. It is expected that the fresh lithium surface reacts with electrolyte to form a passivation layer. This layer becomes

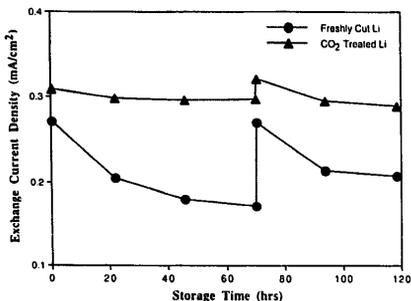


Fig. 3. Effect of lithium electrode surface treatment on exchange current density.

thicker with prolonged storage. As a result, the exchange current density decreases due to the increase in surface film thickness and higher ionic resistivity. In contrast, the i_0 for the CO_2 treated electrode was essentially unchanged, with only a slight decrease within the same time period. Fig. 4 presents the polarization resistance measurements for both electrodes. The maximum resistance increase for the freshly cut lithium electrode is as high as 470 Ω , while for CO_2 treated lithium electrode the increase is below 60 Ω within the same storage time period. It suggests that the lithium carbonate film has effectively passivated the surface of the lithium electrode. The reactions between lithium and the electrolyte, as occurring in the case of freshly cut lithium electrode, are suppressed. Due to the high lithium ion conductivity of the lithium carbonate film, the i_0 was maintained at the same level.

When the working lithium electrodes were galvanostatically discharged under a current density of $\sim 20 \text{ mA}/\text{cm}^2$ for 20 s, the exchange current densities measured immediately after the high current discharge increased significantly, especially for the freshly cut electrode (Fig. 3 at 70 h storage time). This i_0 recovery is probably due to surface film breakage under high current pulses. The resistance of SEI would thus be decreased (Fig. 4). The difference between the CO_2 treated lithium electrode and the nontreated electrode is also apparent after the high current density pulse test. The exchange current density of the untreated electrode decreases very rapidly, while for the CO_2 treated electrode, the decrease proceeds much more slowly (Fig. 3). We attribute this observation to the formation of a compact and strong lithium carbonate film which can withstand high current pulses without significant damage. Therefore, even after the galvanostatic pulse, the dominant SEI component on the lithium electrode surface is still lithium carbonate.

In agreement with the observation of Fujieda et al. [21], the CO_2 treated lithium electrode showed no voltage delay during the galvanostatic pulse (Fig. 5). In contrast, the untreated electrode showed significant voltage delay, as much as 430 mV. These results correlate very well with the data observed for Li/SVO batteries under pulse discharge. The

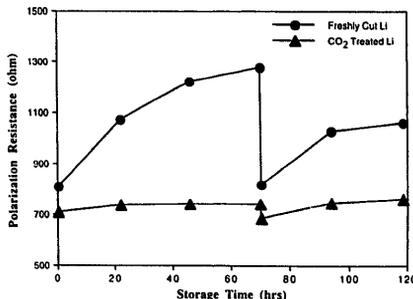


Fig. 4. Lithium electrode/electrolyte storage and SEI polarization resistance.

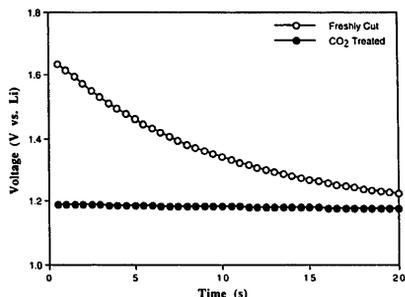


Fig. 5. Effect of lithium electrode surface treatment at a discharge current density of 20 mA/cm².

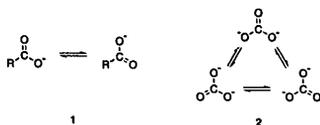


Fig. 6. Charge center delocalization.

untreated lithium electrode or batteries showed substantial voltage delay which disappeared after a high current density pulse. On the other hand, the CO₂ treated lithium electrode or batteries presented no voltage delay, indicating that the lithium carbonate surface film was maintained after the high current density discharge.

3.3. Mechanism of lithium ion transfer across SEI

When an electron is removed from the lithium electrode, the resultant lithium ion transfers from the solid lithium surface to the electrolyte solution by passing through the SEI. The kinetic energy needed to complete this process will be quite different depending on the composition of SEI. In other words, if the ionic resistance of the SEI is high, a high activation energy will be needed for a lithium ion to pass through it. Since the surface passivation layer of a lithium electrode is composed of various lithium salts, the most likely mechanism for lithium ion transfer through the SEI film is lithium ion exchange as demonstrated in the following equation

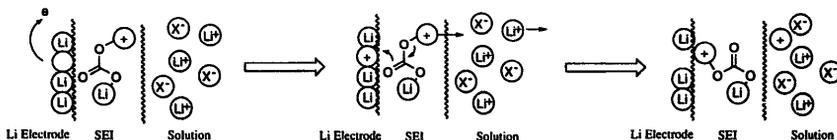
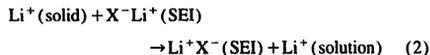


Fig. 7. Mechanism of lithium ion transfer across lithium carbonate SEI surface film.

The maximum current density the SEI surface film can withstand without being damaged is dependent on the rate of lithium ion exchange according to the above equation. The lithium ion exchange rate is proportional to the exchange current density i_0 . The higher the i_0 , the lower the SEI ionic resistance (Figs. 3 and 4), and the lower the activation energy needed for the ion transfer reaction [31]. In a fashion similar to organic carboxylates (1), the charge center in a carbonate (2) can shift from one oxygen atom to the other due to molecular orbital interaction and charge delocalization (Fig. 6). The presence of orbital interaction and charge delocalization in lithium carbonate provides an additional channel for a relatively fast intermolecular lithium ion exchange (Fig. 7). Such a channel, however, does not exist in many other lithium salts, such as lithium oxide, lithium halides and simple alkyl lithium salts. As a result, the lithium anode surface film composed of other types of lithium salt would have a low lithium ion exchange rate or a high ionic resistance [13]. The surface film would be expected to break under high current density discharge. In contrast, the lithium carbonate film should present relatively low ionic resistance and the film should maintain its mechanical integrity after high current density pulses and even after partial dissolution of the lithium metal. Furthermore, Aurbach et al. [13] have shown that the substitution of lithium carbonate by lithium fluoride and other insoluble electrolyte reduction products increases the resistivity of the SEI, which is also consistent with our conclusion. The proposed mechanism of lithium ion transfer across the lithium carbonate SEI is schematically described in Fig. 7. During discharge, the original lithium ion in the SEI is replaced by the lithium ion from the lithium electrode. Carbonate anion in the SEI can move along the surface of the lithium electrode during discharge. As long as the current density is within its limit, the lithium carbonate film will not break off the electrode surface.

4. Conclusions

The formation of a lithium carbonate film on the surface of a lithium electrode improves the electrode behavior by maintaining a low ionic resistance in the SEI. This SEI acts to slow down the electron transfer reactions between lithium metal and the electrolyte, minimizing surface film growth, and as a result minimizes or eliminates voltage delay. Unlike the surface film formed from lithium-electrolyte reactions, the lithium carbonate surface film is relatively strong and can

withstand high current pulses ($\sim 20 \text{ mA/cm}^2$) without significant damage as demonstrated in the present study. An ion exchange mechanism involving the carbonate anion is proposed.

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