

Effect of carbon dioxide on lithium anode cycleability with various substrates

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Abstract

The effect on the enhancement of the charge/discharge behavior of electrodeposited lithium metal on various substrates with CO₂ was investigated in LiClO₄/propylene carbonate electrolyte. The lithium cycleability was enhanced with CO₂ addition to the electrolyte solution when using nickel and titanium substrates, whereas no apparent enhancement was observed with copper and silver substrates. The results obtained from voltammetry indicated that the reduction of CO₂ did not occur on nickel and titanium, but on copper and silver. It is suggested that the enhancement with CO₂ addition is effective with the substrates which do not reduce CO₂ in the electrolyte before lithium deposition. © 1997 Elsevier Science S.A.

Keywords: Lithium anodes, Cycleability, Carbon dioxide

1. Introduction

A rechargeable lithium battery with lithium metal anode has a great advantage in energy density; it has been widely studied, because lithium has the lowest electrochemical equivalent and the most negative redox potential. However, the charge/discharge cycleability of the lithium metal anode is degraded by the formation of dendritic deposits, which causes the isolation of active lithium metal and also short circuit with the cathode [1,2]. Another reason for the poor cycleability of lithium anode is the formation of a passivating layer with low or no ionic and electronic conductivity, which is formed by the reaction of the solution components such as the solvent, the electrolyte, and traces of contaminants (water, oxygen, etc.) because of the high reactivity of lithium metal. Recent studies on lithium anode are focused on the detailed analysis of the surface layer [3,4] and there are some modifications using various methods for preventing the dendritic deposition [5,6].

Carbon dioxide as well as Al₂O₃, SO₂, and p-conjugated organic compounds, etc., have been known as additives to promote cycle efficiency of the lithium anodes [2,5,7,8]. We have already reported that CO₂ dissolved in electrolyte solutions enhances the cycleability of lithium deposited on nickel

substrate when CO₂ is present during lithium deposition [9,10]. In this paper, we report the correlation between the substrate and the effect of CO₂ on lithium cycleability, and discuss the working mechanism of CO₂ in the electrolyte.

2. Experimental

Propylene carbonate, PC (Tomiya pure chemical, lithium battery grade) was used with 1.0 M LiClO₄ (Tomiya pure chemical, lithium battery grade) as a supporting electrolyte. The water content of the solvent and the supporting electrolyte was less than 20 and 26 ppm, respectively. Gaseous CO₂ with 99.99% purity was dissolved until saturation in the electrolyte solutions before lithium deposition. Substrates for lithium deposition were nickel, titanium, copper and silver. All the substrates were mechanically polished to produce mirror-like surfaces. The electrochemical cell was constructed with a Li/Li⁺ reference electrode and a lithium foil counter electrode.

The charge/discharge cycling tests were conducted by the following procedure proposed by Goldman et al. [11]: 1.0 C cm⁻² of lithium was initially deposited on the substrate at 1.0 mA cm⁻² of constant current and 0.2 C cm⁻² of lithium was stripped and then deposited at the same current density. This charge/discharge cycle was repeated until the discharge potential reached +1 V versus Li/Li⁺. From this cycling

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tests, the average efficiency per cycle, E_a , was calculated according to Eq. (1)

$$E_a = \frac{Q_c - Q_{ex}/n}{Q_c} \times 100(\%) \quad (1)$$

where Q_c is the cycling charge of Li (0.2 C cm^{-2} for each cycle), Q_{ex} is the charge of excess Li (0.8 C cm^{-2}) and n is the number of apparent 100% cycles.

The electrochemical reaction occurred on the substrate in the electrolyte was monitored by voltammetry at a scan rate of 5 mV s^{-1} in the potential range from open-circuit potential ($\sim 2.9 \text{ V}$) to 0 V . The electrochemical impedance was measured using 10 mV (zero to peak) a.c. voltage over a frequency range from 10 Hz to 20 kHz with a galvanostat/potentiostat (Hokuto Denko HA-501G) and a frequency response analyzer (NF Electric Instruments FRA S-5720C). Cell assembly and electrochemical measurements were conducted under dry argon gas atmosphere.

3. Results and discussion

3.1. Charge/discharge cycleability with various substrates

Table 1 shows the cycle number which was repeated during the cycling test. These numbers are representative results depending on the initial deposition charge and the cycling charge. When the initial deposition was scaled up to 10 C cm^{-2} the cycle life (at 2% depth-of-discharge (DOD)) became more than 3000 cycles (more than $E_a = 99.8\%$) for the case of lithium deposited on nickel in the presence of CO_2 , as compared with 115 cycles ($E_a = 96.5\%$) for 1 C cm^{-2} of this case (at 20% DOD). In the case of electrolyte solutions without additives, lithium deposited on nickel substrate showed the best cycleability, compared with titanium, copper and silver substrates to/in which the cycleability of lithium was poor. With CO_2 addition, the cycleability of lithium on titanium substrates was enhanced, as well as on nickel. However, it was hardly noticed when copper and silver substrates were used. The effect of CO_2 has already been studied using nickel substrate and showed the following features:

Table 1
Cycleability of lithium anode deposited on the various substrates

Substrate	1 M LiClO_4/PC		
	without CO_2	with CO_2	with CO_2 reduction ^a
Ni	58 ($E_a = 93.1\%$)	115 ($E_a = 96.5\%$)	103 ($E_a = 96.1\%$)
Ti	29 ($E_a = 86.2\%$)	136 ($E_a = 97.1\%$)	118 ($E_a = 96.6\%$)
Cu	22 ($E_a = 81.8\%$)	26 ($E_a = 84.6\%$)	2
Ag	15 ($E_a = 73.3\%$)	18 ($E_a = 77.8\%$)	12 ($E_a = 66.7\%$)

^a Treatment of reduction of CO_2 was conducted at $+1.4 \text{ V}$ vs. Li/Li^+ for 3 min before deposition of lithium.

1. The interfacial resistance of lithium, which was obtained by in situ galvanostatic a.c. impedance method and estimated from the diameter of the semi-circle of the Cole-Cole plots obtained (regarded as a charge-transfer process) in the high frequency region, was lowered with CO_2 addition [10].
2. The dendritic form of lithium deposition observed in the CO_2 -free solutions was suppressed in the presence of CO_2 during lithium deposition [12].
3. The reactivity of lithium against water was much reduced, which indicates the modification of the surface layer on lithium due to the presence of CO_2 [10].

As a result of the impedance measurements, lowering the lithium interfacial resistance in the presence of CO_2 is common to all the substrates. However, the cycleability of lithium on copper and silver substrates was hardly enhanced even in the presence of CO_2 . Thus, it is suggested that the behavior of the lithium anode is affected also by the other factors.

In order to better understand the interaction between the substrates and CO_2 in the electrolyte solutions, the electrochemical behavior of the solutions on various substrates before lithium deposition was investigated by voltammetry.

3.2. Electrochemical behavior on various substrates

The electrochemical behavior of traces of contaminants (water, oxygen, etc.) in a non-aqueous electrolyte gives an important indication about the state of the electrode since they are reduced on substrates before lithium deposition and form a passivating layer [13]. In the case of nickel substrate, two cathodic peaks appear at $+1.9$ and $+0.5 \text{ V}$, as shown in Fig. 1(a). These peaks are attributed to the reduction of oxygen or nickel oxide and the underpotential deposition (UPD) of lithium, respectively. With CO_2 addition, no change of this cathodic behavior is observed. Fig. 1(b) shows similar results on titanium substrate, except for the absence of the cathodic peak around $+1.9 \text{ V}$. On the other hand, in the case of copper and silver substrates, the cathodic behavior is changed and new peaks are observed with CO_2 addition as shown in Fig. 1(c) and (d). On a silver substrate, a new cathodic peak appears at about $+1.4 \text{ V}$ with CO_2 addition, which is considered to be attributed to the reduction of CO_2 dissolved in the electrolyte. On copper, the new cathodic peak is observed at $+1.2 \text{ V}$ with CO_2 addition. Thus, it is considered that the reduction of CO_2 occurs on these substrates, and this reduction leads to the degradation of the lithium cycleability. To investigate the interaction between the lithium cycleability and the reduction of CO_2 , substrates were held at $+1.4 \text{ V}$ in the CO_2 -containing electrolyte solution before lithium deposition. Then, the cycleability of lithium was estimated as shown in Table 1. In the case of nickel and titanium, where no change with CO_2 addition is observed in Fig. 1(a) and (b), the lithium cycleability is degraded only slightly by the reduction of CO_2 at the potentials higher than that of $\text{Li}/$

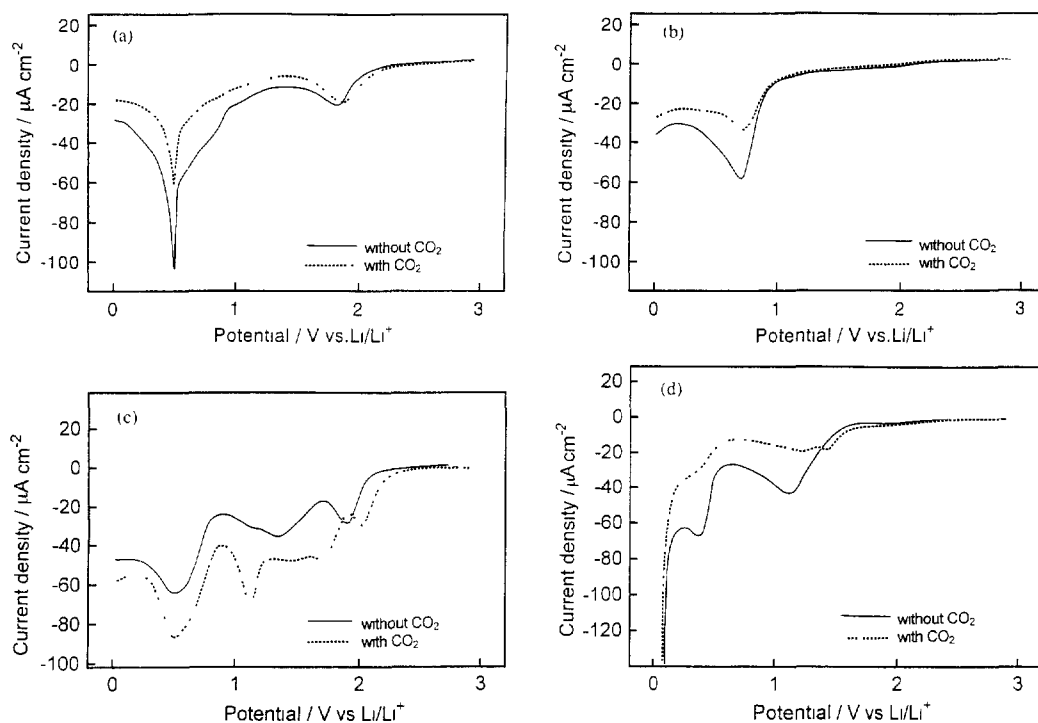


Fig. 1. Voltammograms of (a) nickel, (b) titanium, (c) copper and (d) silver substrates in 1.0 M LiClO₄/PC with or/without CO₂ addition at a scan rate: 5 mV s⁻¹.

Li⁺. As compared with these results, the cycleability of lithium on copper and silver, especially copper, is pronouncedly degraded when CO₂ is reduced on the substrates. Therefore, it is suggested that the precipitation products of the CO₂ reduction on these substrates before lithium deposition prevent the reaction between lithium metal and CO₂, otherwise, these products make adhesion of the deposited lithium weak. Consequently, the addition of CO₂ does not increase the cycleability of lithium in this situation.

3.3. Effect of the surface oxide on substrates

Cycling tests were also carried out using nickel and copper substrates whose surface oxides were eliminated by immersing ~10 vol.% H₂SO₄ solution for 1 min. The anode cycleability was improved when copper substrates were used but very slightly improved with nickel substrates, as shown in Table 2. The addition of CO₂ to the solutions while using the oxide-free copper substrates clearly increased the cycleability. Fig. 2 shows a voltammogram for the oxide-free copper substrate. Comparing Figs. 2 and 1(c), it is clear that using the oxide-free copper substrates, the cathodic peak around 1.9 V is decreased. As has already been reported [1], the copper oxide reacts with lithium ion through several stages, and copper and Li₂O are produced finally. When using the oxide-free substrates, the suppression of this reduction seems to improve the lithium cycleability. It is also suggested that elimination of the oxide from copper surfaces leads to the positive effect of the presence of CO₂ on the lithium cycleability. When using the copper substrate with the oxide on

Table 2
Cycleability of lithium anode deposited on the various substrates eliminated the surface oxide by immersing in ~10 vol.% H₂SO₄ for 1 min

Substrate	1 M LiClO ₄ /PC	
	without CO ₂	with CO ₂
Ni no treatment	58 (<i>E_a</i> = 93.1%)	115 (<i>E_a</i> = 96.5%)
Ni-eliminated surface oxide	69 (<i>E_a</i> = 94.2%)	130 (<i>E_a</i> = 96.9%)
Cu no treatment	22 (<i>E_a</i> = 81.8%)	26 (<i>E_a</i> = 84.6%)
Cu-eliminated surface oxide	50 (<i>E_a</i> = 92.0%)	92 (<i>E_a</i> = 95.7%)

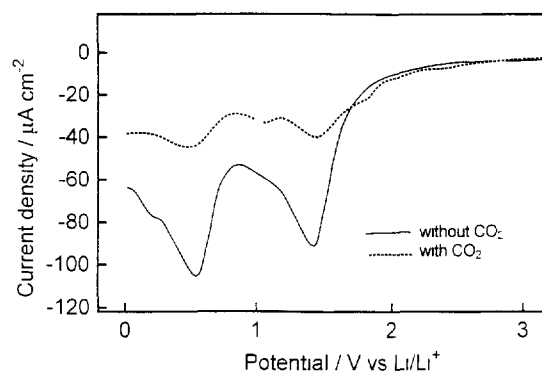


Fig. 2. Voltammograms of copper substrate, immersed in ~10 vol.% H₂SO₄ solution in 1.0 M LiClO₄/PC with and without CO₂ addition at a scan rate: 5 mV s⁻¹.

surface, an Li₂O layer may be produced before lithium deposits and it may prevent the cycling enhancement effect by CO₂. In the case of an oxide-free copper substrate, the surface of the deposited lithium metal forms the ionic conductive layer

by the reaction between lithium metal and CO₂, which depresses the dendritic deposition of lithium, as already discussed in the previous paper [12].

4. Conclusions

An enhancement of the lithium cycleability in the presence of CO₂ in LiClO₄/PC electrolyte occurred with nickel and titanium substrates, while with copper and silver substrates this effect is small. The non-active copper and silver substrates reduce CO₂ in the electrolyte solution before reaching lithium deposition, and they decrease the cycleability of lithium deposited.

Acknowledgements

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