

Surface of lithium electrodes prepared in Ar + CO₂ gas

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Abstract

The surfaces of lithium electrodes prepared in Ar(80%) + CO₂(20%) mixed gas and pure Ar gas have been investigated by X-ray photoelectrospectroscopy (XPS) and a polarization microscope. Electrodes prepared by cutting lithium in the mixed gas do not show a voltage delay at the beginning of discharge in 1 M LiClO₄/propylene carbonate. All parts of the lithium surface prepared in the mixed gas have clear grain boundaries after dissolution during discharge. By contrast, anodic dissolution of the lithium surface prepared in pure Ar gas occurs partially and most of the surface is passivated. XPS studies suggest that the growth of a dense Li₂CO₃ layer on the outer surface of the lithium with storage time is responsible for the voltage delay.

Keywords: Electrodes; Lithium

1. Introduction

Lithium metal or lithium-rich alloys have been studied widely as anodes for lithium batteries with high energy densities. In particular, it is essential to understand the chemistry that takes place on the active lithium surface and to discover means to control it. As a consequence, the reaction products on lithium surfaces have been investigated intensively by techniques such as X-ray photoelectrospectroscopy, infrared spectroscopy and X-ray diffractometry, etc. [1–3].

All electrolytes and solvents are thermodynamically reduced and decomposed on lithium metal. It is believed [4] that the products precipitated on the surface act as solid electrolytes or corrosion-protective films. Nevertheless, there is controversy between different research groups over the details of the surface structure. This is because occasional trace amounts of contaminants are unavoidably present in the atmosphere. Although much attention has been given [5,6] to the effect of contaminants in electrolytes, comparatively few studies have been made of the contaminants in the gas in which the lithium electrodes are initially prepared [7]. The work reported here focuses on the initial film formed on lithium and examines how this film influences the electrochemical behaviour of the electrode.

2. Experimental

The preparation of lithium electrodes and electrochemical experiments was carried out in a glove box filled with 99.99% pure Ar(80%) + CO₂(20%) mixed gas or Ar gas (dew point = -60 °C). A lithium rod (99.9%) was sliced by a steel cutter to obtain a fresh surface. The latter had a mirror-like luster.

Electrochemical measurements were conducted in 1 M LiClO₄/PC (propylene carbonate) (Mitsubishi Petrochemical) with a potentiogalvanostat HA501-G (Hokuto Denko). A conventional three-electrode cell was used in which the reference and counter electrodes were fabricated from lithium ribbon.

The morphology of the lithium electrode surface was observed with a polarization microscope (Nikon) that was located outside the glove box. To avoid exposure of the lithium surface to the outer atmosphere, lithium electrodes were sealed in transparent plastic bags in the glove box. X-ray photospectroscopy (XPS) measurements were performed with an ESCA 5300 (Perkin-Elmer) instrument. Samples were transported via a 'transfer vessel', that made it possible to transfer lithium electrodes from the glove box to an XPS introduction chamber without exposure to the air.

3. Results and discussion

Typical discharge curves for lithium electrodes at 1 mA/cm^2 in $1 \text{ M LiClO}_4/\text{PC}$ are shown in Fig. 1. The electrodes were cut and stored in the gases for 2 weeks before discharge. The discharge curve (curve (a)) for the electrode treated in Ar gas exhibited a large polarization at the beginning of discharge. This causes a voltage-delay problem. By contrast, the electrode treated in the mixed gas displayed a flat discharge curve (curve (b)). Even when the electrode prepared in the mixed gas was immersed in the electrolyte solution for 2 months before discharge, the electrode still gave a flat discharge curve. Clearly, the addition of CO_2 gas to the Ar atmosphere is a very effective means of overcoming the voltage-delay problem.

Typical first-cycle voltammograms for lithium electrodes prepared in both atmospheres are presented in Fig. 2. As predicted from the discharge curves in Fig. 1, a large anodic current flows when the electrode is prepared in the mixed gas (curve (b)). Furthermore, the apparent equilibrium potential shifts noticeably towards a more positive value. The shift could be observed over 20 min and may be due to a mixed redox

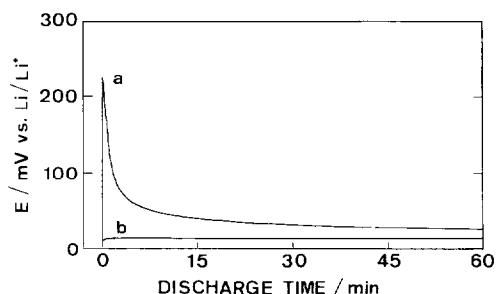


Fig. 1. Typical discharge curves for lithium electrodes at 1 mA/cm^2 in LiClO_4/PC . Electrodes stored for 2 weeks in: (a) Ar, and (b) Ar(80%) + CO_2 (20%).

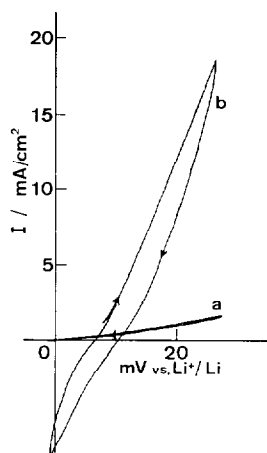


Fig. 2. Typical first-cycle voltammograms for lithium electrodes in LiClO_4/PC . Electrodes stored for 2 weeks in: (a) Ar, and (b) Ar(80%) + CO_2 (20%).

potential between lithium and decomposition of the electrolyte solution and the contaminants. A similar phenomenon has been observed [8] when lithium is cut in the electrolyte solution. In the present case, direct reaction between lithium and the electrolyte solution may not occur because the metal surface is covered initially with a surface film. It should be noted, however, that the porosity of surface films may be sufficient to allow the penetration of solvent [9].

The difference between the discharge curves of the lithium electrodes prepared in both atmospheres is reflected by the appearance of the surface after discharge, as shown in Fig. 3. These micrographs represent the typical surface morphology of the lithium electrodes after 2 h of discharge at 1 mA/cm^2 in $1 \text{ M LiClO}_4/\text{PC}$. The dissolution of the lithium surface prepared in Ar gas was not uniform (Fig. 3(a)). There is a sharp resolution between the insoluble bright regions and the dark regions. The trace left by the cutter can be observed on the bright regions. By contrast, the surface of the electrode prepared in the mixed gas after discharge displayed the fine structure of the lithium grain boundaries (Fig. 3(b)). In this case, it is clear that the lithium surface is dissolved uniformly during discharge. Hence, the initial increase in the discharge potential can be attributed to a decrease in the effective electrode area that has not been passivated.

The differences in passivation are obviously based on differences in the properties of the surface film formed on the lithium. The chemical composition and the state of the surface of lithium prepared in either Ar gas or mixed gas were thus examined by XPS. Fig. 4 shows typical XPS peaks in the C(1S) (carbon 1S), O(1S) (oxygen 1S) and Li(1S) (lithium 1S) regions of the lithium surface prepared in the mixed gas. A change in the spectra was observed with the Ar-ion sputtering time. Other signals were not detected. The initial C(1S) spectrum (before sputtering) is characterized by three peaks at 292.8, 287.6 and 285.2 eV. The peaks at 292.8 and 287.6 eV also appeared in the spectrum of Li_2CO_3 powder which was measured for the purposes of comparison. The former peak was attributed to Li_2CO_3 ,

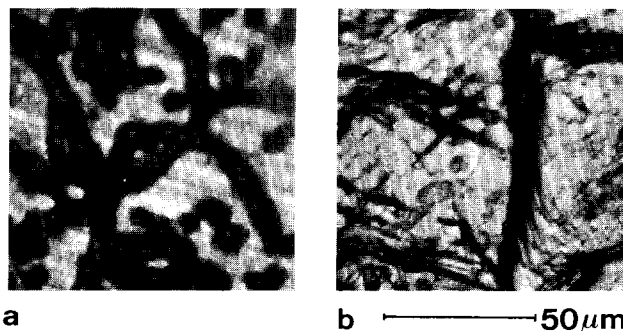


Fig. 3. Surface of lithium electrodes after 2 h discharge at 1 mA/cm^2 in LiClO_4/PC prepared in: (a) Ar, and (b) Ar(80%) + CO_2 (20%).

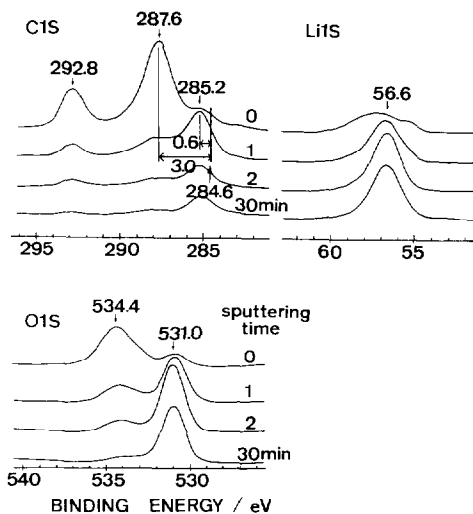


Fig. 4. Depth profiles of XPS spectra for a lithium surface prepared in Ar(80%) + CO₂(20%).

the latter to contaminated hydrocarbons. Generally, an insulating compound irradiated with X-rays during XPS measurement is prone to charge positively and to emit electrons. Then, the peaks for insulating particles in the lithium film can shift to higher binding energies. The difference between the observed value of the binding energy attributed to contaminated hydrocarbons to that reported in the literature [10], namely 284.6 eV, can be explained by this behaviour.

Studies also revealed a further peak at 285.2 eV (Fig. 4). This can also be attributed to contaminated hydrocarbons. There are two peaks at 534.4 and 531.0 eV in the O(1S) region. The peak at 534.4 eV can be attributed to Li₂CO₃. The value should be 531.5 eV after correction for the shift in the contaminated hydrocarbons from 284.6 to 287.6 eV, as noted above. The peak at 534.4 eV decreased with sputtering time and peaks, possibly associated with Li₂O, appeared at 531.0 eV in the O(1S) region and at 56.6 eV in the Li(1S) region. Furthermore, it should be noted that the peak at 285.2 eV in the C(1S) region at first increased, and then decreased, with sputtering time. This suggests that the lithium film may be composed of an outer Li₂CO₃ layer and an inner Li₂O layer. The outermost parts of both these layers can be contaminated with hydrocarbons. It is clear that the particles of Li₂O are charged differently from those of Li₂CO₃ during the XPS measurement. Thus, two peaks are observed for the contaminated hydrocarbons in the XPS spectrum. After a further 2 h of sputtering, a new peak appeared at 55.0 eV (attributed to lithium metal) and all the peaks in the C(1S) region disappeared. By contrast, the peaks for Li₂O persisted. A probable decomposition of Li₂CO₃ to Li₂O and CO₂ with X-ray irradiation makes quantitative analysis impossible.

Fig. 5 shows a typical XPS spectrum for a lithium surface cut and stored for 2 months in Ar gas. A peak,

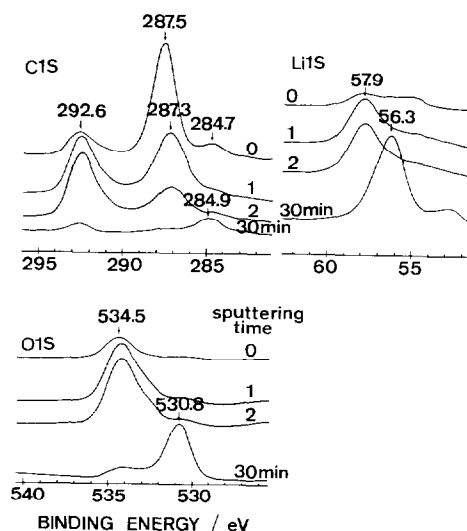


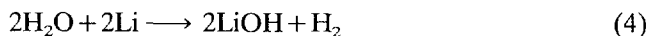
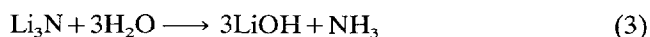
Fig. 5. Depth profiles of XPS spectra for lithium surface prepared in Ar.

that could not be found in Fig. 4, is clearly observed at 57.9 eV in the Li(1S) region. This is attributed to Li₂CO₃. The surface layer of Li₂CO₃ on lithium prepared in Ar gas is expected to be thick and dense. Since the surface of lithium is easily covered with reaction products and contaminants, even in a high-vacuum chamber [11,12], the contaminants in 99.99% pure Ar gas would more readily spoil the lithium metal surface.

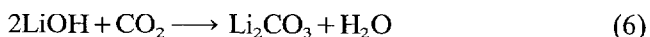
The direct reaction:



occurs in the mixed gas. This reaction accounts for the observed Li₂CO₃ formed on the lithium prepared in the mixed gas. The reaction does not appear, however, to occur exclusively in Ar gas. Since the major contaminants in Ar gas are nitrogen, oxygen and water, other possible reactions in Ar gas are:



These products can gradually react further with traces of CO₂ as follows:



As noted above, the XPS spectrum and its depth profile on the lithium surface cut in Ar gas depend strongly on the storage time. The outer surface of the film appears to change gradually from Li₂O or LiOH to Li₂CO₃ under the influence of contaminants in the Ar gas. Corrosion of lithium can be accelerated by the catalytic action of water according to reactions (4)

and (6). These reactions can carry water inside the film and promote the formation of a thick layer of Li_2CO_3 . This change in the surface is considered to be the cause of the marked voltage delay. The Li_2CO_3 layer is the most stable of the various reaction products formed between lithium and the gases. Thus, it must act as the best protective film towards corrosion and, thereby, increase the initial discharge potential.

The initial discharge potentials of lithium electrodes prepared in Ar gas and the mixed gas are plotted against storage time in the gases in Fig. 6. For treatment with mixed gas, there is no increase in the initial discharge potential, even after 2 months of storage. On the other hand, the initial discharge potentials of the electrodes prepared in Ar gas increase markedly with storage time. This corresponds well with the results of the XPS studies, namely, there is an increase in the thickness of Li_2CO_3 .

These results should not lead to the conclusion that pure Ar gas contains considerably more contaminants than the mixed gas. Fig. 7 presents typical discharge

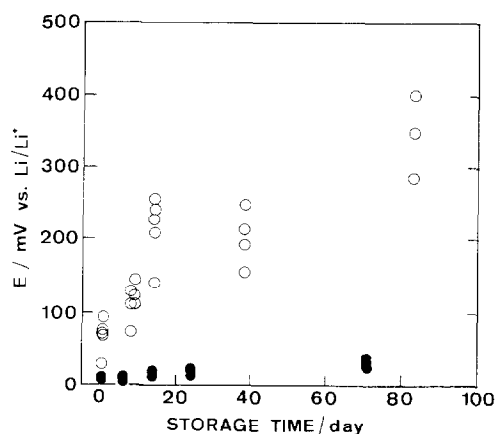


Fig. 6. Discharge potential of lithium electrodes as a function of storage time in: (O) Ar, and (●) Ar(80%)+CO₂(20%).

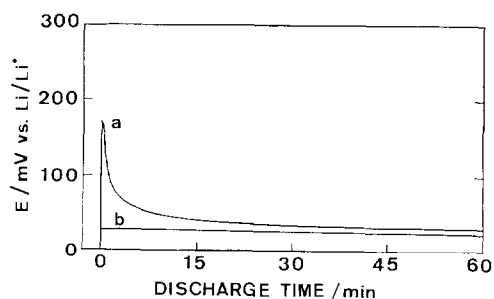


Fig. 7. Typical discharge curves for lithium electrodes in LiClO_4/PC . Electrodes prepared by: (a) cutting in Ar and stored in mixed gas for 2 weeks, and (b) cutting in mixed gas and stored in Ar for 2 weeks.

curves for lithium electrodes prepared either by cutting in Ar gas and then storing in mixed gas for 2 weeks (curve (a)), or by cutting in mixed gas and storing in Ar for 2 weeks (curve (b)). Comparison with the data given in Fig. 1 shows that the former is similar to that obtained for electrodes cut and stored in Ar gas alone, while the latter is similar to that cut and stored in the mixed gas. Therefore, the characteristics of the lithium surface are defined by the gas to which the metal is first exposed. Changing the atmosphere after the formation of the initial film on lithium produces no further modification to the film.

4. Conclusions

Electrodes prepared by cutting lithium in mixed gas do not display a voltage delay at the beginning of discharge in 1 M LiClO_4/PC . All parts of the surface of these electrode dissolve uniformly during discharge and, thereby, display sharp grain boundaries. By contrast, electrodes prepared in Ar gas exhibit a voltage delay due to only partial dissolution of the surface. The growth of a passivating Li_2CO_3 layer, which is probably the cause of the voltage delay, is slow when a lithium surface is created in the mixed gas.

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