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Effect of surface modification using various acids on electrodeposition of lithium

S. SHIRAISHI, K. KANAMURA, Z. TAKEHARA

Division of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto 606-01, Japan

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Surface modification of lithium was carried out using the chemical reaction of the native film with acids (HF, H_3PO_4, HI, HCl) dissolved in propylene carbonate (PC). The chemical composition change of the lithium surface was detected using X-ray photoelectron spectroscopy. The electrodeposition of lithium on the as-received lithium or the modified lithium was conducted in PC containing 1.0 mol dm^{-3} $LiClO_4$ or $LiPF_6$ under galvanostatic conditions. The morphology of electrodeposited lithium particles was observed with scanning electron microscopy. The lithium dendrites were observed when lithium was deposited on the as-received lithium in both electrolytes. Moreover the dendrites were also formed on the lithium surface modified with H_3PO_4, HI, or HCl. On the other hand, spherical lithium particles were produced, when lithium was electrodeposited in PC containing 1.0 mol dm^{-3} $LiPF_6$ on the lithium surface modified with HF. However spherical lithium particles were not obtained, when PC containing 1.0 mol dm^{-3} $LiClO_4$ was used as the electrolyte. The lithium surface modified by H_3PO_4, HI, or HCl was covered with a thick film consisting of Li_3PO_4, Li_2CO_3, LiOH, or Li_2O. The lithium surface modified with HF was covered with a thin bilayer structure film consisting of LiF and Li_2O. These results clearly show that the surface film having the thin bilayer structure (LiF and Li_2O) and the use of PC containing 1.0 mol dm^{-3} $LiPF_6$ enhance the suppression of dendrite formation of lithium.

1. Introduction

Recently, rechargeable lithium batteries with lithium metal anodes have been proposed as power supplies because of their theoretical high energy and power densities. However, they have not been widely used because of their low rechargeability [1–3]. The low rechargeability is caused by the chemical reaction of lithium with nonaqueous electrolytes and the dendrite formation of lithium during the charging process [4, 5]. The lithium dendrites sometimes lose electrical contact with current collectors during charge/discharge cycles. This makes part of the lithium inaccessible to discharge. Such lithium has been called 'dead lithium'. The morphology of lithium is crucial to high rechargeability. Some studies have proposed that the morphology of electrodeposited lithium is strongly related to the surface states of lithium. The presence of some organic and inorganic compounds in the surface film have been confirmed by various methods (FT–IR [6, 7], XRD [8], SIMS [9], AES [10]). However, the relationship between the surface state of lithium and its morphology has not been completely explained. This may be due to the variety in the surface states of lithium used by each researcher (for example; as-received lithium foil [11], *in situ* cutting lithium wire [12], electrodeposited lithium [8], lithium prepared by vapour–deposition [13], amalgamated lithium [9], etc.). Moreover, another complication arises from the kind of electrolyte used for the electrodeposition (for example, propylene carbonate, γ-butyrolactone, tetrahydrofuran, or dimethoxyethane containing $LiClO_4$, $LiAsF_6$, $LiBF_4$, $LiPF_6$, or $LiCF_3SO_3$). When the electrodeposition of lithium is performed on as-received lithium foils, the morphology of electrodeposited lithium may depend on the surface state of the lithium foil or the kind of electrolytes. Therefore, the surface state of the lithium foil must be known to study the electrodeposition of lithium on the lithium foil. Recently we have found that the surface state of a lithium foil changes with the immersion time in propylene carbonate containing $LiPF_6$, leading to the morphological change in the lithium particles electrodeposited on it [14]. Consequently, we have proposed that the morphology of lithium is related to the surface state of the lithium foil. The surface state change of the lithium foil is caused by the acid-base reaction of the native film with acids present in electrolytes as impurities.

In this study, the surface modification of lithium was conducted by the acid-base reaction of the native film with acids (HF, H_3PO_4, HCl, or HI) added in pure PC. The electrodeposition of lithium was performed in PC containing 1.0 mol dm^{-3} $LiClO_4$ or $LiPF_6$ using the modified lithium. The effects of this surface modification and the effect of electrolyte on the morphology of electrodeposited lithium were discussed.

2. Experimental details

2.1. *Surface modification and electrodeposition*

As-received lithium foils (Kyokuto Co.) were used. The surface states of these lithium foils were analyzed by X-ray photoelectron spectroscopy (XPS). The surface state of all lithium foils used were as reported previously [11]. The as-received lithium foils were covered with the native film. Its outer part consisted of a mixture of Li_2CO_3 and LiOH, and the inner part consisted of Li_2O. The lithium foil was immersed in PC containing 2×10^{-4} mol dm^{-3} HF, H_3PO_4, HI, or HCl for three days. PC was treated using molecular sieves (Wako pure Chemical Co.) for two days to remove water before use. After this dehydration, the residual water in PC was less than 5 ppm, determined by Karl Fischer Moisture Titrator (MKC-210, Kyoto Denshi Kogyo Co.). PC containing acid was prepared from this pure PC and HF (46% by weight), H_3PO_4 (85% by weight), HCl (36% by weight), or HI (47% by weight) (Wako Pure Chemical Co.). The water contents of PC solutions containing acids were estimated to be less than 20 ppm. After this treatment, these modified lithium foils were washed with pure PC (Mitsubishi Yuka Co.).

The electrodeposition of lithium on the modified lithium surface (1 cm^2) was performed in PC containing 1.0 mol dm^{-3} $LiClO_4$ or $LiPF_6$ (Mitsubishi Yuka Co.) under galvanostatic conditions. The current density was 0.2 mA cm^{-2} and the duration was 80 min. The total quantity of electric charge was 0.96 C cm^{-2}. Lithium foil was used as counter (8 cm^2) and reference electrodes. The water contents of these electrolytes were estimated to be less than 20 ppm. These procedures were conducted in an argon dry box (dew point < −90° C) at room temperature.

Table 1. Binding energies of various lithium compounds

Compounds	*Binding energy**/eV						
	Li1*s*	O1*s*	C1*s*	F1*s*	P2*p*	I3$d_{5/2}$	Cl2*p*
Li	52.2						
Li_2O	53.6	528.7					
LiOH	54.4	531.7					
Li_2CO_3	55.5	532.1	290.2				
LiF	56.5			685.5			
Li_3PO_4	55.3	531.6			133.5		
LiI	56.3					619.8	
LiCl	56.3						198.7

* The chemical shifts were referred to C1*s* of a residual hydrocarbon (285.0 eV) for compensation of electrostatic charging.

2.2. *XPS analysis*

The characterization of the modified lithium surface was carried out using XPS (ESCA 850s, Shimadzu). The XPS analysis was performed under ultra-high

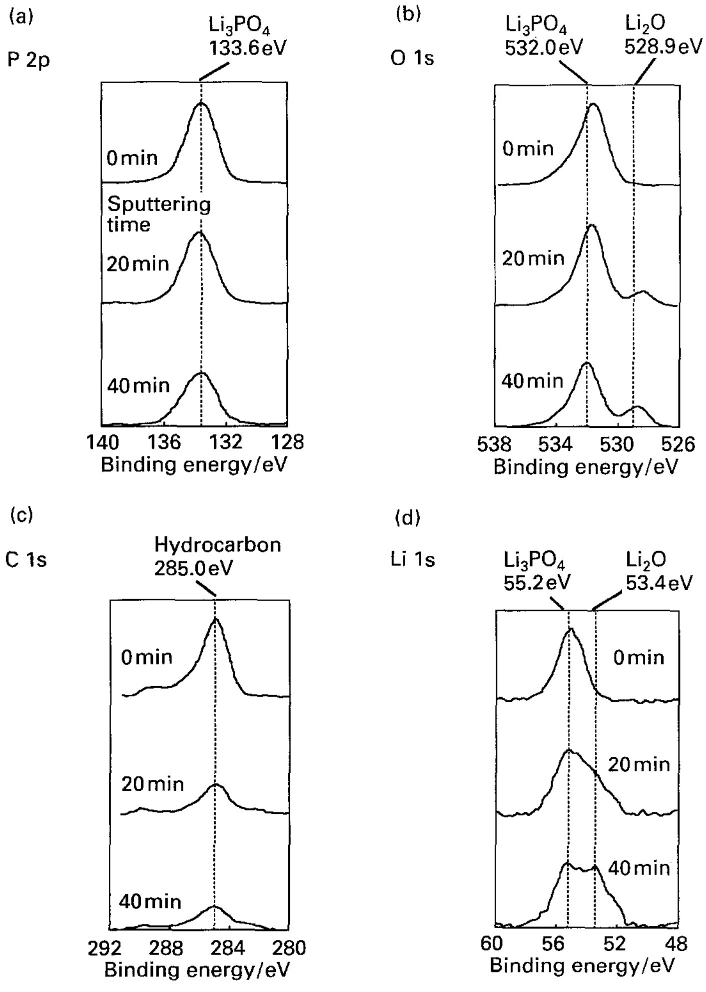

Fig. 1. The XPS spectra of (a) P2*p*, (b) O1*s*, (c) C1*s*, and (d) Li1*s* for the film formed on the lithium surface after the immersion in PC containing 2×10^{-4} mol dm^{-3} H_3PO_4 for three days, after the argon ion sputtering (2 keV, 7~8 μA) for 0 min (upper spectrum), 20 min (middle one), and 40 min (bottom one).

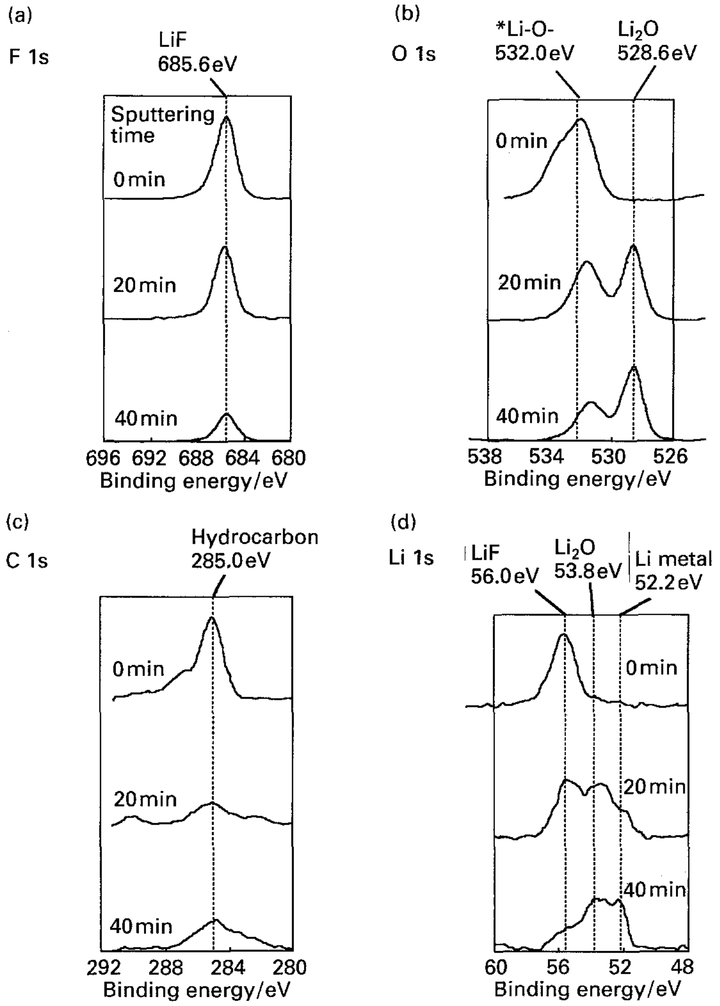

Fig. 2. The XPS spectra of (a) F1*s*, (b) O1*s*, (c) C1*s*, and (d) Li1*s* for the film formed on the lithium surface after the immersion in PC containing 2×10^{-4} mol dm^{-3} HF for three days, after the argon ion sputtering (2 keV, 7~8 μA) for 0 min (upper spectrum), 20 min (middle one), and 40 min (bottom one), * : Li_2CO_3 or LiOH.

vacuum conditions (less than 5×10^{-7} Pa). Before the XPS analysis, the modified lithium was dried under vacuum (less than 1×10^{-3} Pa) at room temperature for one hour in a dry box. The transfer procedure for samples to the introduction chamber of the XPS equipment has been described in our previous paper [11]. MgK_α (1253 eV) X-ray source was used (8 kV, 30 mA). The depth profile of each element was obtained from the XPS measurement with argon ion sputtering (ultra-high pure argon; Kyoto Teisan Co., ion beam; 2 keV, 8 μA). The binding energy of the C1*s* peak at 285.0 eV was used as an internal standard. The binding energy for each compound was referred to in Table 1.

2.3. *SEM observation*

The morphology of electrodeposited lithium was observed using scanning electron microscopy (JSM-25D, JEOL). The sample was washed with pure PC and dried under vacuum for 1 h before being introduced to the SEM under an argon atmosphere.

3. Results and discussion

3.1. *Surface modification using HF or H_3PO_4 dissolved in propylene carbonate*

Figure 1 presents the XPS spectra of P2*p*, O1*s*, C1*s*, and Li1*s* for the lithium surface after the immersion in PC containing 2×10^{-4} mol dm^{-3} H_3PO_4 for three days. The upper spectrum was obtained before the argon ion sputtering, the middle and bottom spectra were obtained after the argon ion sputtering for 20 min and 40 min, respectively. These spectra correspond to the depth profile of each element in the surface film. The peak observed at 133.6 eV in the XPS spectra of P2*p* is attributed to Li_3PO_4. The intensity of this peak was unchanged with argon ion sputtering. This means that a thick Li_3PO_4 layer is formed on the lithium surface. Peaks at 532.0 eV and 528.9 eV in the O1*s* spectra correspond to Li_3PO_4 and Li_2O, respectively. The peak corresponding to Li_2O was observed after the argon ion sputtering for 20 min. These spectra indicate that a layer of Li_2O is present under the thick layer of Li_3PO_4. The peak at 285.0 eV in the C1*s* spectra is attributed to hydrocarbon, which is an impurity in the XPS measurement chamber. In the XPS spectra of Li1*s*, the peak attributed to Li_3PO_4 was observed at 55.2 eV before and after the argon ion sputtering. The peak corresponding to Li_2O was observed at 53.4 eV after the argon ion sputtering for 20 min. These results were in good agreement with those obtained for the P2*p* and O1*s* spectra. Therefore, it can be concluded that the film formed on the lithium surface after the immersion in PC containing H_3PO_4 has a bilayer

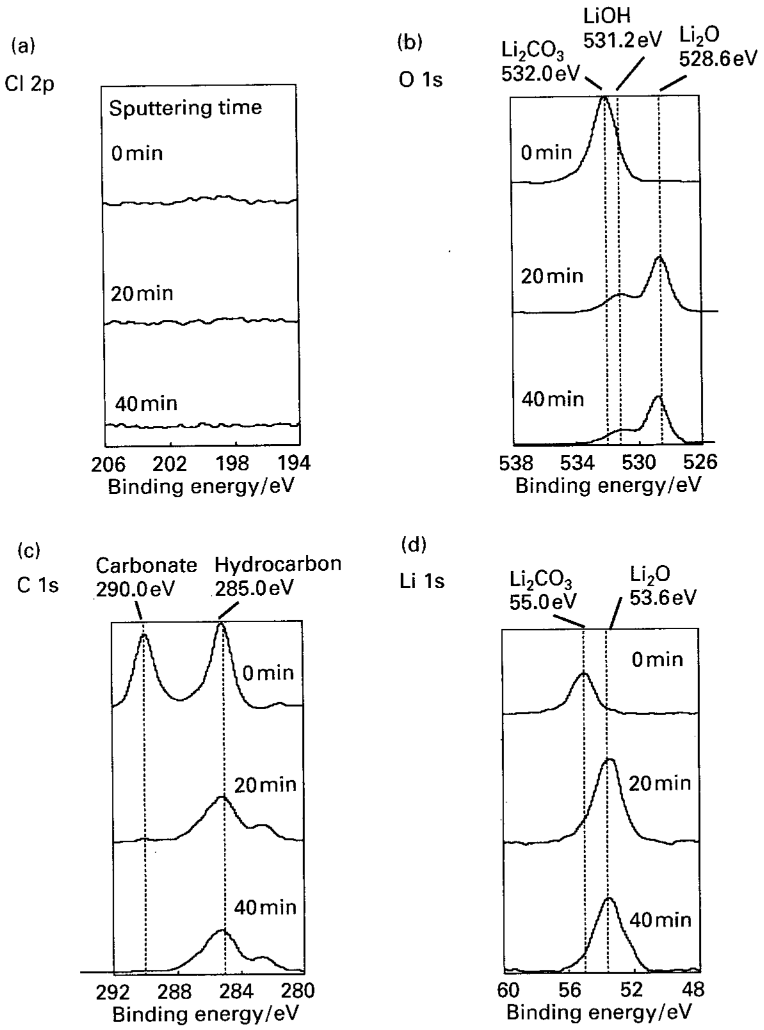

Fig. 3. The XPS spectra of (a) Cl2*p*, (b) O1*s*, (c) C1*s*, and (d) Li1*s* for the film formed on the lithium surface after the immersion in PC containing 2×10^{-4} mol dm^{-3} HCl for three days, after the argon ion sputtering (2 keV, 7~8 μA) for 0 min (upper spectrum), 20 min (middle one), and 40 min (bottom one).

structure film consisting of the thick Li_3PO_4 and Li_2O.

Figure 2 shows the XPS spectra of F1*s*, O1*s*, C1*s*, and Li1*s* for the lithium surface after immersion in PC containing 2×10^{-4} mol dm^{-3} HF for three days. The peak observed at 685.6 eV is attributed to LiF. This peak intensity decreased significantly with argon ion sputtering showing that LiF is formed at the outer part of the lithium surface film. In the XPS spectra of O1*s* the peak around 532 eV can be attributed to Li_2CO_3 or LiOH while the peak at 528.6 eV is attributed to Li_2O. These peak intensities were changed with argon ion sputtering. This indicates that Li_2CO_3 or LiOH exists at the outer part of the surface film and Li_2O exists at the inner part of the film. The peak attributed to hydrocarbon was observed at 285.0 eV in the C1*s* spectra. The peak attributed to Li_2CO_3 (290.0 eV) could not be observed. This fact indicates that Li_2CO_3 is not present in the film. The peak attributed to LiF was observed at 56.0 eV in the XPS spectra of Li1*s* before argon ion sputtering, while peaks corresponding to Li_2O and Li metal were also observed at 53.8 eV and 52.2 eV after argon ion sputtering. The peak of Li metal was clearly observed after argon ion sputtering for 40 min. The peak of Li metal was not observed in the XPS spectra for the as-received lithium used in this study even after argon ion sputtering for 40 min [11]. These results show that the surface film after immersion in PC containing HF is thinner than the native film. It can be concluded that the lithium surface is modified by HF and consists of a thin bilayer structure film consisting of LiF and Li_2O.

The formation of Li_3PO_4 and LiF may be explained by the chemical reaction of lithium compounds (Li_2CO_3, LiOH, and Li_2O) consisting of the native film with acids (H_3PO_4, HF) in PC. These reactions can be described as follows:

$$\begin{aligned} Li_2CO_3 + 2/x\,H_xA &\longrightarrow 2/x\,Li_xA + H_2CO_3 \\ LiOH + 1/x\,H_xA &\longrightarrow 1/x\,Li_xA + H_2O \\ Li_2O + 2/x\,H_xA &\longrightarrow 2/x\,Li_xA + H_2O \\ &(H_xA; H_3PO_4 \text{ or } HF) \end{aligned}$$

Moreover, the surface state of lithium after immersion in PC containing HF was very similar to that after immersion in PC containing 1.0 mol dm^{-3} $LiPF_6$ for three days [11, 14]. This indicates that the surface state change of the as-received lithium in PC containing $LiPF_6$ is caused by the acid-base reaction of the native film with HF dissolved in the electrolyte as an impurity. Other possible schemes for the formation of LiF on the lithium surface in the electrolyte are the reduction of salt with lithium metal [15] and the decomposition of salt itself [12].

3.2. *Surface modification using HCl or HI dissolved in PC*

Figure 3 presents the XPS spectra of Cl2*p*, O1*s*, C1*s*, and Li1*s* for the lithium surface after the immersion in PC containing 2×10^{-4} mol dm^{-3} HCl for three days. No peaks were observed in the XPS spectra of Cl2*p* neither before or after argon ion sputtering. This indicates that compounds involving chlorine are not present in the lithium surface film. The peak at 532.0 eV in the XPS spectra of O1*s* before the argon ion sputtering corresponds to Li_2CO_3. Peaks attributed to LiOH and Li_2O were observed at 531.2 eV and 528.6 eV after argon ion sputtering, respectively. The peak at 290.0 eV in the C1*s* spectra is attributed to Li_2CO_3. This peak was diminished with argon ion sputtering. The peak corresponding to Li_2CO_3 was observed at 55.0 eV in the Li1*s* spectra before sputtering. The peak attributed to Li_2O was observed at 53.6 eV after sputtering. These XPS spectra show that the outer part of the surface film consists of Li_2CO_3 and LiOH, and that of the inner part consists of Li_2O.

Figure 4 shows the XPS spectra of I3$d_{5/2}$, O1*s*, C1*s*, and Li1*s* for the lithium surface after immersion in PC containing 2×10^{-4} HI for three days. The peak attributed to LiI was observed at 629.8 eV in the I3$d_{5/2}$ spectra. The intensity of this peak was much smaller than those of other elements. Probably, compounds containing iodine are at low concentration in the lithium surface film. The O1*s*, C1*s*, and Li1*s* spectra in Fig. 4 were very similar to those in Fig. 3. This result shows that the lithium surface after the immersion in PC containing HI is also covered with a bilayer structure film consisting Li_2CO_3/LiOH and Li_2O.

From these XPS spectra, it can be said that the structure of the lithium surface after immersion in PC containing HCl or HI resembles that of the native film. This may be explained as follows. HCl and HI may not have high enough acidity in PC to react with Li_2CO_3, LiOH, and Li_2O, so that the native film remained on the lithium surface after the immersion in PC solutions containing these acids. Another possible explanation is the difference in solubility of lithium compounds in PC. Li_3PO_4 and LiF hardly dissolve in PC, while LiCl and LiI dissolve readily. Therefore, the lithium surface after immersion in PC containing HCl or HI is still covered with insoluble Li_2CO_3, LiOH, and Li_2O. These compounds probably remain to react with acid, or are produced by chemical reaction of PC or residual water with lithium metal. The reactivity of the acid can be estimated from the proton affinity in the gas phase which corresponds to the basicity of ions in an aprotic nonaqueous solvent. F^- (1553 kJ mol^{-1})

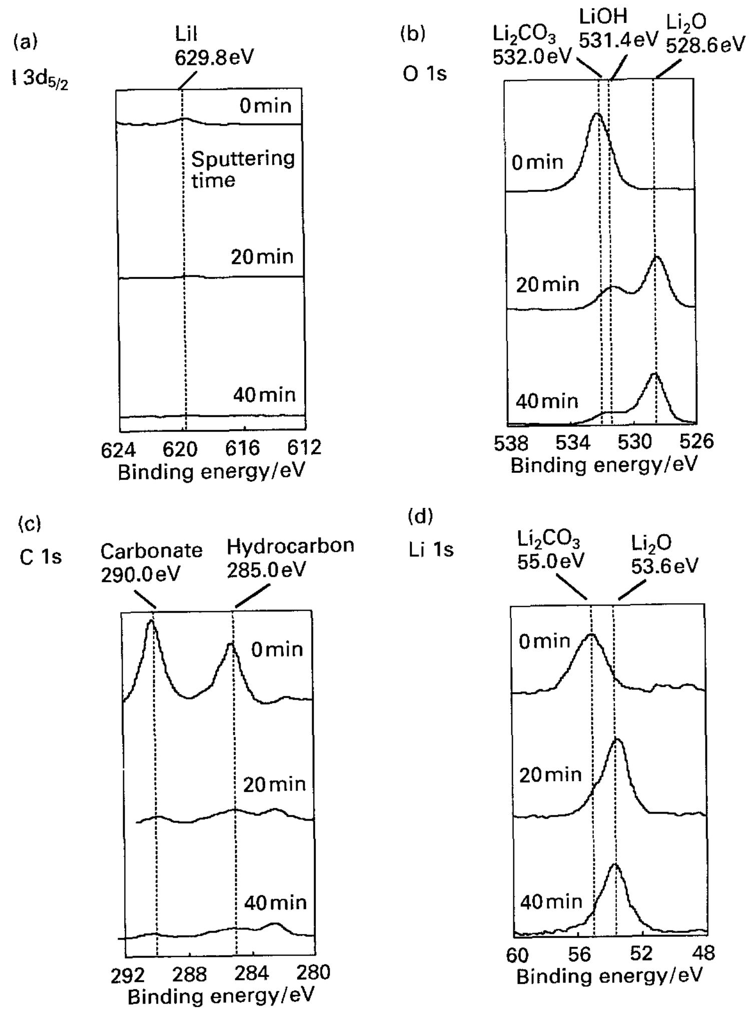

Fig. 4. The XPS spectra of (a) I3$d_{5/2}$, (b) O1*s*, (c) C1*s*, and (d) Li1*s* for the film formed on the lithium surface after the immersion in PC containing 2×10^{-4} mol dm^{-3} HI for three days, after the argon ion sputtering (2 keV, 7~8 μA) for 0 min (upper spectrum), 20 min (middle one), and 40 min (bottom one).

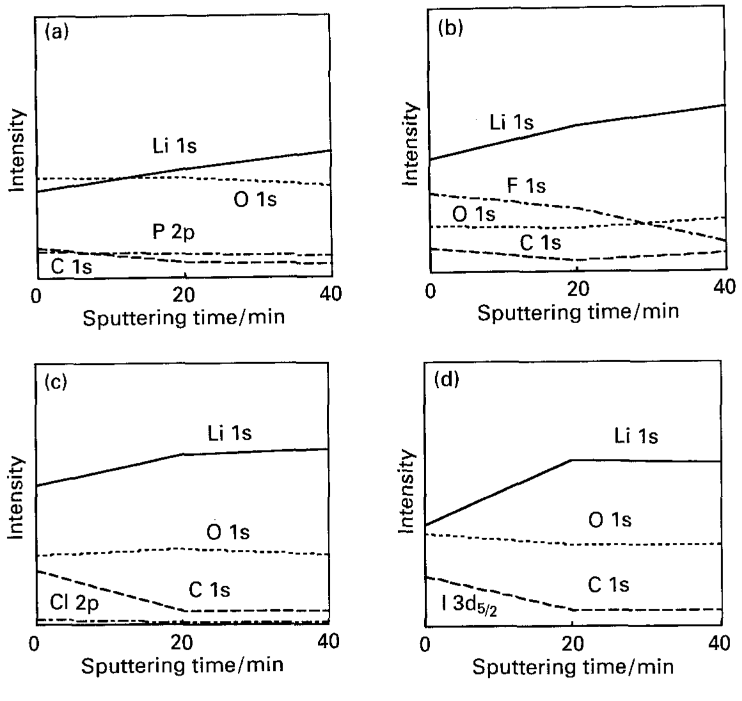

Fig. 5. Depth profiles of various elements in the film formed on the lithium surface after the immersion in PC containing (a) 2×10^{-4} mol dm^{-3} H_3PO_4, (b) 2×10^{-4} mol dm^{-3} HF, (c) 2×10^{-4} mol dm^{-3} HCl, or (d) 2×10^{-4} mol dm^{-3} HI.

has a larger proton affinity compared with those of Cl^- (1393 kJ mol^{-1}) or I^- (1314 kJ mol^{-1}) [16]. From these values, it can be seen that HF is the weakest among the three acids. HCl and HI should react with Li_2CO_3, LiOH, and Li_2O to form lithium halides on the lithium surface. Therefore the surface states of lithium after immersion in PC containing HCl and HI may be due to the high solubility of LiCl and LiI. LiF is so insoluble in PC that LiF remains on the surface film as a reaction product of HF and the native film. The LiF layer may be sufficiently dense to suppress the further reaction of the native film [11].

3.3. *Depth profile of the modified lithium surface*

Figure 5 shows the depth profile for each element in the lithium surface film after immersion in PC containing (a) H_3PO_4, (b) HF, (c) HCl, or (d) HI. The depth profiles can be obtained from the relative peak intensities in the XPS spectra for each element before and after argon ion sputtering, and approximately indicates the relative molar ratio of each element in the surface film. They were calculated from the following equation [17].

$$I = I_0/\sigma \qquad (1)$$

I, I_0, and σ mean the relative integrated intensity of

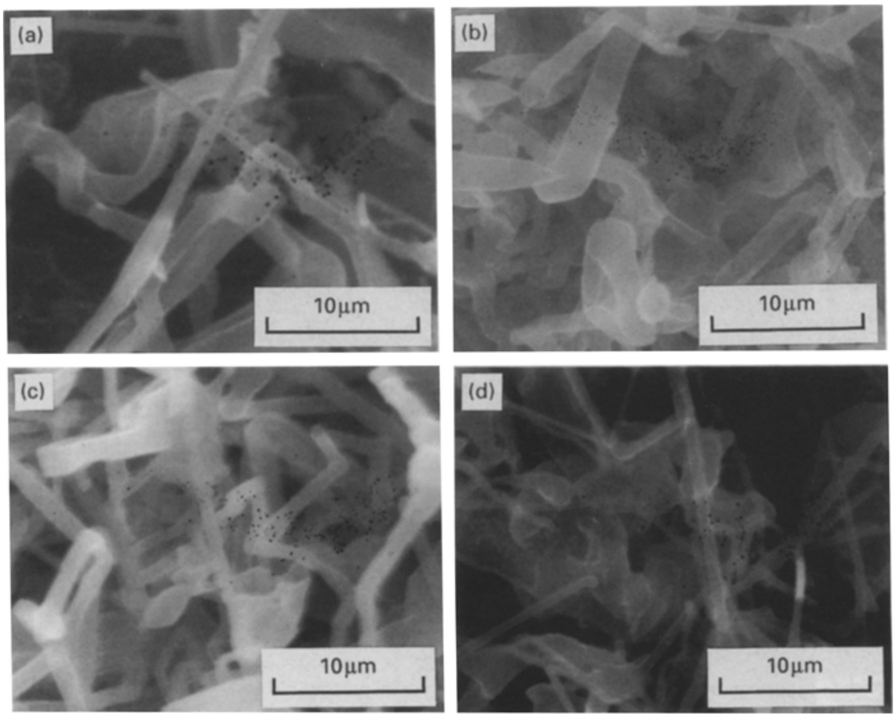

Fig. 6. The scanning electron micrographs of lithium deposited on lithium foils after the immersion in PC containing (a) 2×10^{-4} mol dm^{-3} H_3PO_4, (b) 2×10^{-4} mol dm^{-3} HF, (c) 2×10^{-4} mol dm^{-3} HCl, or (d) 2×10^{-4} mol dm^{-3} HI for three days (the electrodeposition current: 0.2 mA cm^{-2}; duration: 80 min; electrolyte: PC containing 1.0 mol dm^{-3} $LiClO_4$).

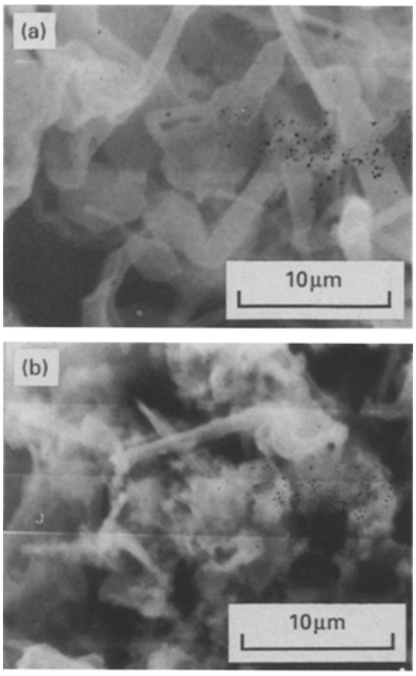

Fig. 7. The scanning electron micrographs of lithium deposited in PC containing (a) 1.0 mol dm^{-3} $LiClO_4$ or (b) 1.0 mol dm^{-3} $LiPF_6$ on the as-received lithium foils (electrodeposition current: 0.2 mA cm^{-2}; duration: 80 min).

the XPS peak, the observed integrated intensity, and the cross section for ionization (relative sensitivity), respectively. Figure 5(a) shows that phosphorus uniformly distributes in the surface film after immersion in PC containing H_3PO_4. The ratio among P, O, and Li in the film roughly corresponds to that for Li_3PO_4. Figure 5(b) indicates that the amount of fluorine is concentrated on the outer part of the surface film after immersion in PC containing HF for three days, demonstrating that the main compound in the outer part of the film is LiF. On the other hand, it is clear that the amount of chlorine in the surface after immersion in PC containing HCl for three days is much less than those of Li and O, as shown in Fig. 5(c). Additionally, the ratio of Li, O, and C in this profile resembles that in the native film. The depth profile in Fig. 5(d) was similar to that in Fig. 5(c), indicating that iodine is hardly present in the surface film after immersion in PC containing HI for three days.

3.4. *SEM observation of electrodeposited lithium*

Figure 6 shows the scanning electron micrographs of lithium electrodeposited in PC containing 1.0 mol dm^{-3} $LiClO_4$ on the lithium surface after immersion in PC containing H_3PO_4, HF, HCl or HI for three days. The typical dendritic form was observed for lithium electrodeposited on all lithium surfaces. A similar result was obtained for propylene carbonate containing 1.0 mol dm^{-3} $LiBF_4$ or $LiAsF_6$. Moreover, the morphology of lithium deposited on the as-received lithium without surface modification was dendritic and independent of the kind of electrolyte, as shown in Fig. 7. On the other hand lithium electrodeposited in PC containing 1.0 mol dm^{-3} $LiPF_6$ after immersion in PC containing HF for three days had a spherical morphology, as shown in Fig. 8. However, the morphology of lithium electrodeposited in PC containing 1.0 mol dm^{-3} $LiClO_4$ was not dependent on the surface modification. Dendrites were always observed. Thus, the surface treatment of lithium by HF dissolved in PC is very effective for the suppression of dendrite formation on lithium when PC containing $LiPF_6$ is used.

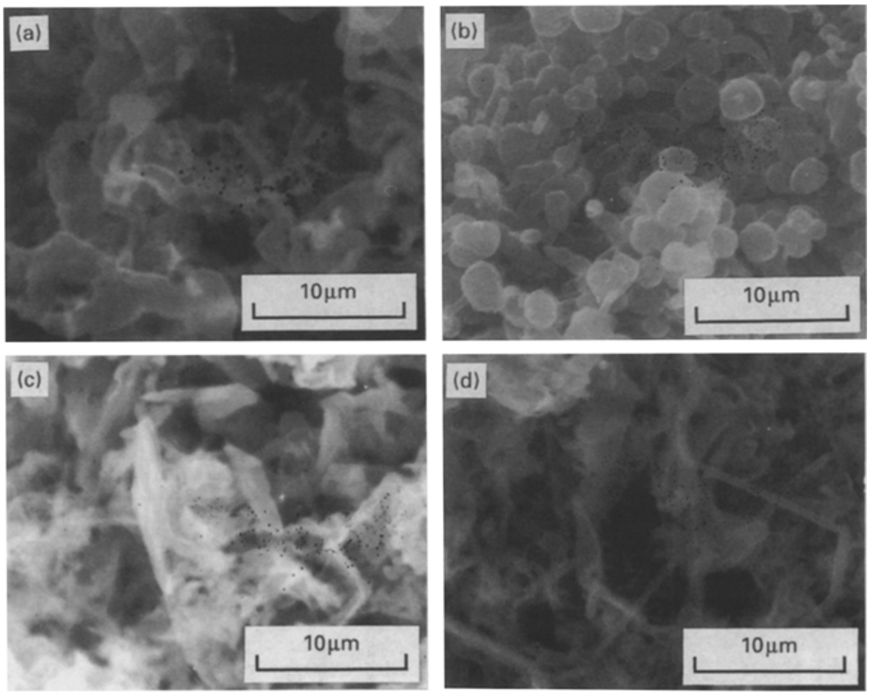

Fig. 8. The scanning electron micrographs of lithium deposited on lithium foils after the immersion in PC containing (a) 2×10^{-4} mol dm^{-3} H_3PO_4, (b) 2×10^{-4} mol dm^{-3} HF, (c) 2×10^{-4} mol dm^{-3} HCl or (d) 2×10^{-4} mol dm^{-3} HI for three days (electrodeposition current: 0.2 mA cm^{-2}; duration: 80 min; electrolyte: PC containing 1.0 mol dm^{-3} $LiPF_6$).

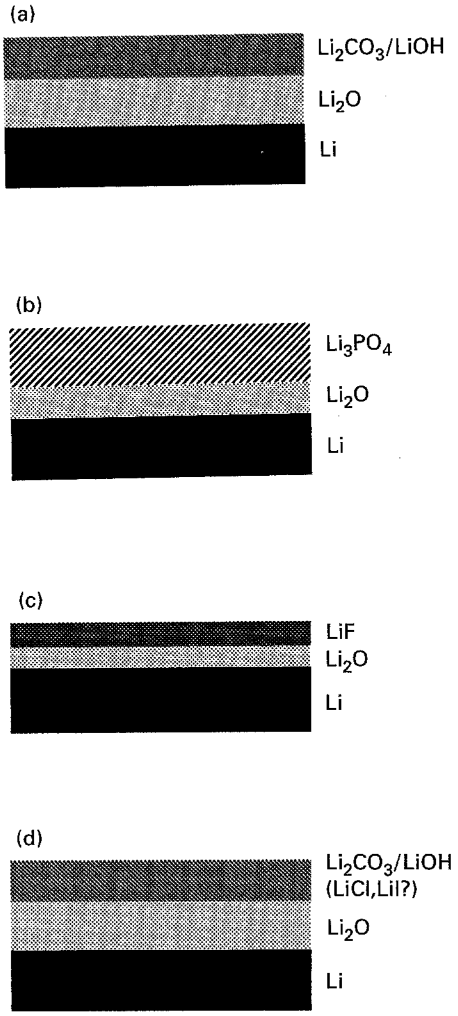

Fig. 9. Schematic illustrations for lithium surfaces (a) before the modification (the native film), (b) after the modification using 2×10^{-4} mol dm^{-3} H_3PO_4, (c) after the modification using 2×10^{-4} mol dm^{-3} HF and (d) after the modification using 2×10^{-4} mol dm^{-3} HI or HCl dissolved in PC.

4. Conclusion

Some results obtained from XPS analyses are summarized in Fig. 9. The surface state of lithium was treated by the acid-base reaction of the native film of lithium with acids dissolved in PC. It was found that HF produces the most favorable surface state of lithium for the suppression of dendrites when using PC containing 1.0 mol dm^{-3} $LiPF_6$. The surface film has a thin bilayer structure consisting of LiF and Li_2O. This indicates that the thin bilayer structure film of LiF and Li_2O may enhance spherical lithium formation. However, when using PC containing 1.0 mol dm^{-3} $LiClO_4$, even though the lithium surface is modified by HF dissolved in PC, lithium dendrites were formed during electrodeposition. The electrolyte salt may be related to the morphology of lithium deposited on the substrate. Species in PC containing $LiPF_6$ may have a significant effect on the electrodeposition process. One possibility species may be HF involved in the electrolyte; PF_6^- ion is hydrolysed to form HF. If PC containing 1.0 mol dm^{-3} $LiClO_4$ containing a small amount of HF is used, dendrite formation can be suppressed. This study demonstrates that the suppression of dendrite formation is enhanced by surface modification of lithium with HF dissolved in PC and also the use of PC containing 1.0 mol dm^{-3} $LiPF_6$.

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