XPS Analysis of the Surface of a Carbon Electrode Intercalated by Lithium Ions

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Surface states of carbon electrodes reduced in nonaqueous electrolytes containing 1.0 mol dm^{-3} $LiClO_4$ were analyzed by an X-ray photoelectron spectroscopy (XPS) in order to decide chemical compositions of surface films formed on two different carbon materials. One is a low crystalline carbon, and the other is a highly crystalline carbon. The XPS spectra measured in this study suggest that the chemical compositions of the surface film formed on the highly crystalline carbon depends on the type of solvent. The carbon surface was almost bare when using propylene carbonate. On the other hand, a well-defined surface film mainly consisting of LiOH was formed in a mixed solvent of ethylene carbonate and diethyl carbonate. When the low crystalline carbon was used, the surface films formed in both electrolytes were a well-developed layer mainly consisting of LiOH. The electrochemical characteristics of these carbon materials in the two electrolytes showed that irreversible reactions were suppressed by the formation of a well-developed LiOH layer. These results suggested that such a well-developed LiOH layer formed on carbon materials has a function to suppress the irreversible reactions occurring on carbon materials during the first cathodic reduction process.

Introduction

Carbon electrodes have exhibited various electrochemical features in nonaqueous electrolytes depending on their surface states and crystal structures when lithium ions are inserted into their interstitial space.[1−8] It has been reported that, at the first lithium intercalation process, irreversible processes occur, corresponding to the surface state of carbon and the type of solvent used. When propylene carbonate electrolyte is used as the solvent, the electrode potential during a cathodic reduction process becomes constant at around 1.0 V vs Li/Li$^+$, showing that the decomposition of propylene carbonate takes place instead of lithium intercalation.[1] On the other hand, the decomposition of the solvent can be suppressed by using other solvents, such as a mixed solvent of ethylene carbonate and diethyl carbonate.[4,9] When lithium ions are inserted into carbon materials, the electrode potential of carbon becomes more negative than 1.0 V vs Li/Li$^+$. At such a negative electrode potential, solvents may be reduced, or a co-intercalation of solvents may occur. However, some carbons show an excellent reversibility for intercalation and deintercalation cycles when the proper electrolyte is used. If the decomposition of solvent takes place on the carbon electrode, a reversibility of intercalation and deintercalation cycle will be very low. This means that the decomposition of solvent can be strongly suppressed under proper conditions. In some experimental results reported, this phenomenon has been observed. They have suggested that the surface state of the carbon is very important for the reversible intercalation and deintercalation cycle.[4,8,9] Especially, recent studies have been done to explain the difference in surface states of carbon materials reduced in various electrolytes. However, the chemical compositions of the surface films on carbon materials in nonaqueous electrolytes are not completely understood.

The surface analysis of graphite intercalation compounds, such as A_xC (A: alkali-metal ions) have been performed by using an ultrahigh-vacuum system.[10−13] An X-ray photoelectron spectroscopy (XPS) study has also been conducted using a graphite intercalated with lithium.[13] This experiment provided well-defined binding energies for Li and C in LiC_6 prepared in an ultrahigh-vacuum system. We studied the surface states of carbon electrodes before and after the first cathodic reduction in two representative electrolytes by using XPS in order to investigate the chemical compositions of the surface films.

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Table 1. Various Parameters of MCMBs Used in This Study[a]

samples	purity [%]	density [g cm^{-3}]	d_{002} [Å]	L_c [Å]	L_a [Å]
$MCMB_{1000}$	99.65	1.881	3.50	18	
$MCMB_{2800}$	99.88	2.184	3.37	190	324

[a] d_{002}, the spacing between (002) planes. L_c, crystallite size along the *c* axis. L_a, crystallite size along the *a* axis.

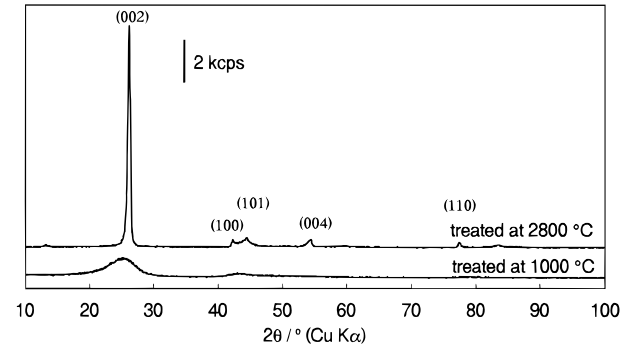

Figure 1. X-ray diffraction patterns of the $MCMB_{2800}$ and $MCMB_{1000}$ used in the electrochemical experiments.

Experimental Section

Mesophase carbon microbeads (MCMB, SEC Ltd., Japan) were used with a heat treatment at 1000 or 2800 °C. These MCMBs are referred to by the designations $MCMB_{1000}$ and $MCMB_{2800}$, respectively. The purity and density of these MCMBs were shown in Table 1. The X-ray diffraction patterns for these MCMBs were measured and are shown in Figure 1. The main peaks (002 line) were observed at $2\theta = 26.4°$ and 25.4° for $MCMB_{2800}$ and $MCMB_{1000}$, respectively. The peak width of $MCMB_{1000}$ was much larger than that of $MCMB_{2800}$. The peak intensity for $MCMB_{1000}$ was much smaller than that for $MCMB_{2800}$. The *d* spacings of these carbon materials were determined from the 002 lines, and crystallite sizes of these MCMBs were determined from the full width at half-maximum of the 002 and 110 lines, respectively.[14] These structural parameters are summarized in Table 1. From the X-ray diffraction results, it can be said that $MCMB_{2800}$ has a graphite structure and $MCMB_{1000}$ has a relatively low crystallinity.

The MCMB (7 mg) was mixed with Teflon binders with a weight ratio of 90:10. The mixture was pressed onto a Ni mesh at 5×10^5 Pa for 10 min to prepare pellet electrodes. Propylene carbonate (PC) or a mixed solvent of ethylene carbonate and diethyl carbonate (EC+DEC) containing 1.0 mol dm^{-3} $LiClO_4$ (Mitsubishi Chemicals, Co., Japan) were used as electrolytes without further purification. The water content of the electrolytes was estimated to be less than 30 ppm, by using a Karl Fischer moisture titrator (MKC-210, Kyoto Denshi Kogyo Co., Japan). The MCMBs were cathodically reduced under galvanostatic conditions at 0.05 mA in two electrolytes using a standard three-electrode cell. Lithium metal (Honjoh Metal Co., Japan) was used as the reference and counter electrodes. After the cathodic reduction, the MCMBs were washed with pure PC or DEC to remove electrolyte salts remaining on the MCMBs. All procedures were conducted in an argon drybox (dew point <−90 °C) at room temperature. Before an XPS analysis, the MCMBs were dried under vacuum (less than 10^{-3} Pa) for 1 h in the argon drybox.

The XPS analysis was performed under about 10^{-7} Pa (ESCA 850s, Shimadzu, Japan). The Mg Kα line was used as an X-ray source. The minimum resolution was 0.7 eV. When the XPS analysis was carried out using a clean silver standard sample (Ag $3d_{5/2}$; 368.2 eV), hydrocarbon gas was observed as the only contaminant in the XPS equipment, and no peaks showing adsorption of O_2, H_2O, or CO_2 were observed for 1 h. Since hydrocarbons are less active, this does not interfere with the XPS analysis of the MCMBs or those intercalated by lithium. The MCMBs were transferred from the argon drybox to a subchamber connected to the XPS equipment filled with an argon. A glass bottle with a ground stopper was used as a transfer vessel to avoid undesirable reactions with atmosphere during the transfer process. More details regarding the transfer procedure to the subchamber of the XPS equipment have been described in our previous paper.[15,16] Some chemical species formed on the MCMBs (especially, after the cathodic reduction of the MCMBs) may cause an insulating layer from the XPS spectrometer. As a result of this insulation, electrostatic charging and a lack of contact of the Fermi edge of the MCMBs with the spectrometer sometimes occur in the XPS measurement. These effects provide a serious problem in the determination of binding energies. Therefore, the binding energies have to be determined by using an internal standard. For example, a hydrocarbon adsorbed on a sample is sometimes used as the internal standard. However, residual hydrocarbon gas adsorbed on the MCMBs is not suitable as the internal standard. This is due to strong peaks for the MCMBs near the hydrocarbon peak. On the other hand, a peak attributed to LiF was observed in the F 1s XPS spectra of the MCMB intercalated by lithium. LiF may be produced by the reduction of the Teflon binder. A peak assigned to LiCl was observed in the XPS spectra of Cl 2p. LiCl may be formed by the reduction of $LiClO_4$ salt. In this study, either the F 1s binding energy of LiF or the Cl 2p binding energy of LiCl was used as the internal standard. The F 1s binding energy of LiF is 685.5 eV and the Cl 2p binding energy of LiCl is 199.0 eV. Using these binding energies, the peak positions were calibrated. The chemical states of the species were determined by referring to the binding energies for various lithium compounds in Table 2. After the determination of the binding energies, the surface states of the MCMBs were derived from the XPS spectra of Li 1s, C 1s, F 1s, Cl 2p, and O 1s.

Table 2. Binding Energies of Various Lithium Compounds

compounds	binding energy[a]/eV Li 1s	O 1s	C 1s	F 1s	C 2p
Li_2O	53.7 ± 0.1	528.8 ± 0.1			
LiOH	54.6 ± 0.1	531.6 ± 0.1			
Li_2CO_3	55.0 ± 0.1	532.0 ± 0.1	290.1 ± 0.1		
LiF	56.0 ± 0.1			685.5 ± 0.1	
LiCl	56.0 ± 0.1				199.0 ± 0.1

[a] The binding energies were calibrated by the C 1s peak (285.0 eV) of a residual hydrocarbon gas adsorbed on samples in an XPS analysis chamber.

A depth profile for each element was calculated from the integrated peak intensity and an ionization constant for each element. The etching process was performed using an argon (ultrapure argon; Kyoto Teisan Co., Japan) ion beam (accelerating voltage 2 keV, ion beam current 7−8 μA). Since the surface of carbon electrodes are not ideally uniform and smooth, it was too difficult to measure the practical etching rate of various compounds from the experimental method. On the other hand, it has been reported in the literature[17] that the etching rate can be estimated by a calculation involving the atomic weight, material density, ion beam current density, and sputtering coefficient, ideally. In this study, the etching rate was estimated to be 5 Å min^{-1} by such a calculation according to reference 17. Though the etching rate would be slightly changed by surface morphology and matrix effect, the etching rate obtained by the above calculation is good enough to estimate the thickness of the surface film on the carbon electrodes as a first rough approximation.

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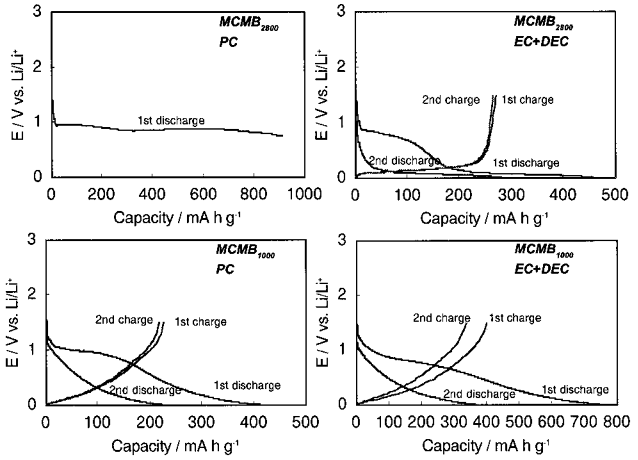

Figure 2. Electrode potential changes of $MCMB_{2800}$ and $MCMB_{1000}$ at a 0.05 C (the current at which the theoretical capacity (372 mA h g^{-1}) is consumed for 20 h) rate in $LiClO_4$/PC or $LiClO_4$/EC+DEC.

Results and Discussion

Figure 2 shows the electrode potential changes of $MCMB_{1000}$ and $MCMB_{2800}$ in PC or EC+DEC containing 1.0 mol dm^{-3} $LiClO_4$ ($LiClO_4$/PC and $LiClO_4$/EC+DEC) during the cathodic reduction (discharge) and the anodic oxidation (charge). The electrode potential of $MCMB_{1000}$ shifted toward the negative direction during the cathodic polarization in both electrolytes and finally reached 0 V vs Li/Li^+. These electrode potential changes were in agreement with a typical electrode potential change for the intercalation of lithium into a low crystalline carbon.[18−24] This suggests that the intercalation of lithium into $MCMB_{1000}$ takes place during the cathodic polarization. On the other hand, the electrode potential for $MCMB_{2800}$ in $LiClO_4$/PC remained at around 1.0 V vs Li/Li^+ even after the cathodic reduction for more than 120 h at 0.05 mA, which would be equivalent to a carbon capacity of 900 mA h g^{-1}. This potential change shows that the intercalation of lithium into $MCMB_{2800}$ does not occur during the galvanostatic cathodic polarization when using $LiClO_4$/PC. Probably, the decomposition of PC or ClO_4^- takes place instead of the lithium intercalation process. On the other hand, lithium intercalation into $MCMB_{2800}$ was observed when $LiClO_4$/EC+DEC was used. Some potential plateaus in the electrode potential changes (especially in the second cathodic polarization) were observed, corresponding to the formation of the different stage compounds for graphite intercalated with lithium. The electrode potential changes for $MCMB_{1000}$ in both electrolytes were different from those of $MCMB_{2800}$, which gradually shifted to a more negative potential during the cathodic polarization process and did not show any potential plateaus corresponding to the formation of stage compounds. These phenomena were also confirmed by the X-ray diffraction method. The X-ray diffraction patterns of these carbons after the cathodic polarization in both electrolytes were in agreement with previous results that have been reported by many researchers.[18−24] Although the structure of the MCMBs is related to the electrochemical behavior, the different behavior of $MCMB_{2800}$ in two electrolytes is not explained by the structural factors. Thus, the intercalation of lithium into the MCMBs is influenced by the type of carbon materials as well as the type of electrolyte solvent. A possible reason for these influences may be given by the difference in the surface state of the MCMBs. The nature of the surface state of carbons has been discussed by many researchers.[4,8,9]

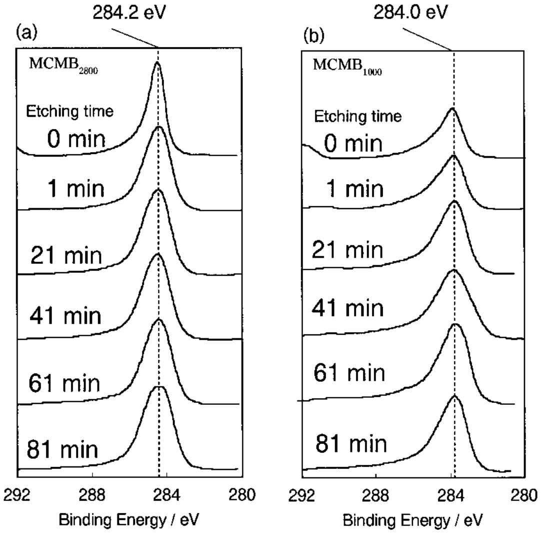

Figure 3. XPS spectra of MCMB before cathodic reduction: (a) $MCMB_{2800}$; (b) $MCMB_{1000}$.

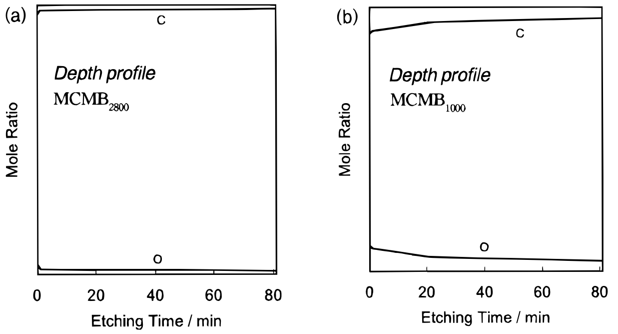

Figure 4. Depth profiles of MCMB before cathodic reduction: (a) $MCMB_{2800}$; (b) $MCMB_{1000}$. The etching rate was roughly estimated to be 5 Å min^{-1}.

In the case of the MCMBs, edge planes mostly touch the electrolytes,[24] so that the electrochemical activity of the edge plane is very important. Figures 3 and 4 show the XPS spectra and the depth profile for $MCMB_{2800}$ and $MCMB_{1000}$. Since carbon materials have a high electronic conductivity, electrostatic charging for these carbon materials does not occur.[25] Therefore, the C 1s binding energies of both samples were obtained without calibration. The C 1s binding energy of $MCMB_{2800}$ was 284.2 eV. Other researchers reported that the binding energy of highly oriented pyrolytic graphite (HOPG) is 284.3[10] or 284.4 eV.[13] The difference

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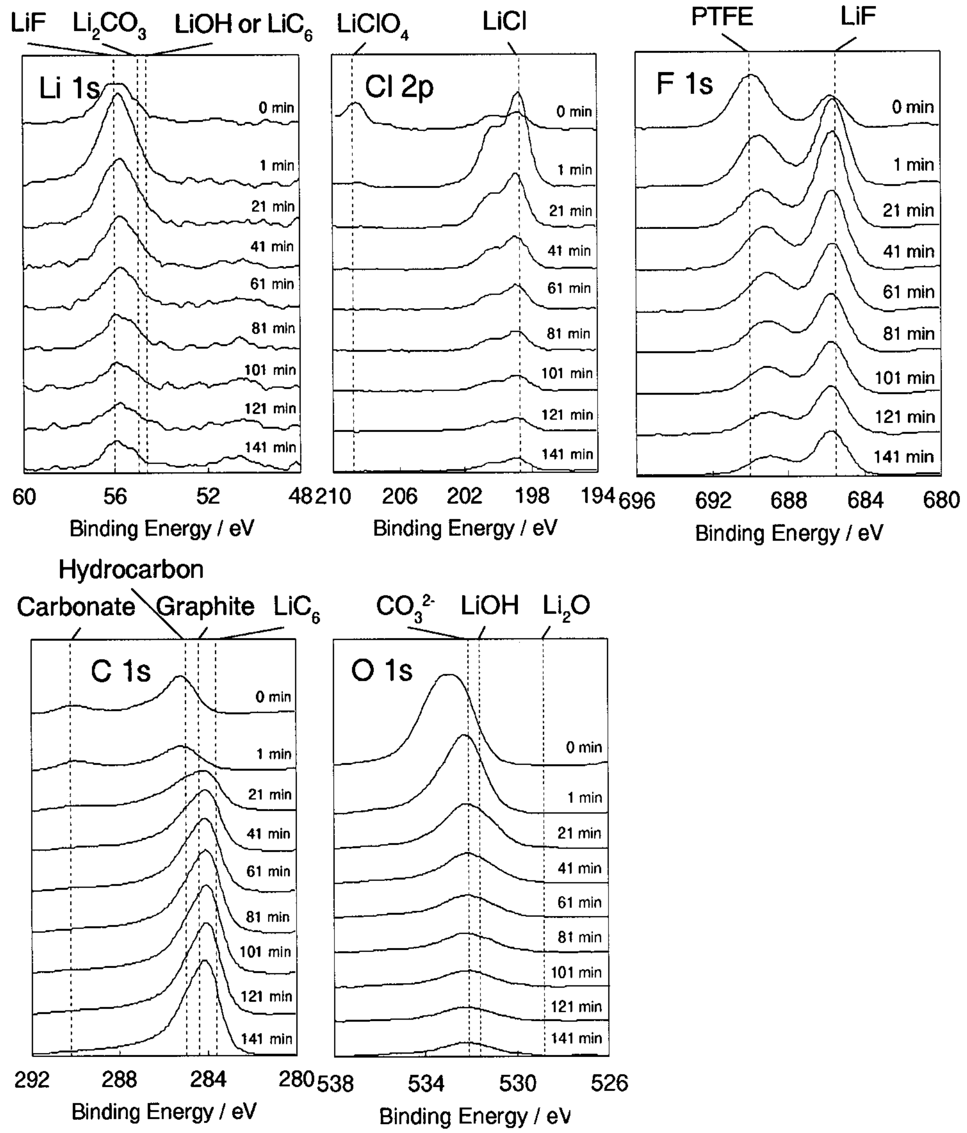

Figure 5. XPS spectra of Li 1s, C 1s, O 1s, F 1s, and Cl 2p for $MCMB_{2800}$ reduced at 0.05 mA in $LiClO_4$/PC for 120 h; the times in the figure indicates the duration of the argon ion etching (2 keV, 7−8 μA).

among these measurements may be caused by the calibration process for binding energy. In this study, we calibrated this binding energy using an internal standard in the following sections in which this binding energy was estimated to be 284.4 eV. Therefore, these results show that the C 1s binding energy of $MCMB_{2800}$ is in good agreement with that of graphite, such as HOPG (284.4 eV). The full width at half-maximum (fwhm) of the peak in the XPS spectra of C 1s is related to the crystallinity of the MCMB.[25] The fwhm of $MCMB_{2800}$ was 1.1 eV, while the fwhm of $MCMB_{1000}$ was 1.6 eV. This result shows that $MCMB_{2800}$ is more crystalline than $MCMB_{1000}$, which is consistent with the X-ray diffraction patterns in Figure 1. The fwhm of $MCMB_{2800}$ was found to increase with the argon ion etching, suggesting that the surface structure of $MCMB_{2800}$ was disordered by the argon ion beam radiation.[25] Wertheim et al. reported that a long tailing peak toward a high binding energy was observed for HOPG. They have discussed the long tailing peak in terms of the interaction of the electrons in conduction band with an emission of photoelectrons from the C 1s level.[13] Therefore, the tailing of $MCMB_{2800}$ or $MCMB_{1000}$ is also explained by the effect of electrons in the conduction band. The depth profile (Figure 4) showed that the surface of $MCMB_{1000}$ contains a larger amount of oxygen than that of $MCMB_{2800}$. The peak shape and the depth profile show that the chemical bond characteristics of C−C in $MCMB_{1000}$ are distributed in a wide range. These different surface states of the MCMBs may influence the electrochemical activity of the MCMBs in nonaqueous electrolytes.

Figure 5 shows the XPS spectra of the Li 1s, Cl 2p, C 1s, O 1s, and F 1s states and the depth profile of each element for $MCMB_{2800}$ reduced for 120 h at 0.05 mA in $LiClO_4$/PC. The total charge for this reduction would be equivalent to a carbon capacity of 900 mA h g^{-1}. A peak was observed at 56.0 eV in the XPS spectra of Li 1s before and after the argon ion etching. This peak is assigned to LiF. Since elemental F was not included in this electrolyte, the Teflon binder is probably the source of the LiF. Peaks were observed at 690.0 and 685.5 eV in the XPS spectra of the F 1s states. These peaks correspond to elemental F in Teflon and LiF, respectively. Both XPS spectra of F 1s and Li 1s show the presence of LiF in the pellet electrode. In the XPS spectra of Li 1s, a very weak shoulder was observed at a slightly lower binding energy than 55.0 eV after the

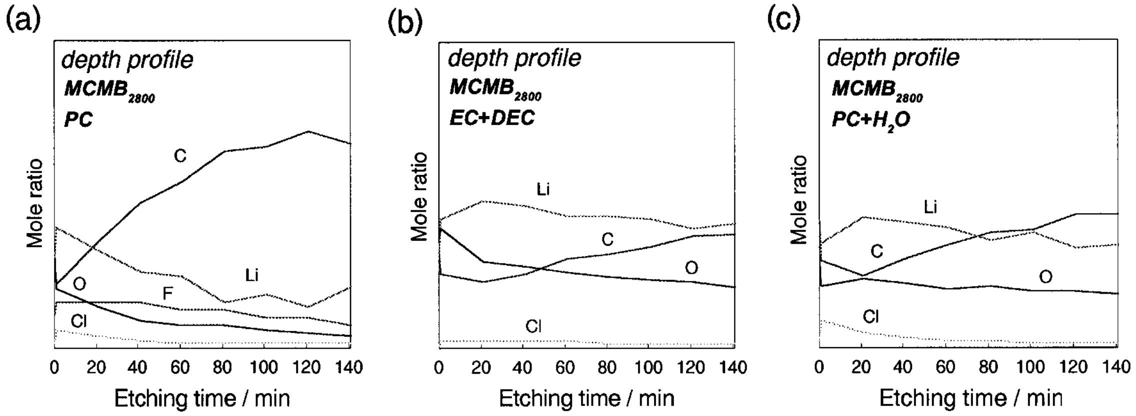

Figure 6. Depth profiles of $MCMB_{2800}$ reduced at 0.05 mA in (a) $LiClO_4$/PC, (b) $LiClO_4$/EC+DEC, and (c) $LiClO_4$/PC with 300 ppm H_2O. The etching rate was roughly estimated to be 5 Å min^{-1}.

argon ion etching. Probably, a small amount of Li_2CO_3 and LiOH are present in the surface film on $MCMB_{2800}$. Two peaks were observed at 208.0 and 199.0 eV in the XPS spectra of Cl 2p before the argon ion etching. The peak at 208.0 eV is due to ClO_4^- anions remaining on $MCMB_{2800}$. Another peak is assigned to LiCl which may be produced by the reduction of ClO_4^- ions. A peak was observed at 290.2 eV in the XPS spectra of C 1s before the argon ion etching. This peak is attributed to carbonate species, showing the presence of Li_2CO_3 or organic products involving carbonate bonds. The peak intensity was very weak and almost disappeared after the argon ion etching for 21 min. A peak at 285.0 eV is attributed to hydrocarbon existing in the XPS analysis chamber as a contaminant or is assigned to organic compounds of the surface film. A new peak appeared in the XPS spectra of C 1s at 284.4 eV after the argon ion etching for 21 min. This peak position did not change during the further argon ion etching process. The C 1s binding energy of LiC_6 against the Fermi level was reported to be 285.2 eV.[13] Since the work function changes with the chemical state of the species, the work function change must be considered in a determination of the chemical shifts in XPS spectra.[26] The work functions of graphite and LiC_6 were reported to be 4.4 and 2.8 eV, respectively, so that the difference in these work functions is 1.6 eV.[13] Therefore, the C 1s binding energy of LiC_6 is expected to be 283.6 eV (=285.2 eV − 1.6 eV). This means that the chemical shift of the C 1s core level in LiC_6 relative to that in graphite is estimated to be 0.8 eV when the C 1s binding energy of graphite is 284.4 eV. Therefore, the peak at 284.4 eV in Figure 5 suggests that the formation of LiC_6 did not take place when using $LiClO_4$/PC. A peak was observed at 533.0 eV in the XPS spectra of the O 1s spectra before the argon ion etching procedure. This peak is not assigned to any possible lithium compounds. Probably, it is attributed to some organic compounds having alkyl carbonate groups. After the argon ion etching, a new peak was observed at 532.0 eV which corresponds to Li_2CO_3 or LiOH. Although the presence of Li_2CO_3 can be adopted from this result, a strong peak corresponding to carbonate was not observed in the XPS spectra of C 1s. Therefore, the surface film does not mainly consist of Li_2CO_3, but it consists of LiOH whose binding energy is 531.6 eV.

The depth profiles of these elements are also shown in Figure 6a. The amount of elemental C markedly increased with increasing argon ion etching duration. The amount of the other elements markedly decreased with increasing argon ion etching duration. From these depth profiles, it can be seen that a surface film consisting of organic and inorganic compounds exists on the carbon electrode reduced in $LiClO_4$/PC. However, the thickness of this surface film was extremely small. If the variation in the argon ion beam radiation is considered, it can be said that a part of the carbon surface is not covered with the surface film. Moreover, the amount of Li was much smaller than that of elemental C. This means that the intercalation of lithium into the graphite structure does not occur in $LiClO_4$/PC. From these results, it can be proposed that the surface of $MCMB_{2800}$ is still partly bare and active for the electrochemical reduction of electrolyte taking place around 1.0 V vs Li/Li^+. This reduction of electrolyte prevents the intercalation of lithium. This behavior has been extensively discussed by many researchers. Especially, Fong et al.[4] have suggested that the co-intercalation of solvent causes a partial exfoliation of graphite surfaces and exposure of fresh graphite surface to electrolytes. Arakawa et al.[3] also suggested that PC decomposes on a graphite surface by the co-intercalation leading to no intercalation of lithium for the PC electrolyte.

Figure 7 shows the XPS spectra of $MCMB_{2800}$ reduced for 63 h at 0.05 mA in $LiClO_4$/EC+DEC. The total charge for this reduction is equivalent to carbon capacity 450 mA h g^{-1}. A broad peak was observed at 55.6 eV in the XPS spectra of Li 1s before the argon ion etching. This peak is assigned to LiOH, Li_2CO_3, and LiF. After the argon ion etching, the peak shifted to a slightly lower binding energy, 55.0 eV. This peak is attributed to Li_2CO_3 and LiOH. After the further argon ion etching procedure, the peak shifted to a lower binding energy than 55.0 eV. Wertheim et al. reported that the chemical shift of the Li 1s core level in LiC_6 from that in lithium metal was 2.6 eV. In our previous paper,[15] we reported that the Li 1s binding energy of lithium metal was 52.2 eV against the C 1s binding energy (285.0 eV) of an adsorbed hydrocarbon. From these previous studies, the Li 1s binding energy of LiC_6 is expected to be 54.8 eV. Therefore, another possible compound corresponding to this binding energy is LiC_6. A peak was observed at 532.0 eV in the XPS spectra of

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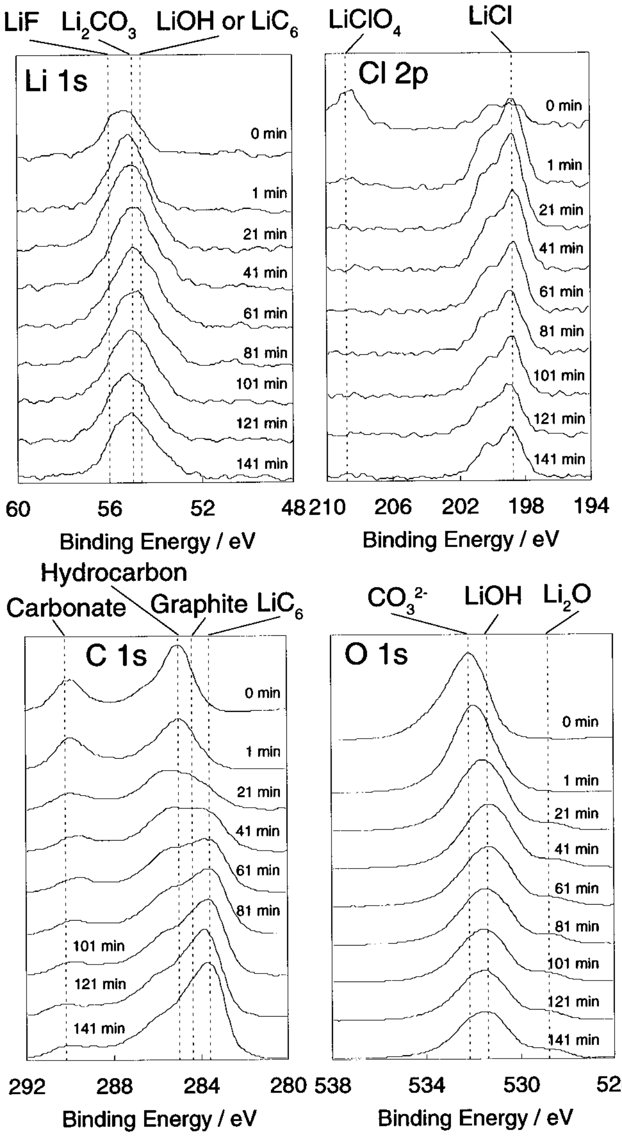

Figure 7. XPS spectra of Li 1s, C 1s, O 1s and Cl 2p for $MCMB_{2800}$ reduced at 0.05 mA in $LiClO_4$/EC+DEC, the cathodic reduction was terminated at 0 V vs Li/Li^+; the times in the figure indicates the duration of the argon ion etching (2 keV, 7−8 μA).

O 1s before the argon ion etching, showing that Li_2CO_3 was present in the surface film. However, this peak had disappeared after the argon ion etching for 21 min. Instead of a Li_2CO_3 peak, a strong peak was observed at 531.6 eV, and its intensity did not change during the following argon ion etching process. This peak is assigned to LiOH. The peak observed at 290.0 eV in the XPS spectra of C 1s is assigned to carbonate. Li_2CO_3 formation on carbon electrodes was evidenced by a FTIR analysis of Aurbach et al.[9] After argon ion etching for 21 min, the peak for carbonate species had almost disappeared. This indicates that carbonate species are present at the outer part of the surface film on $MCMB_{2800}$ and its amount is not very large. From the Li 1s, C 1s, and O 1s spectra, it can be said that the surface film on $MCMB_{2800}$ mainly consists of a thick LiOH inner layer and a thin Li_2CO_3 outer layer. Probably, the amount of Li_2CO_3 in the surface film is not enough to cover the entire surface of $MCMB_{2800}$. In the XPS spectra of C 1s, another peak was observed at 285.0 eV before the argon ion etching. This peak corresponds to the hydrocarbon in the XPS analysis chamber. Its intensity decreased with the argon ion etching process. A new peak was observed at 283.6 eV, which binding energy is in agreement with that of elemental C in LiC_6. This peak intensity increased during the argon ion etching. These results show that the intercalation of Li into the graphite structure takes place in this electrolyte. The formation of LiC_6 was also confirmed by the X-ray diffraction method. A comparison of the XPS spectra of C 1s and Li 1s shows that the peak at around 55.0−54.7 eV in the XPS spectra of Li 1s is attributed to LiOH and Li_2CO_3 after the etching duration ranging from 0 to 21 min, but the peak at 54.7 eV after the argon ion etching for 41 min is also attributed to LiC_6. Two peaks were observed in the XPS spectra of Cl 2p, which were assigned to $LiClO_4$ and LiCl, respectively. This Cl 2p spectra were very similar to that for $MCMB_{2800}$ reduced in $LiClO_4$/PC. However, other XPS spectra were completely different from those for $MCMB_{2800}$ reduced in $LiClO_4$/PC.

Figure 6b shows the depth profile for each element involved in the surface film formed on $MCMB_{2800}$ reduced in $LiClO_4$/EC+DEC. This depth profile was different from that for $MCMB_{2800}$ reduced in $LiClO_4$/PC in which a stable surface film was not formed. The amount of elemental C gradually increased and that of O gradually decreased with the argon ion etching. From these results, it can be seen that the surface film formed on $MCMB_{2800}$ is thicker than that on $MCMB_{1000}$. On the other hand, the amount of Li did not decrease even after the argon ion etching, indicating that $MCMB_{2800}$ was intercalated by lithium. The Li:O ratio in the depth profile was more than 1:1, corresponding to LiOH, and increased with further argon ion etching. This is because the mole ratio of lithium reflects both of the amount of lithium in LiOH and that in Li-intercalated carbon. Therefore, it can be seen that the depth profile is consistent with the assignment of the spectra.

From the XPS analysis of $MCMB_{2800}$ reduced in both electrolytes, it can be said that the most important point is the surface films formed on $MCMB_{2800}$. A well-defined surface film (several hundred angstroms, main species LiOH) was formed when the $LiClO_4$/EC+DEC was used. On the other hand, the surface film on $MCMB_{2800}$ reduced in $LiClO_4$/PC was very thin. This difference in the surface condition of $MCMB_{2800}$ provides different electrochemical characteristics for $MCMB_{2800}$. Therefore, it can be said that the LiOH film works as a key factor in the intercalation of lithium. The function of $LiClO_4$/EC+DEC may be explained by a stabilization of the thick LiOH layer on carbon materials. Since we have already confirmed that Li_2CO_3 powder does not decompose to LiOH with the radiation of Ar ion beam in our XPS equipment, it can be concluded that the LiOH layer is produced by a reductive reaction involving residual H_2O in electrolytes. If this is correct, the formation of LiOH should be enhanced by a larger supply of OH^- ions. Recently, Aurbach et al. have proposed that the addition of H_2O (500 ppm) is useful to obtain a more reversible intercalation/deintercalation of lithium into carbon materials when using dimethyl carbonate (DMC) as a solvent.[9] In our study, H_2O (300 ppm) was added to $LiClO_4$/PC.

The electrode potential change for $MCMB_{2800}$ in $LiClO_4$/PC was clearly improved by the addition of H_2O, as is shown in Figure 8. As discussed above, the

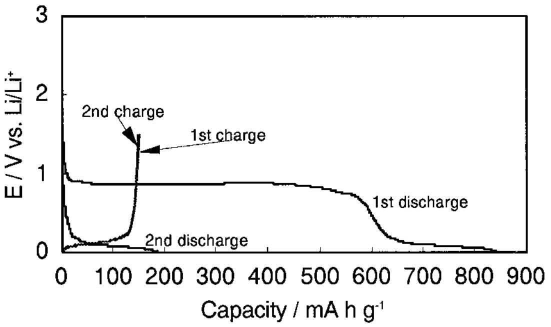

Figure 8. Electrode potential change of $MCMB_{2800}$ at the 0.05 C (the current at which the theoretical capacity (372 mA h g^{-1}) is consumed for 20 h) rate in $LiClO_4$/PC with 300 ppm H_2O.

electrode potential did not become more negative than 1.0 V vs Li/Li^+, when $LiClO_4$/PC was used as a solvent. On the other hand, when H_2O was added into $LiClO_4$/PC, the electrode potential of $MCMB_{2800}$ became more negative than 1.0 V vs Li/Li^+ after the cathodic reduction for 600 mA h g^{-1} and then finally reached 0 V vs Li/Li^+. This potential change not only shows the decomposition of $LiClO_4$/PC but also indicates the intercalation of lithium. The charge capacity of $MCMB_{2800}$ in $LiClO_4$/PC without H_2O was almost 0. On the other hand, that of $MCMB_{2800}$ in $LiClO_4$/PC containing 300 ppm H_2O was 150 mA h g^{-1}. Moreover, the electrode potential change during the reduction and oxidation cycle became more reversible. This result indicates that the intercalation/deintercalation of lithium into/from $MCMB_{2800}$ occurs with a high reversibility. Probably, the addition of small amount of H_2O into $LiClO_4$/PC influences the surface reaction of $MCMB_{2800}$. The following XPS analysis was performed for $MCMB_{2800}$ reduced in this electrolyte to observe the surface film on $MCMB_{2800}$.

Figure 9 shows the XPS spectra of Li 1s, Cl 2p, C 1s, and O 1s for $MCMB_{2800}$ reduced for 120 h at 0.05 mA in $LiClO_4$/PC containing 300 ppm H_2O. The total charge for this reduction is equivalent to carbon capacity 850 mA h g^{-1}. Peaks corresponding to LiOH were observed at 54.7 and 531.6 eV in the XPS spectra of Li 1s and O 1s, respectively, indicating that the surface film on $MCMB_{2800}$ consists of the thick LiOH layer. In the XPS spectra of C 1s, a peak corresponding to Li_2CO_3 was observed at the outer part of the surface film, but its amount was small. A peak attributed to LiC_6 was also detected after the argon ion sputtering for 21 min. These results indicate that the surface state of $MCMB_{2800}$ is very sensitive to H_2O. Thus, the XPS spectra obtained for $MCMB_{2800}$ reduced in $LiClO_4$/PC containing 300 ppm H_2O was very similar to those in $LiClO_4$/EC+DEC. From this result, it can be said that the addition of H_2O promotes the formation of the LiOH layer on $MCMB_{2800}$. Probably, the LiOH surface film operates as a solid−electrolyte interface and prevents the co-intercalation of PC.

Figure 6c also shows the depth profile for $MCMB_{2800}$ reduced in $LiClO_4$/PC containing 300 ppm H_2O. The depth profiles for elements were very similar to those for $MCMB_{2800}$ reduced in $LiClO_4$/EC+DEC. This result indicates that the surface state of $MCMB_{2800}$ can be modified by a small amount of additives, as well as the type of solvent.

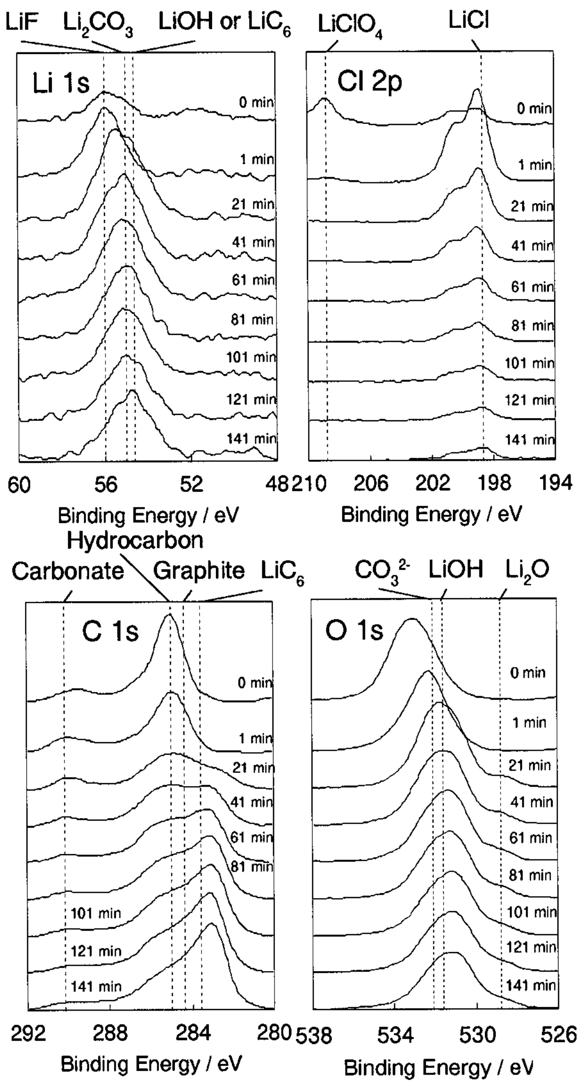

Figure 9. XPS spectra of Li 1s, C 1s, O 1s, and Cl 2p for $MCMB_{2800}$ reduced at 0.05 mA in $LiClO_4$/PC and 300 ppm H_2O, the reduction was terminated at 0 V vs Li/Li^+; the times in the figure indicates the duration of the argon ion etching (2 keV, 7−8 μA).

Various products are formed on the MCMBs during the cathodic reduction through chemical and electrochemical reactions. Probably, these surface reactions are affected not only by the type of electrolyte but also by a surface structure of the MCMBs. The surface structure of the MCMBs is related to the crystallinity of the carbon materials. In fact, the electrode potential change of $MCMB_{1000}$ was different from those of $MCMB_{2800}$, as shown in Figure 2. This may be due to the different surface state of $MCMB_{1000}$ from $MCMB_{2800}$.

Figure 10 shows the XPS spectra of Li 1s, Cl 2p, C 1s, and O 1s for $MCMB_{1000}$ reduced for 59 h at 0.05 mA in $LiClO_4$/PC. The total charge for this reduction is equivalent to carbon capacity 420 mA h g^{-1}. The XPS spectra of Li 1s was similar to those for $MCMB_{2800}$ reduced in the $LiClO_4$/EC+DEC rather than those for $MCMB_{2800}$ reduced in $LiClO_4$/PC. The XPS spectra of O 1s shows the surface film on $MCMB_{1000}$ consists of a LiOH layer. In the XPS spectra of C 1s, the peak corresponding to LiC_6 was clearly observed at 283.6 eV, indicating that lithium intercalates into $MCMB_{1000}$ even when using $LiClO_4$/PC. These results also indicate that

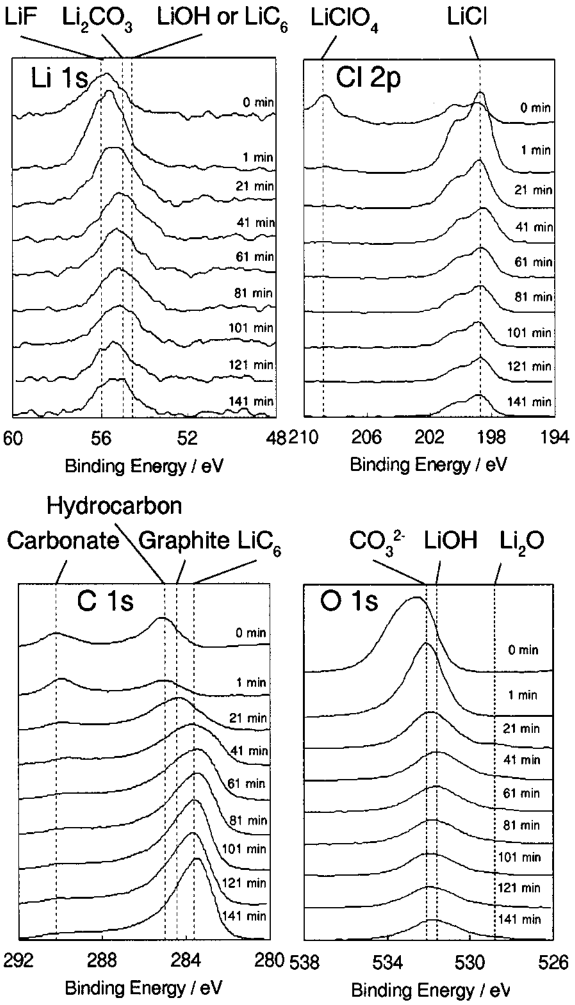

Figure 10. XPS spectra of Li 1s, C 1s, O 1s, and Cl 2p for $MCMB_{1000}$ reduced at 0.05 mA in $LiClO_4$/PC; the reduction was terminated at 0 V vs Li/Li^+; the times in the figure indicates the duration of the argon ion etching (2 keV, 7−8 μA).

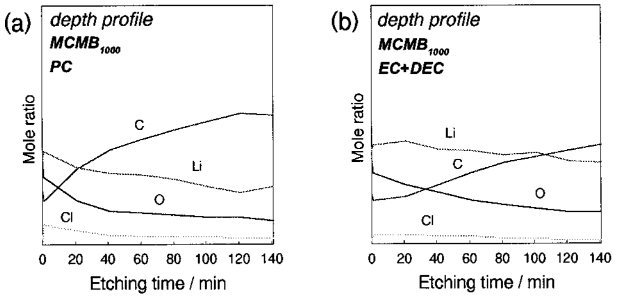

Figure 11. Depth profiles of $MCMB_{1000}$ reduced at 0.05 mA in (a) $LiClO_4$/PC and (b) $LiClO_4$/EC+DEC. The etching rate was roughly estimated to be 5 Å min^{-1}.

the intercalation of lithium is related to the formation of a LiOH layer on $MCMB_{1000}$. Figure 11a shows the depth profile for each element involved in the surface film formed on $MCMB_{1000}$ reduced in $LiClO_4$/PC. The thickness of this LiOH layer seems to be smaller than that on $MCMB_{2800}$ reduced in $LiClO_4$/EC+DEC (Figure 6b). Therefore, it can be said that lithium intercalates into $MCMB_{1000}$ even if the thickness of the LiOH layer is relatively thin. This may be due to the disordered surface structure of $MCMB_{1000}$.

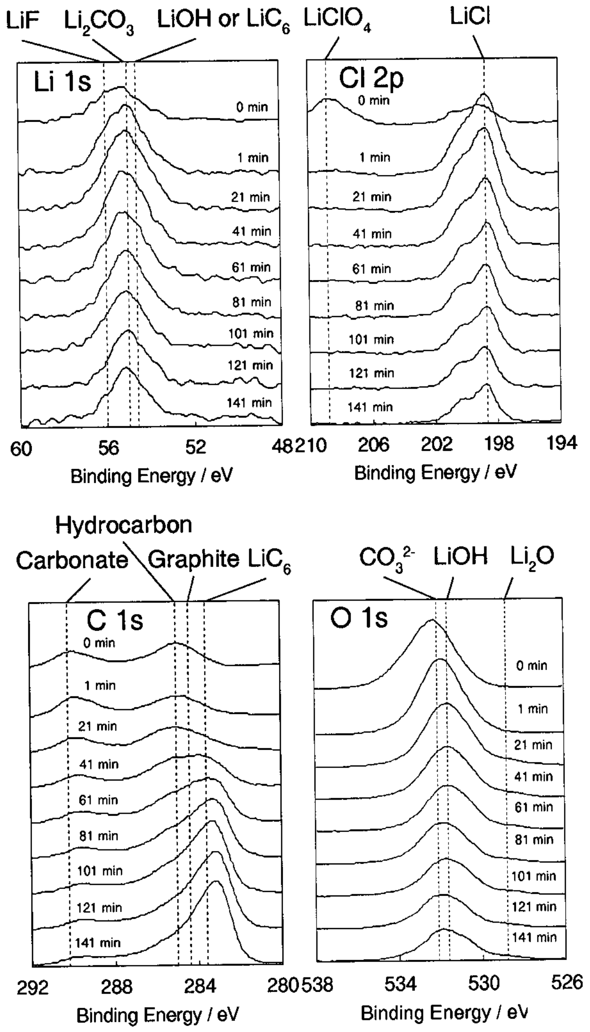

Figure 12. XPS spectra of Li 1s, C 1s, O 1s, and Cl 2p for $MCMB_{1000}$ reduced at 0.05 mA in $LiClO_4$/EC+DEC; the reduction was terminated at 0 V vs Li/Li^+; the times in the figure indicates the duration of the argon ion etching (2 keV, 7−8 μA).

Figure 12 shows the XPS spectra of Li 1s, Cl 2p, C1s, and O 1s for $MCMB_{1000}$ reduced for 105 h at 0.05 mA in $LiClO_4$/EC+DEC. The total charge for this reduction is equivalent to carbon capacity 750 mA h g^{-1}. Figure 11b also showed the depth profile of each element involved in the surface film. From these XPS analysis, it can be seen that the surface film consists of a thick LiOH layer which avoids the reduction of electrolytes. As a result of such a surface film, lithium can intercalate into a graphite structure. These results were very similar to those for $MCMB_{2800}$ reduced in $LiClO_4$/EC+DEC.

Conclusions

The XPS analysis on the MCMBs in two electrolytes shows that the surface state of the MCMBs is very important for the reversible intercalation and deintercalation of lithium during the reduction and oxidation processes of these carbons. Specially, the formation of a LiOH layer on the MCMBs is one of critical factors for the intercalation of lithium and is influenced by the crystallinity of the MCMBs and the type of electrolytes. Furthermore, the addition of a small amount of H_2O into $LiClO_4$/PC was effective in forming a LiOH layer on $MCMB_{2800}$. This result demonstrates that we can modify the surface state of carbon materials using small amount of additives in nonaqueous electrolytes.

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