

A STUDY OF SURFACE LAYERS ON LITHIUM FOILS FOR BATTERIES

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Summary

Parts of the surfaces of lithium foils sometimes turn faint-brown or yellow in colour during storage. This phenomenon has been investigated both by ESCA and by X-ray diffraction techniques. The performances of cells having coloured lithium foils have also been examined.

The colouring of the lithium foils has been attributed to optical interference resulting from the formation of very thin oxide layers on the metal surface.

Introduction

Metallic lithium used as electrodes in batteries is usually in the form of a thin foil. On some occasions, the surface of the lithium foil takes on a faint-brown or yellow colouration during storage, in spite of the foils being maintained in a sealed condition. The reason for this phenomenon has been investigated using electron spectroscopy for chemical analysis (ESCA) and X-ray diffraction (XRD) techniques. In addition a study has been made of the effect of lithium surface tarnishing on battery performance.

Experimental

Three differently coloured samples of aged lithium foil (faint brown, bluish-silver and yellowish-silver) were investigated; a fresh, silver-white sample of lithium foil was used as reference. The surface of each sample was analysed with a LAB-Mk II ESCA instrument (VG Corporation). Further oxidation of the lithium was prevented by quick insertion into the ESCA instrument in an inert gas (*i.e.*, N₂) atmosphere.

Surface analysis was also carried out by XRD using a Rotaflex RU-200 RAX-12 spectrometer (Rigaku Denki Corporation). In these measurements, the lithium surfaces were covered with a Mylar film in order to prevent further oxidation [1, 2].

Determination of the elements contained in the lithium foil was achieved by means of a Type GE 170 spectroscopic analyser (Shimadzu Corporation).

The characteristic electrode behaviour of each sample of lithium foil was examined in the test cell shown in Fig. 1. All the electrodes were circular with a diameter of 10.6 mm and a weight of ~ 10 mg. The positive active material was a composite of 90 wt.% MnO_2 (EMD, heat-treated at 380°C), 6 wt.% graphite, and 4 wt.% polytetrafluoroethylene (PTFE). The mixture (0.30 g) was pressed at 2 t cm^{-2} to form a disc (10.6 mm dia.). The electrolyte consisted of 1 M LiClO_4 in a 1:1 (by volume) mixed solvent of propylene carbonate and 1,2-dimethoxyethane. Each reagent was dried by the usual methods before use.

Cell performance was compared on the basis of the discharge capacity, which was calculated from the curve obtained from a constant-current discharge test. For each cell, the discharge was carried out with a load of $2.5 \text{ k}\Omega$ at 20°C . At the same time, the internal impedance of each cell was measured between 1 Hz and 65 kHz by means of a Type 1250 frequency response analyser (Solartron Corporation).

Results and discussion

Shaving off the surface layer of all three tarnished lithium surfaces with a knife revealed that the underlying metal had the same silver-white colour as the reference piece of lithium foil. This observation clearly indicates that the different colours of each piece of aged lithium foil resulted from differences in the surface conditions of the metal.

The ESCA spectra obtained from the lithium samples are shown in Fig. 2. Only the peaks corresponding to lithium, carbon, and oxygen were observed. Thus, it can be concluded that no unusual compounds were formed on the surface, nor was there any concentration of foreign elements. The surface film corresponded to the formation of an oxide.

A more detailed study of the observed lithium, carbon, and oxygen was undertaken by conducting ESCA measurements after etching the lithium surfaces with argon ions. The peak corresponding to carbon was detected in

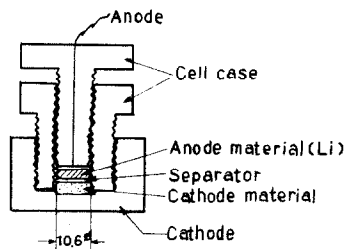


Fig. 1. Design of test cell.

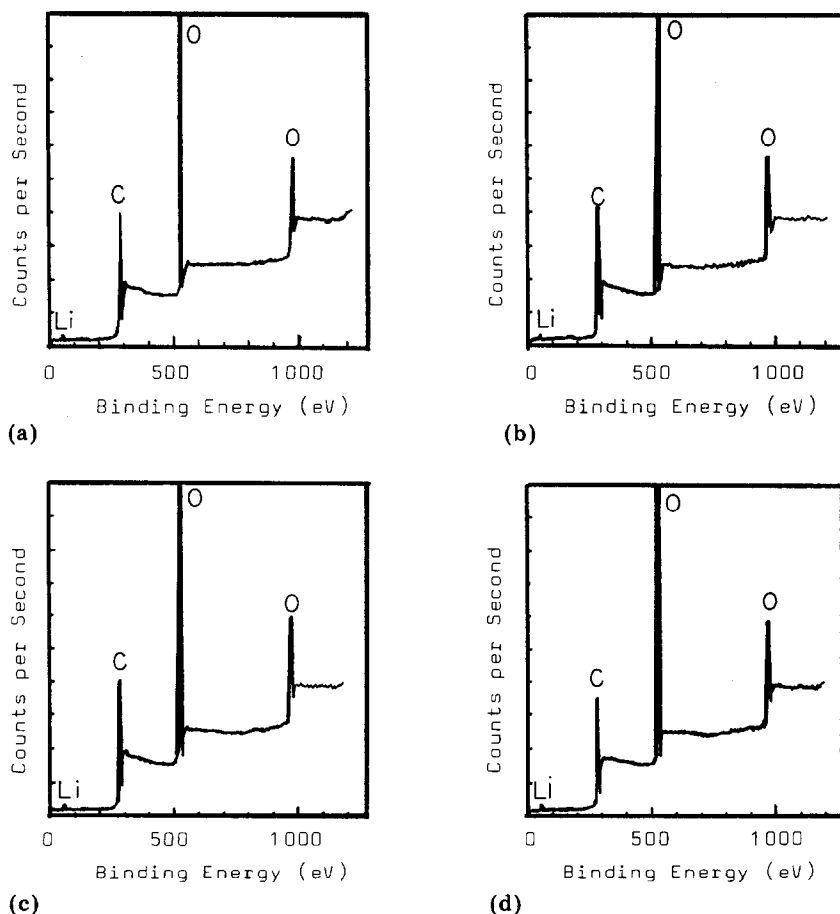


Fig. 2. ESCA spectra of (a) silver-white, (b) faint-brown, (c) bluish silver, and (d) yellowish-silver lithium foil.

both the fresh (silver-white) and the three coloured varieties of the samples. In all cases the carbon peak disappeared when the etching reached a depth of about 100 Å; at this point the respective spectra were virtually identical (Fig. 3).

Argon-ion etching revealed that the thickness of the lithium-oxide layer differed between specimens. Figure 4 shows the oxygen/lithium molar ratio plotted against depth on the three types of lithium foil. It can be seen that the thickness of the oxide layer increased in the order: silver-white < yellowish-silver < faint-brown. It should be further noted that the differences in layer thickness were great, ranging from several hundred to several thousand angstroms.

Figure 5 shows the results from an XRD examination of the lithium surfaces. In all four samples, the pattern exhibits only the peaks due to

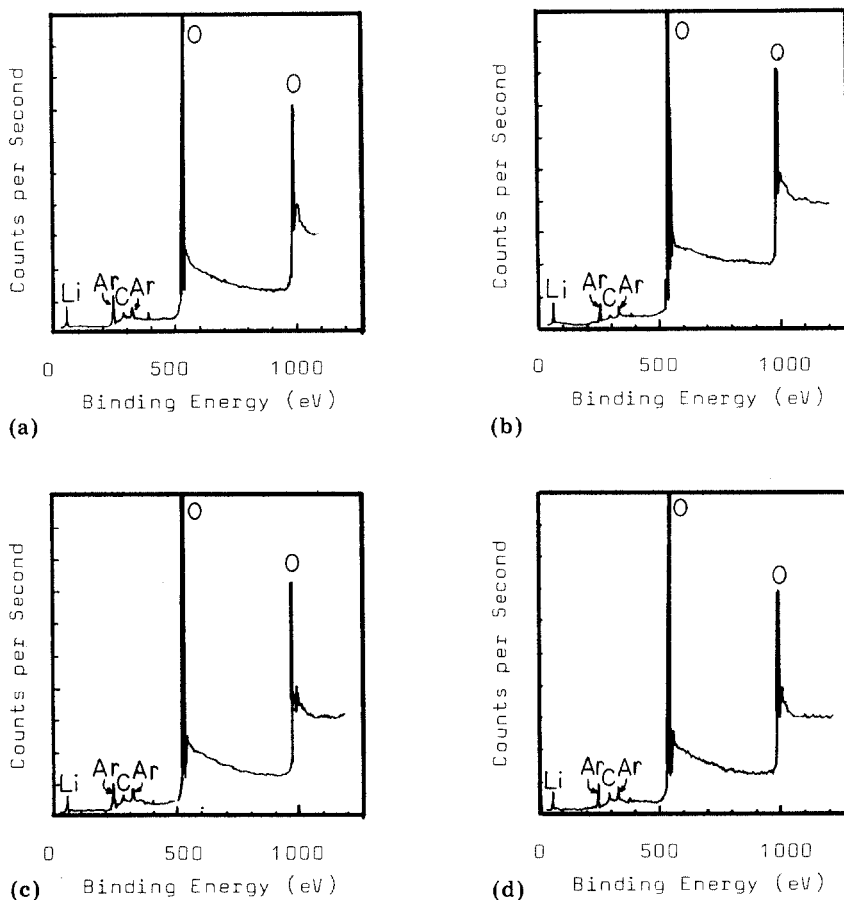


Fig. 3. ESCA spectra after 100 Å etching (determined from etching time) of (a) silver-white, (b) faint-brown, (c) bluish-silver, and (d) yellowish-silver lithium foil.

metallic lithium. However, differences in surface orientation were found among the samples. In particular, there was a decrease in the peak height of the (200) plane. This may be attributed to differences in the conditions under which the samples were processed.

When the silver-white foil was subjected to forced oxidation in air, the peak due to LiOH appeared on the XRD pattern. After this treatment, the surface of the lithium foil had turned gray-black. The same situation developed when the three coloured pieces of lithium foil were processed in a like manner. On removing the gray-black surface of the lithium foil, a silver-white colour was observed beneath each surface layer. These results demonstrate that the growth of the oxide layer can be determined from XRD patterns, and that discolouration takes place due to the formation of hydroxides.

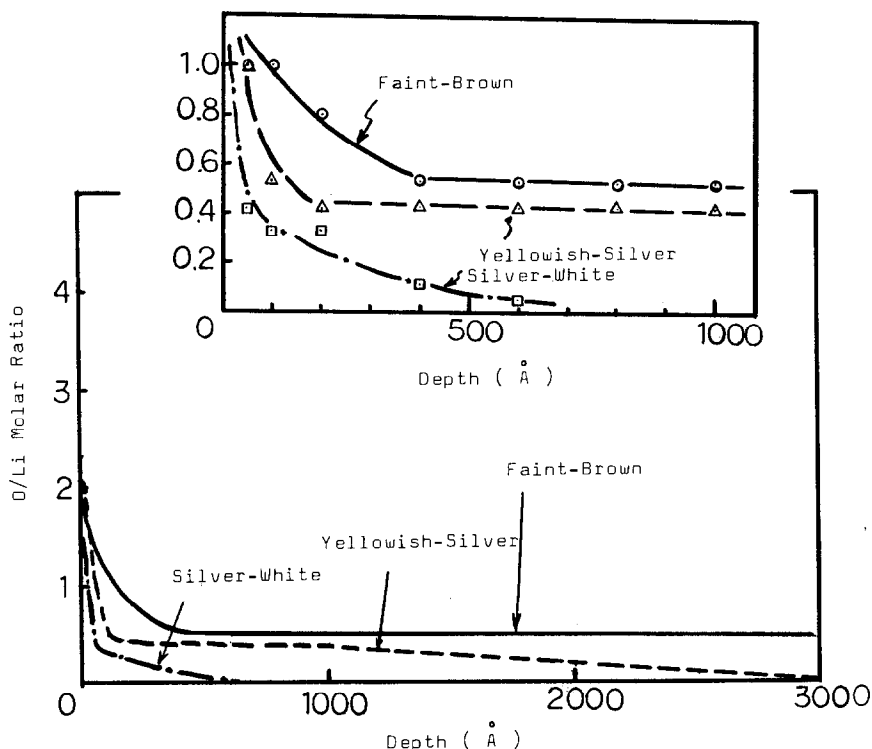


Fig. 4. Dependence of O/Li molar ratio on depth of surface layer on lithium foil (depth determined from argon-ion etching time).

The possible presence of trace metal elements was investigated by spectroscopic analysis. The findings are given in Table 1. As with ESCA studies, no difference was observed between the four types of lithium foil.

The above observations suggest that the differences in the appearance of the four lithium samples arise from interference colours due to different thicknesses in the oxide layers formed on the lithium surfaces [3].

In cell discharge tests, the capacity of the MnO_2 cathode was much larger than that of the lithium anode, so that the discharge characteristics were determined by the latter electrode. Table 2 gives the percentage of utilization of the lithium-active material under these conditions. The data show that there is no significant difference in the utilization of the three differently-coloured and the silver-white samples of lithium foil. Equally, the internal impedance remained unchanged (Fig. 6).

Discharge tests were also conducted on lithium foil that had been exposed to air until a gray-black surface had formed. This material yielded a lower degree of utilization (Table 2) together with an increase in internal resistance (Fig. 6).

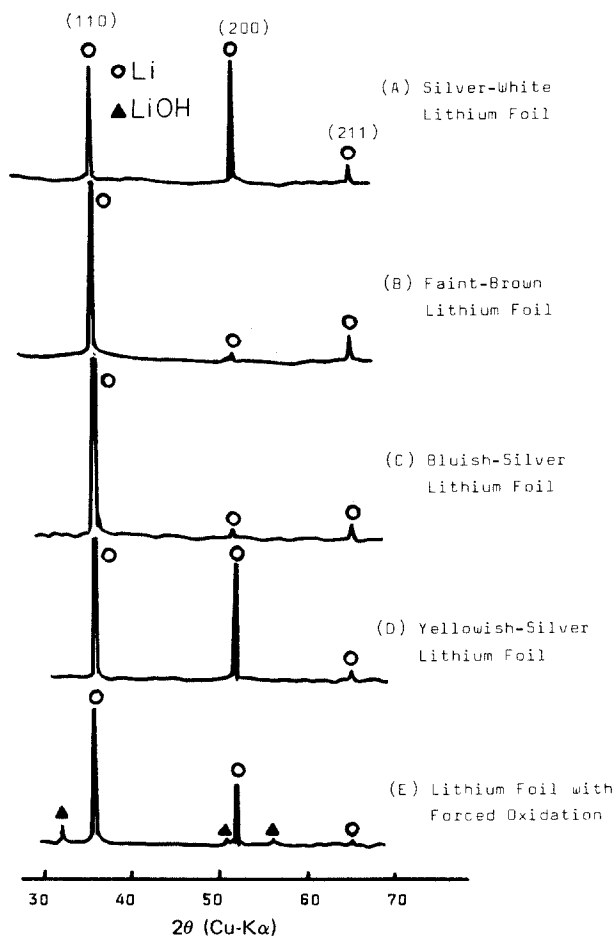


Fig. 5. XRD patterns of lithium foils.

TABLE 1

Spectroscopic analysis of various lithium foils

	Si	Pb	Sn	Fe	Al	Cu	Na	Ag
Silver-white lithium foil	+	±	±	+	+	±	+	±
Faint brown lithium foil	+	±	±	+	+	±	+	±
Bluish-silver lithium foil	+	±	±	+	+	±	+	±
Yellowish-silver lithium foil	+	±	±	+	+	±	+	±

^aDetected intensity: 20 > 19 > 18... > 2 > 1 > + > ± > not detected.

^bOther trace metal elements not detected.

TABLE 2

Discharge tests on various lithium foils (20 °C; 2.5 k Ω load; cut-off voltage 2.0 V)

Type	Theoretical capacity (mA h)	Experimental value			Index	Remarks
		Discharge performance		Average (%)		
		Capacity (mA h)	Utilization (%)			
(A) Silver-white lithium foil	36.4	36.2	99.5	97.5	100	(Li foil thickness) 0.200 mm
		34.4	94.5			
		34.4	94.5			
		36.3	99.7			
		36.2	99.5			
(B) Faint brown lithium foil	40.4	39.0	96.5	95.4	98	0.222 mm
		36.9	91.3			
		38.7	95.8			
		40.1	99.3			
		38.0	94.1			
(C) Bluish-silver lithium foil	40.4	40.0	99.0	98.5	101	0.222 mm
		40.3	99.8			
		39.3	97.3			
		39.8	98.5			
		39.6	98.0			
(D) Yellowish-silver lithium foil	37.4	37.1	99.2	98.2	101	0.206 mm
		36.1	96.5			
		36.1	96.5			
		37.3	99.7			
		37.0	98.9			
(E) Lithium foil with forced oxidation	40.9	31.3	76.5	76.5	78	0.225 mm
		31.2	76.3			
		31.4	76.8			

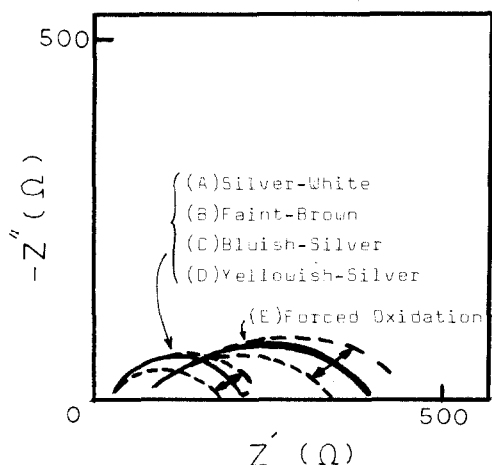


Fig. 6. Complex-plane analysis of charged Li/MnO₂ cells using different types of lithium foil. Frequency range from 1 Hz to 65 kHz.

Conclusions

Studies have shown that the tarnishing of lithium foils is caused by optical interference due to the formation of very thin oxide layers on the metal surface. When these foils are used as anodes in a Li/MnO₂ cell, the presence of the surface layers exerts little effect on the discharge characteristics.

Acknowledgements

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References

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