

# Electrochemical characterization of various metal foils as a current collector of positive electrode for rechargeable lithium batteries

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## Abstract

Electrochemical characterization of various metal foils as a current collector of the positive electrode for rechargeable lithium batteries was carried out by cyclic voltammetry, potentiostatic electrolysis and a.c. impedance measurement. Products of the potentiostatic electrolysis were determined by atomic absorption spectroscopy and gas chromatography/mass spectrometry. As a result, it was found that an aluminum foil seems to be the most suitable material as a current collector of the positive electrode, whose electrochemical stability in 1 M LiClO<sub>4</sub>/ethylene carbonate–diethyl carbonate and 1 M LiPF<sub>6</sub>/ethylene carbonate–diethyl carbonate solutions increases with increasing aluminum purity. © 1997 Elsevier Science S.A.

**Keywords** Rechargeable lithium batteries; Current collectors; Positive electrodes; Metal foils

## 1. Introduction

In general, a current collector of the positive electrode plays an important part in rechargeable lithium batteries and has to satisfy the following requirements: (i) mechanical strength, light weight and thinness; (ii) chemical and electrochemical stabilities in an electrolyte solution, and (iii) acceptability of and adhesiveness to cathode mix (cathode active material, binder and conducting material). To date, however, there have been only a few reports on the electrochemical characteristics of the current collectors [1,2]. In the present work, the electrochemical characteristics of various metal foils were investigated in two kinds of electrolyte solution in order to decide the best choice of materials for use in rechargeable lithium batteries.

## 2. Experimental

The chemical compositions of metal foils (Al, Cu, Fe, Ni, SUS304 and Ti) used in this work are given in Table 1. Prior to use, the metal foils were polished with 0.03 μm alumina suspension and then washed with distilled water and acetone.

Electrochemical measurements were carried out in a beaker-type cell, using lithium metal foils as the counter and reference electrodes. A 1 M solution of lithium perchlorate (LiClO<sub>4</sub>) or lithium hexafluorophosphate (LiPF<sub>6</sub>) in a mixture of ethylene carbonate (EC) and diethylcarbonate (DEC) (1:1 by volume), supplied from Mitsubishi Chemical Corporation, was used as an electrolyte solution. The contents of H<sub>2</sub>O in 1 M LiClO<sub>4</sub>/(EC–DEC) and 1 M LiPF<sub>6</sub>/(EC–DEC) solutions were less than 30 and 20 ppm, respectively. Products of the potentiostatic electrolysis were determined by atomic absorption spectrometry and gas chromatography/mass spectrometry (GC/MASS). A.c. impedance spectra were measured at equilibrium potential. The amplitude of the perturbation signal was 10 mV and the frequency range was 1 Hz–10 kHz. Electron spectroscopy for chemical analysis (ESCA) was carried out using a Mg Kα X-ray excitation source (8 kV, 30 mA).

## 3. Results and discussion

Cyclic voltammograms of various metal foils in 1 M LiClO<sub>4</sub>/(EC–DEC) and 1 M LiPF<sub>6</sub>/(EC–DEC) solutions are shown in Fig. 1. In the case of 1 M LiClO<sub>4</sub>/(EC–DEC) solution, anodic currents at the Al and Ti foils were very

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Table 1  
Chemical compositions of materials used in this work

Material	Content (ppm)						
	Si	Fe	Cu	Mn	Mg	Cr	Zn
Al (99.99%)	8	10	49	<1	<1	<1	<1
Al (99.85%)	41	62	11	7	5	2	7
Al (99.3%)	150	510	200	30	40	30	40
Al (96.9%)	2500	4300	1700	10800	25000	40	50
SUS304	37	<sup>a</sup>		120		1856	
Cu			<sup>a</sup>	<1			<1
Fe	1000	<sup>a</sup>		3000			
Ni		50	4	47			
Ti		104	10	8			

Material	Content (ppm)						
	Ti	Ni	C	P	S	Co	Al
Al (99.99%)		<1				<1	<sup>a</sup>
Al (99.85%)		3				<1	<sup>a</sup>
Al (99.3%)		10				<10	<sup>a</sup>
Al (96.9%)		20				<10	<sup>a</sup>
SUS304		829	6	31	7		
Cu		<1					
Fe			800	<400	<500		
Ni		<sup>a</sup>				66	
Ti	<sup>a</sup>					3	

<sup>a</sup> Main component

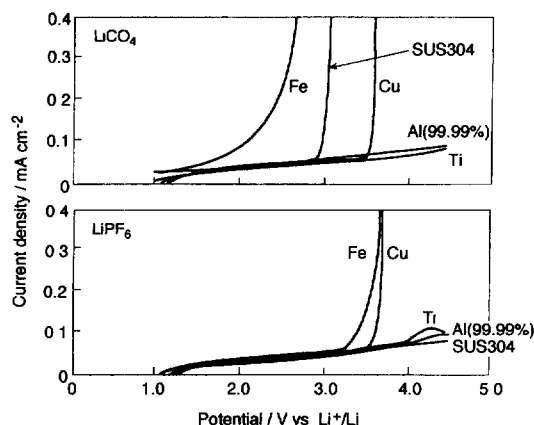


Fig. 1. Anodic polarization curves of Al (99.99%), Cu, Fe, SUS304 and Ti electrodes in 1 M LiClO<sub>4</sub>/(EC-DEC) and 1 M LiPF<sub>6</sub>/(EC-DEC) solutions, first cycle, potential scan rate = 5 mV s<sup>-1</sup>.

small over the measured potential range, suggesting that they are much more stable against electrochemical oxidation, compared with the Fe, SUS304 and Cu foils. In the case of 1 M LiPF<sub>6</sub>/(EC-DEC) solution, on the other hand, anodic oxidation potential of the Fe foil was greatly shifted to the more anodic side, compared with data shown in Fig. 1(a). Furthermore, it is evident that the electrochemical stability of SUS304 foil was greatly improved by using this electrolyte solution.

Cyclic voltammograms of Al foils with different purities were measured. According to the results, the anodic current

at the Al foils with higher impurities increased with increasing number of potential scan, while the anodic current at the Al foil with high purity scarcely changed, suggesting that the electrochemical stability of the Al foil is influenced by aluminum purity.

When the metal foils were allowed to stand in the electrolyte solutions without electrolysis, there was no detectable amount of dissolved metal ions except for the case of the Fe foil. However, every metal anodically dissolved more or less in both electrolyte solutions used. So, metal ions dissolved in the electrolyte solutions by the potentiostatic electrolyses at 4.5 V versus Li/Li<sup>+</sup> for 10 h were determined. In both electrolyte solutions, number of charges passed in anodic oxidation of metal foils showed the similar tendency to that observed on the cyclic voltammograms. The quantity of dissolved metal ions was relatively small at the Al and Ti foils in both electrolyte solutions and at the SUS 304 foil in 1 M LiPF<sub>6</sub>/(EC-DEC) solution, compared with the other metal foils. Moreover, the quantity of dissolved metal ions for the Al foils decreased with an increase in aluminum purity, indicating that the Al foil with high purity is desirable for use as a current collector of positive electrode.

Fig. 2 shows time course of anodic current density for the Al foils with different purities in potentiostatic electrolyses at 4.5 V versus Li<sup>+</sup>/Li using two different electrolyte solutions. In the case of 1 M LiClO<sub>4</sub>/(EC-DEC) solution, the anodic current density increased with increasing electrolysis time and depended on the aluminum purity, but it was negligibly small in the case of 1 M LiPF<sub>6</sub>/(EC-DEC) solution. In the latter case, the formation of fluoride on the surface of the Al films was confirmed by ESCA, and the fluoride seems to play a protective role for the corrosion of the Al foils. In all cases, any decomposition product of the electrolyte solutions could not be detected by GC/MASS under the present experimental conditions.

A.c. impedance spectra for the Al (99.99%) and Ti foils in 1 M LiClO<sub>4</sub>/(EC-DEC) solution are shown in Fig. 3. As

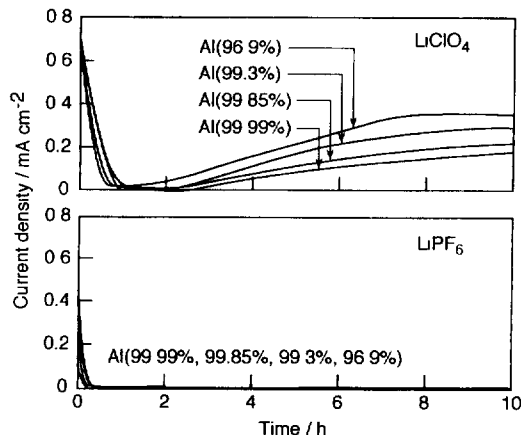


Fig. 2. Time course of anodic current density for Al foils with different purities in potentiostatic electrolyses using 1 M LiClO<sub>4</sub>/(EC-DEC) and 1 M LiPF<sub>6</sub>/(EC-DEC) solutions; applied potential 4.5 V vs. Li<sup>+</sup>/Li.

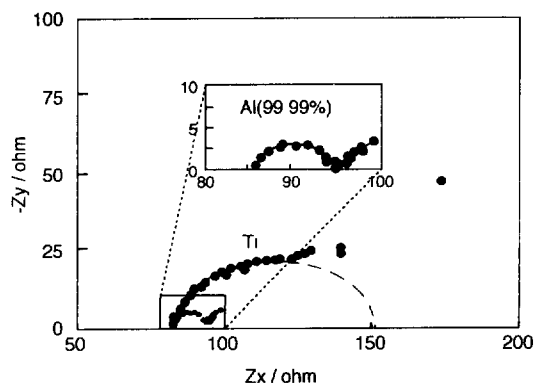


Fig. 3. A.c. impedance spectra of Al (99.99%) and Ti in 1 M LiClO<sub>4</sub>/(EC-DEC) solution.

can be seen from this figure, the electrical resistance of the surface oxide film on the Al (99.99%) foil evaluated from a diameter of a semi-circle which was much smaller than that on the Ti foil. This seems to be responsible for the relatively small quantity of dissolved metal ions in the case of the Ti foil. It was also found by a.c. impedance measurements in 1 M LiPF<sub>6</sub>/(EC-DEC) solution that the electrical resistance of the surface oxide film on the Al (99.99%) was smaller than that on the SUS304 foil for the same reason. The differ-

ence in electric resistance of Al (99.99%) in both electrolytes was hardly discernible.

#### 4. Conclusions

Judging from the above-mentioned results, an Al foil with a high purity seems to be the most suitable material as a current collector of the positive electrode.

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#### References

- [1] K. Kanamura, T. Okagawa, M. Ohashi and Z. Takehara, *Proc. 36th Battery Symp. in Japan*, 1995, p. 307.
- [2] K. Kanamura, S. Toriyama, S. Shiraishi and Z. Takehara, *J. Electrochem. Soc.*, 142 (1995) 1383.