



Short communication

## Effects of current collectors on power performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode for Li-ion battery

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## ABSTRACT

The effects of current collector on the charge/discharge capacity and cycle stability of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (LTO) electrode under high C-rates (up to 20C) have been investigated by applying five types of current collectors, including a Al foil, an anodization-etched Al (E-Al), the same etched Al with a conformal C coating (C-E-Al), a Cu foil (Cu) and the same Cu foil with a C coating (C-Cu). The C coatings on both metal current collectors are deposited by a chemical vapor deposition process using  $\text{CH}_4$  at 600 °C. The capacities of the LTO electrodes above 1 C rate are in the order of  $\text{Al} < \text{E-Al} < \text{Cu} \sim \text{C-E-Al} < \text{C-Cu}$ , exhibiting remarkable enhancement in rate performance by the C-coating for both metals. Surface analyses indicate that the enhancement can be attributed to the combination of two factors, including removal of the native oxide layer and modification of surface hydrophobicity, which improves adhesion of active layer, on the current collector surface. Both contribute to the reduction of the resistance at the current-collector/active layer interface. All electrodes show good cycle stability.

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### 1. Introduction

$\text{Li}_4\text{Ti}_5\text{O}_{12}$  (LTO) exhibits a capacity of 175  $\text{mAh g}^{-1}$ , a flat potential plateau at ca. 1.5 V vs.  $\text{Li}/\text{Li}^+$ , and most significantly negligible volume change [1,2] upon electrochemical lithiation/de-lithiation. The dimension-invariable property allows the material to undergo high-rate charge/discharge with high reversibility and good cycling stability. Therefore, it has been considered as a very promising anode material for both high-power lithium battery and hybrid supercapacitor applications [3–8]. The basic principle for achieving high-power capability of an electrode is minimizing the overall resistance of the electrochemical system. For Li-ion batteries, the ionic diffusion resistances and electronic resistance associated with the electrode active materials have been of major concern in the past. On the other hand, the resistance of the interface between the current collector and active layer has received much less attention in the literature, presumably because it has long been considered of less significance for the low-power Li-ion electrode materials. However, the rapid advancement in material synthesis technologies may in some cases have reduced the ionic and electronic resistances of the active materials to the point that they become competitive to the other resistance sources. Indeed, the power performances of supercapacitor and a high-power cathode material,

namely  $\text{LiFePO}_4$ , have recently been shown to be markedly enhanced by C coating on their Al current collectors [9–11]. Such enhancement has been attributed mainly to the reduction in the current collector/active layer (CC/AL) interfacial resistance.

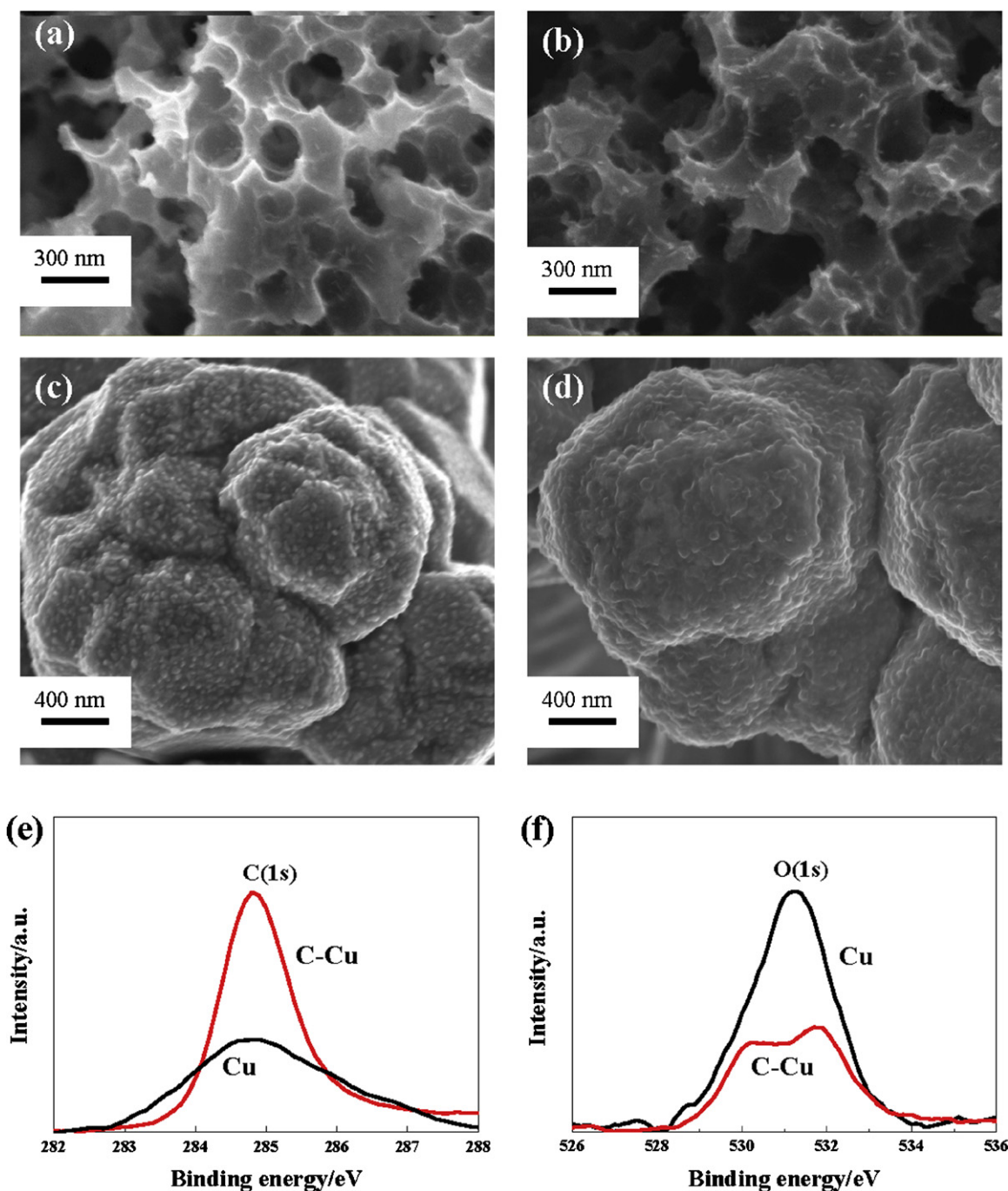
We study in this work the effects of the CC/AL interfacial resistance on the power performance of LTO electrode by employing five different types of current collectors, including a Al foil, an etched Al (E-Al), the etched Al with a C coating (C-E-Al), a Cu foil (Cu) and the same Cu foil with a C coating (C-Cu). The C coating is produced by a high temperature chemical vapor deposition process. These current collectors have different surface chemistry, hydrophobicity and roughness, and they shall provide valuable information regarding the role of the CC/AL interfacial resistance on the high-power performance of the LTO electrode.

### 2. Experimental

The Al (Intelcoat Technologies), Cu (Copper Foil Division, Furukawa Electric Co., Ltd.) and etched Al (Japan Capacitor Industrial Co., Ltd.) are commercial products and they have been used as received. To prepare the C coating, the foils were placed inside a horizontal hot-wall reactor and subjected to heat treatment in flowing  $\text{CH}_4$  at 600 °C for 20 h. The electrodes were prepared by conventional slurry-coating method. The active layer consisted of, on a dry basis, 80 wt.% LTO powder (BTR Energy Materials Co., Ltd; average particle size (vendor's value: ca. 100 nm), 13 wt.% carbon black, and 7 wt.% binder (polyvinylidene difluoride; Aldrich). The

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**Fig. 1.** Material characterizations. (a)–(d) are SEM micrographs of E-Al (a), C-E-Al (b), Cu (c) and C-Cu current collectors. (e)–(f) show the XPS C(1s) and O(1s) spectra for the Cu and C-Cu current collectors.

electrodes were roll-pressed and finally dried at 120 °C for 6 h in vacuum. The resulting LTO electrodes were assembled together with Li-foil counter electrodes to make CR2032 coin cells, and the electrolyte was 1 M LiPF<sub>6</sub> in a 1:2 (v/v) mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC; Mitsubishi Chemical). All the cells were assembled in a dry room where the dew point was maintained at between –40 and –45 °C. The active layers have a mass of ca. 2.8 mg cm<sup>-2</sup>.

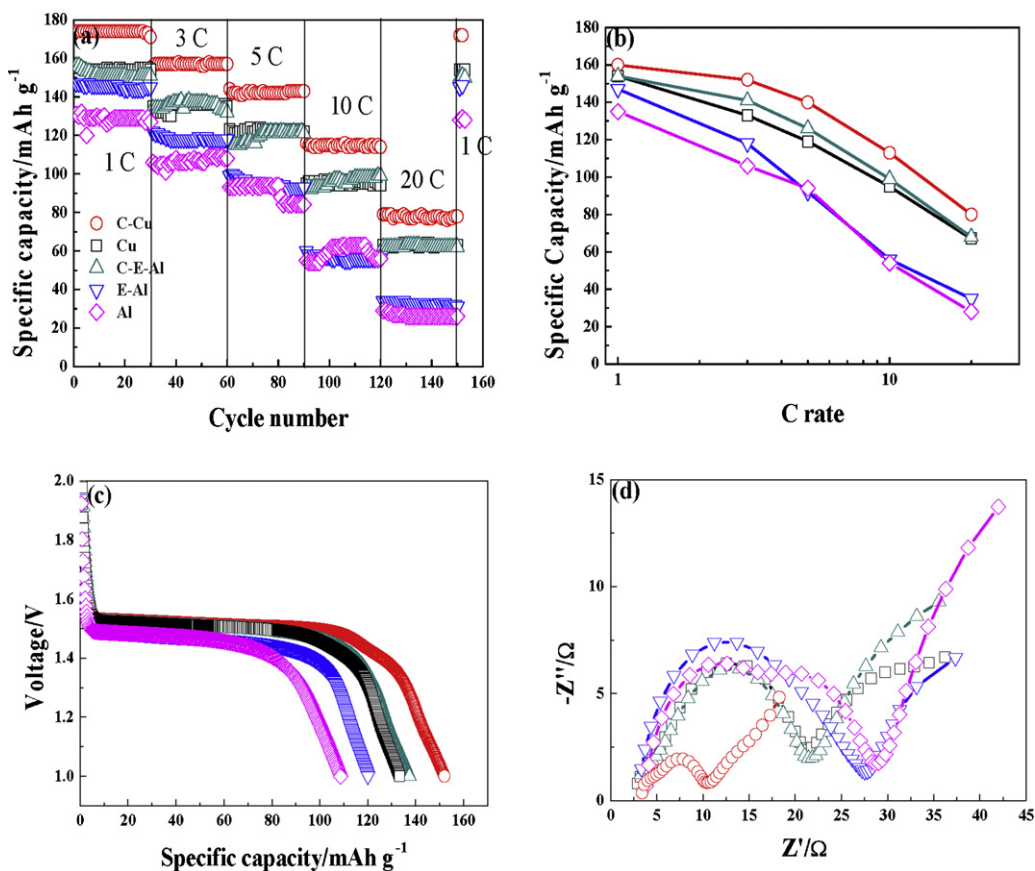
Electrochemical characterizations include constant current charge/discharge (C/D) test and electrochemical impedance spectroscopy (EIS). The C/D tests were carried out with selected current rate between 3.0 and 1.0 V at room temperature on a battery tester (Arbin, model: MCN6410). EIS analysis (AUTOLAB, Eco

Chemie PGSTAT30) was conducted with the frequency ranging from 10 mHz to 60 kHz and a voltage amplitude of 10 mV at 1.5 V. The morphologies of the materials and electrodes were characterized by scanning electron microscopy (SEM; LEO1530).

### 3. Results and discussion

#### 3.1. Materials analyses

The Al foil has a smooth surface except for some mechanical scratches. Fig. 1a–d shows the surface morphologies of E-Al, C-E-Al, Cu and C-Cu current collectors, which have more profound surface features. E-Al foil has a porous surface structure showing circular



**Fig. 2.** Electrochemical characterizations. (a) Capacity data vs. cycle number; (b) capacity data vs. current rate; (c) discharge voltage curves (3 C rate); and (d) Nyquist plots for cells using different current collectors (○: C-Cu; □: Cu; △: C-E-Al; ▽: E-Al; ◇: Al).

pores overlapping with one another to form void opening of  $\sim 1 \mu\text{m}$  at surface (Fig. 1a). After the high-temperature C-coating process, the porous structure remains (Fig. 1b), while the interior surface is coated with a conformal C layer. The surface chemical compositions of the Al-based current collectors have been characterized in detail in a previous study [10] by using X-ray photoelectron spectroscopy (XPS). In brief, both the Al and E-Al current collector possesses a native oxide surface layer with decreasing oxygen content with depth. The C-E-Al current collector has a composite surface layer that consists of a top C layer and a bottom  $\text{Al}_4\text{C}_3$  layer. The C-coating thickness is greater than  $\sim 70 \text{ nm}$ , varying from one location to another. The original surface oxide layer has been broken into debris dispersed within the C layer.

The Cu current collector possesses a rough surface structure that shows large particles of  $1\text{--}3 \mu\text{m}$  in diameter with smaller particles of ca.  $20\text{--}30 \text{ nm}$  at their surfaces (Fig. 1c). After the CVD process, the foil surface is covered with a conformal C layer (Fig. 1d). The XPS data confirm that the C-Cu current collector has a higher C content on surface than the Cu current collector, while the latter has a higher oxygen content. The thickness of the carbon layer on C-Cu is ca.  $45 \text{ nm}$ , according to the secondary ion mass spectroscopy (SIMS) analysis (not shown).

### 3.2. Electrochemical analyses

Fig. 2a plots the capacity data under different C-rates for the five different electrodes. 25 cycles have been conducted under every selected current rate and the average values are summarized in Fig. 2b. Selected discharge voltage curves (under 3 C rate) are shown in Fig. 2c. For brevity, the coin-cells will be referred to with the same notation as the electrodes they contain. As shown, the Al cell shows

the lowest capacities for all the adopted current rates. Using the etched Al foil (the E-Al cell), which gives a higher CC/AL interfacial area than smooth Al, results in slight increase in capacities below 5 C rate. The C-E-Al cell shows remarkable capacity improvement under all current rates, and the improvement is particularly strong under high current rate. Compared with the Al cell, the capacity has been increased by 20% and 150% under 1 C and 20 C rates, respectively.

The Cu cell exhibits higher capacities than the Al and E-Al cells at all current rates and performs closely to the C-E-Al cell. C-coating on the Cu surface further markedly enhances the capacity. Overall, the power performance of these cells is in the order of  $\text{Al} < \text{E-Al} < \text{Cu} \sim \text{C-E-Al} < \text{C-Cu}$ . For achieving a capacity of  $130 \text{ mAh g}^{-1}$ , the current rate has been increased from 1 C for the Al cell to 5 C for C-E-Al and to 7 C for C-Cu.

It is also worth noting that after cycling 150 cycles under various high rates as shown in Fig. 2a, the cells show essentially no fading. This reflects the cycling stability nature of the active material.

For all these cells, their Nyquist plots show a distorted semi-circle above ca. 20 Hz (Fig. 2d). Theoretically, any interface that can be described by a parallel RC equivalent circuit unit will give a semi-circle in the Nyquist plot. The semi-circle over this frequency range for a Li-ion battery electrode has typically been attributed to the impedance associated with the electrode/electrolyte interface, and the width of the semi-circle along the real-part ( $Z'$ ) axis to the charge-transfer resistance. However, in studying the C-based electric double-layer capacitor (EDLC), Portet et al. [9] showed that the use of Al current collector, which has a native surface oxide layer, gave rise to a semi-circle above ca. 80 Hz, while the use of C-coated Al current collector did not. This has also been confirmed in our previous study on another C-coated Al current collector

**Table 1**  
Contact angles of water on current collectors.

Type of current collector	Contact angle
Al	74°
E-Al	87°
C-E-Al <sup>a</sup>	116°
Cu	102°
C-Cu <sup>a</sup>	129°

<sup>a</sup> C-coating is produced at 600 °C in CH<sub>4</sub> for 20 h.

[10]. As EDLC does not involve charge transfer across the electrode/electrolyte interface, the semi-circle seen on the Al current collector must originate from the CC/AL interface, and the associated capacitor element of the RC unit arises from the thin oxide layer as well as patches of thin electrolyte film between the active layer and the current collector due to poor adhesion (see further discussion below). Therefore, it is believed that the semi-circles shown in Fig. 2d include both the charge-transfer and CC/AL interfacial impedances, and the width of these semi-circles are the sum of the charge-transfer and CC/AL interfacial resistances. Since all the electrodes studied here have the same active material and electrolyte, one expects the same electrochemical behaviors at the solid/electrolyte interface. Therefore, the differences shown in their semi-circle resistances are caused primarily by the different resistances at the CC/AL interface. Accordingly, it can be concluded that the CC/AL interfacial resistance follows the order of Al > E-Al > Cu ~ C-E-Al > C-Cu, which is exactly the reverse order of their capacities.

The reduction of the CC/AL interfacial reduction by the C coating may be understood in terms of the surface chemistry of the current collector. The presence of insulating oxide layers at the pristine Al and Cu current collectors would impose significant resistance to current flow across the CC/AL interface. Furthermore, the oxide

surface is hydrophilic, while the coating slurry and dried active layer are both hydrophobic in nature. The different polarities would result in poor film adhesion and hence high interfacial resistance. Replacing the surface oxide layer with the C layer can significantly reduce these problems. Firstly, it directly reduces the surface resistance by destroying the native oxide layer. Secondly, it can turn the current-collector surface from being hydrophilic to hydrophobic, and hence improve the adhesion of the active layer. To demonstrate such a property change, Table 1 compares the contact angle data of water on these current collectors. The higher the contact angle, the greater is the surface hydrophobicity. As shown, after the CVD C deposition treatment, the surfaces of both Al and Cu current collectors exhibit very significant increase in hydrophobicity.

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