



# Crater-like architectural aluminum current collectors with superior electrochemical performance for Li-ion batteries



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## ABSTRACT

Crater-like architectural aluminum current collectors is prepared by a simple chemical etching method with NaOH-based solutions, and investigate the effect of aluminum surface morphology on its electrochemical performance as cathode current collector in Li-ion batteries. Characterization data reveal an acceptable tensile strength and surface hydrophilicity in the etched aluminum current collector, together with the creation of a rough surface with many reticular crater-like pits. In Li-ion cells using LiCoO<sub>2</sub> as the active material, the crater-like architectural aluminum foil is electrochemically stable as the current collector, when in contact with other cell components during the charge–discharge processes. The improved electrochemical performance is attributed to the good electrical contact between cathode material particles and the current collector, and the resulting efficient electron transfer.

## 1. Introduction

Li-ion batteries are the most important power source in portable devices, because of their high energy density, long cycle life, and absence of memory effect. Furthermore, concerns of global warming have accelerated the development of Li-ion batteries for electric vehicles and large/medium-sized batteries [1–3]. However, the commercial battery industry is still not satisfied with the rapid advances of the mobile, automotive and stationary storage applications markets. These markets desire further gravimetric/volumetric energy densities, long-term use, and safety. These challenging requirements need alternative active electrode materials beyond conventional LiCoO<sub>2</sub> and graphite [4–6]. In this regard, many researchers have studied active cathode and anode materials for Li-ion batteries, and proposed new electrical energy storage devices such as Li–S, Na-ion, and metal-air batteries [7–15]. Though these attempts are ingenious, they are not ready for commercialization in terms of chemical/electrochemical stability, durability, stable cycle life, safety issues, and/or cost of starting materials. In addition, these novel materials are in early stages of development and still require significant research time and cost.

Besides the core materials, other components of Li-ion batteries can be improved to increase the energy density of the cell, by reducing the cell weight or volume. These components include: current collectors, lead taps, and external cases [16,17]. In particular, the thinner anode and cathode current collectors can easily enhance battery performance

while using existing materials. Generally, the current collector is a thin foil 15–20 μm thick, which serves as a bridge for electrons to/from the laminated active material film. It has to satisfy the following requirements: (i) thin, light but with adequate mechanical properties, (ii) has good adhesion to the films of the laminated active materials, and (iii) being electrochemically and chemically stable during charge and discharge processes [18,19]. However, there have been few studies of the current collector in Li-ion batteries, possibly because compared to the core materials, the current collector appears to be a conventional topic that lacks the luster of dramatically changing the battery technologies.

The aim of this study was to investigate the correlation between crater-like architectural Al current collector and electrochemical properties for Li-ion batteries. In order to improve the adhesion on Al current collector, wet chemical etching was performed as a surface modification method [20]. Then, the performance of Li-ion cells using crater-like architecture and smooth current collectors were compared. Care was taken to avoid forming pinholes on the Al collector, because the pinholes not only contribute to the generation of defective electrodes during the lamination of the active material film, but also can cause local heating problems due to the intensive current distribution. Moreover, in order to exclude the electrochemical performances in the current collector according to the characteristics of the cathode material, we used the most commonly attested LiCoO<sub>2</sub> as cathode active material.

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**Table 1**  
Concentrations in the various basic solutions.

Solution	NaOH	Na <sub>2</sub> CO <sub>3</sub>	C <sub>6</sub> H <sub>11</sub> NaO <sub>7</sub>	NaNO <sub>3</sub>
Solution 1	50 g/L	5 g/L	0.5 g/L	-
Solution 2	10 g/L	5 g/L	0.5 g/L	-
Solution 3	50 g/L	-	0.5 g/L	10 g/L
Solution 4	10 g/L	-	0.5 g/L	10 g/L

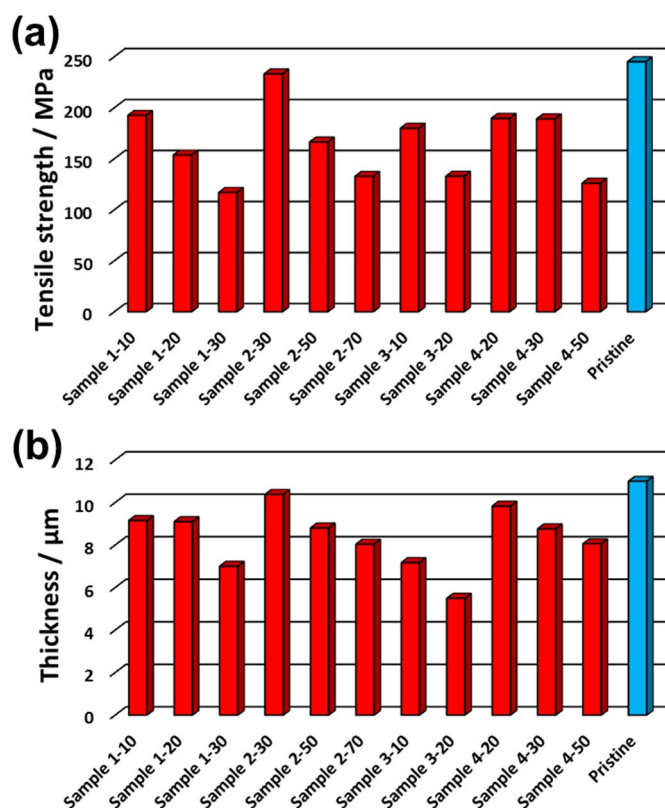
## 2. Experimental

AA1100 alloy Al foils (11  $\mu\text{m}$  thickness, DONG-IL Aluminum Corp.) manufactured by Corona treatment to remove the remaining grease and oil were used in this work. The clean Al foils with a size of 15 cm  $\times$  6 cm were immersed in two type solutions with different chemical etching rates. One solution contained sodium hydroxide (NaOH, > 98%, Alfa), sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>, > 98%, Alfa), and sodium gluconate as a chelating agent (C<sub>6</sub>H<sub>11</sub>NaO<sub>7</sub>, > 97%, Alfa). The other one contained NaOH, sodium nitrate (NaNO<sub>3</sub>, > 98%, Alfa), and sodium gluconate. Table 1 presents the various concentrations used in these solutions. The etching temperature was set at 60  $^{\circ}\text{C}$ , and the etching time was 10–70 s. The obtained samples were named by the solution label (1–4) and etching time: 1–10, 1–20, 1–30, 2–30, 2–50, 2–70, 3–10, 3–20, 4–20, 4–30, and 4–50. The etched Al foils were rinsed with deionized water and dried in an oven for several hours prior to characterization. The etched Al foils were prepared three specimens for each sample and analyzed. All Al samples for tensile strength measurements were prepared in sizes of 10 cm  $\times$  1.27 cm and tested on a universal testing machine (UTM, Shimadzu AG-X), according to the standard procedure described in ISO 6892. The foil thickness was measured by a Dektak 150 alpha step surface profiler. The morphology and microstructure were examined by scanning electron microscopy (SEM, Tescan Mira LM). The water contact angles were measured using a Phoenix 300 apparatus, and the values were averages over five measurements at different parts of the surface. The surface roughness was observed by atomic force microscopy (AFM, Shimadzu SPM-9700) in dynamic mode.

The cathodes were prepared with active material (LiCoO<sub>2</sub>), carbon black (super P), and polyvinylidene fluoride (PVDF) binder mixed in *N*-methylpyrrolidone (NMP) at a weight ratio of 8:1:1. The mixture was coated on the crater-like architectural Al foils, and drying at 120  $^{\circ}\text{C}$  for 2 h under vacuum. Coin-type battery-test cells (CR2032) were assembled in an argon-filled glove box, using polypropylene separator, Li metal anode, and 1 M LiPF<sub>6</sub> in ethylene carbonate (EC)/ethyl-methyl carbonate (EMC) (1:2 v/v) as the electrolyte. The charge–discharge experiments were performed galvanostatically at a constant current density of 30 mA g<sup>-1</sup> (with regard to the active material) in the voltage range of 3.5–4.5 V vs. Li<sup>+</sup>/Li. Electrochemical impedance spectroscopy (EIS) was carried out with a ZIVE SP2 instrument by applying a 10-mV amplitude signal in the frequency range from 10 kHz to 0.01 Hz. The impedance response was measured after the 1st and 20th cycles, and the data were fitted with the ZMAN software.

## 3. Results and discussion

During the manufacturing process, the electrodes are generally coated in roll form under an appropriate tension. Therefore, sufficient tensile strength is a basic physical requirement for current collectors. Fig. 1(a) shows the tensile strength of Al foils after chemical etching. After immersion in solution 1 for 10 s, the Al foil exhibited a tensile strength of about 193 MPa, which was lower than that of the pristine foil (245 MPa). Prolonging the etching time to 30 s further lowered the tensile strength to  $\sim$ 117 MPa. The strong alkalinity of solutions 1 and 3 had caused drastic surface etching and therefore lowered the tensile strength. In the cases of the other two solutions (2 and 4), there was also



**Fig. 1.** (a) Tensile strength and (b) thickness of pristine Al foil and chemically etched Al foil (i.e., crater-like architectural Al foil) samples.

a similar gradual decline in the tensile strength as the etching time was increased, as Al atoms broke away from the surface. Despite the lowered tensile strengths that negatively affects the electrode coating process, however, reasonable values above 190 MPa were still observed in some samples, such as 1–10, 2–30, 4–20, and 4–30. Next, we measured the thickness of the etched Al foils (Fig. 1(b)), all of which were < 11  $\mu\text{m}$  thick. Those with sufficient tensile strength, namely 1–10, 2–30, 4–20, and 4–30 were 9.2, 10.4, 9.8, and 8.8  $\mu\text{m}$  in thickness, respectively. These values are all below that of the pristine sample (11  $\mu\text{m}$ ).

Table 2 shows the water contact angle for the Al foils. The pristine Al surface exhibited a water contact angle of 71 $^{\circ}$ , which is greater than the values for the etched planar samples (65.5 $^{\circ}$ –40.5 $^{\circ}$ ). The Al surface became hydrophilic after the alkaline treatment. After treatment in solution 1 for 30 s, the contact angle was rapidly reduced to 49.8 $^{\circ}$  due to the increased surface roughness. This tendency was also observed in the strongly basic solution 3. The contact angles on the foils etched in solution 3 for 10 and 20 s were 60.2 $^{\circ}$  and 52.5 $^{\circ}$ , respectively. Treatment

**Table 2**  
Water contact angles on Al foils etched for various times.

Solution	Etching time (sec)	Contact angle (deg)
Solution 1	10	61.5
Solution 1	20	53.9
Solution 1	30	49.8
Solution 2	30	65.5
Solution 2	50	58.3
Solution 2	70	40.5
Solution 3	10	60.2
Solution 3	20	52.5
Solution 4	20	50.3
Solution 4	30	47.3
Solution 4	50	45.3
Pristine aluminum	-	71

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