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High Performance of Nano-sized $LiFePO_4$ Positive Electrode Using Etched Al Current Collector

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Abstract : The electrodes comprising nano-sized $LiFePO_4$, carbon black and binder are prepared with two different Al current collectors. One is the generally used normal Al foil and the other is the chemically etched Al foil. Surface characteristics of each Al foil and electrochemical performance of the cathodes using each foil are investigated. The electrode from the etched Al foil exhibits better physical and electrochemical properties as compared to those of the normal Al foil because the etched Al foil has rough surface with sub-micron pores which improve the adhesion between the electrode materials and the substrate. The electrode on the etched Al foil has such a strong peel strength that the impedance is smaller than that of normal one. Indeed the $LiFePO_4$ electrode from the etched Al foil exhibits a better rate capability and remains intact even after storage for 1 week at the charged state at the elevated temperature 60°C.

Keywords : Lithium ion batteries, $LiFePO_4$, Etched aluminum current collector, Peel strength, Area-specific impedance

1. Introduction

Olivine structured $LiFePO_4$ has been extensively studied due to its advantages of high thermal stability, low cost and low toxicity.[1-2] However, $LiFePO_4$-based electrodes show the poor high rate performances because of the low electronic conductivity ($\sim 10^{-8}$ S cm^{-1}) and low ionic diffusivity ($\sim 10^{-16}$ cm^2 s^{-1}).[3-4] In order to overcome these disadvantages, many researchers have successfully performed the reduction of particle size to shorten transport path, the coating of the particles with carbon to improve the conductivity and the doping with other elements to enhance the electrical conductivity.[5-10] As the primary particle size of $LiFePO_4$ has been reduced to nano-scale, it has caused the difficulties of electrode fabrication process, which are inhomogeneous mixing of the electrode slurry and peeling off the electrode materials from the current collector. To increase the peel strength between the electrode materials and current collector, K. Striebel and her coworkers[11] reported that the electrodes made by casting the electrode slurry onto a carbon-coated Al current collector, which is prepared with very thin coatings of carbon black and polymer binder from the same type of slurry, exhibit good electrochemical performance. According to their report, the very thin carbon layer on the current collector appears to greatly reduce the contact resistance between the electrode layer and current collector. But this method must be added one step, coating carbon on the Al current collector, in the electrode fabrication process. M. Yao *et al.*[12] proposed a new methodology using a three-dimensional porous current collector made from nickel-chromium alloy. The cell using the three-dimensional current collector exhibited a superior rate capability and the size reduction of a semicircle for the charge-transfer resistance as compared to the conventional-type cell fabricated with a normal Al current collector.

In this work, we propose the etched Al foil as a new current collector to improve the electrochemical performances of the nano-sized $LiFePO_4$ electrode. The use of

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etched Al current collector is a simple and convenient method compared to the carbon-coated Al current collector or three-dimensional porous current collector. To investigate the properties of the two current collectors, the images of surface and the cross section were obtained to compare the two current collectors and the surface was analyzed using X-ray photoelectron spectroscopy (XPS). After the electrode fabrication with the two current collectors, we measured the peel strength between the electrode material and the current collector. Electrochemical performances of the resulting $LiFePO_4$ electrodes were compared in terms of cell resistances and rate capability.

2. Experimental

The two current collectors, the normal Al current collector (Sam-A Aluminum Co., Korea, 20 μm, more than 99.4 % purity) and the etched Al current collector (JCC Co., Korea, 20 μm, more than 99.7% purity, made by chemical etching), were crosscut using an argon ion beam (Cross Section Polisher (CP) SM-09010, JEOL) and their field-emission scanning electron microscope (FE-SEM) images were obtained by using a JEOL JSM-7000F.

To investigate the chemical compositions of the two current collectors, the XPS data were collected in an ultra-high vacuum multipurpose surface analysis system (Sigma probe, Thermo, U.K.) operating at a base pressure of $< 10^{-10}$ mbar. The photoelectrons were excited by an Al Kα (1486.6 eV) anode operating at a 100 W constant power (15 kV and 10 mA), and the spot size of X-ray was 400 μm. During data acquisition, the constant-analyzer-energy mode was used at a pass energy of 30 eV and a step of 0.1 eV. The binding energy was calibrated by the C 1 s peak at 285 eV obtained from hydrocarbon contamination.

The slurries were prepared with a carbon-coated nano-sized $LiFePO_4$ power (EIG2, Korea, primary particle size = 100~200 nm), Denka Black (Denka, average particle size = 35 nm) as the conductive additive, and polyvinylidenefluoride (PVdF, Kureha KF-1100) as the binder (90 : 3 : 7 wt. ratio). The PVdF and *N*-methylpyrrolidinone (NMP, Aldrich) as the solvent were mixed for 30 min by homogenizer (2000 rpm), into which the $LiFePO_4$ and Denka Black powders pre-mixed in an agitated mortar were added, and mixed for additional 2 h at the same condition. The prepared slurries were coated onto the two current collectors by using an automatic doctor blade. The electrodes were dried at 120°C in convection oven for 1 h to evaporate the solvent and pressed through a roll press. Before cell assembly, the electrodes were further dried in a vacuum oven at 120°C for 12 h.

To investigate of the interface between the electrode materials and the current collector, the cross sectional images of the composite electrodes were obtained by the same method above.

For the purpose of measuring the peel strength between the electrode materials and the current collector, the 180° peel test (MultiTest-i, Mecmesin Co., E.U.) was used. The peel strength was tested with a peel test using an ISO 8510 1 standard. The electrodes uniformly attached to a slice glass plate with a width of 25 mm and a length of 50 mm. It was measured the requiring force to peel off the electrode material from the current collector.

Coin-type cells were assembled with the composite electrode, Li foil as a counter electrode, and polypropylene film as a separator. The used electrolyte was 1.0 M $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC) and ethylmethyl carbonate (EMC) (1 : 1 vol. ratio), where 1.0 wt.% of vinylene carbonate (VC) was added. The cells were fabricated in a dry room (dew point = −50°C). The cells were charged at a constant current at 0.2 *C* to 4.0 V (*vs*. Li/Li^+) and discharged at 0.2, 1, 2, 3, 5 and 10 *C* to 2.4 V (*vs*. Li/Li^+), respectively. Electrochemical measurements were made at room temperature using a Wonatech (Model WBC-3000).

In order to measure the area-specific impedance (ASI) as a function of depth of discharge, the hybrid pulse power characterization (HPPC) test was performed, in which the 10-second discharge-pulse and the 10-second charge-pulse resistance at each 10% depth-of-discharge (DOD) increment were obtained.[13] The test was made up of single repetitions, separated by 10% DOD constant current discharge segments, each followed by 1 h rest period to allow the cell to return to an electrochemical and thermal equilibrium condition before applying the test profile. The test began with a fully charged state after 1 h rest and terminated after completing the final profile at 90% DOD.

To compare the degradation of the electrodes at the severe state, the storage test was accomplished. The cells charged to 4.0 V (*vs*. Li/Li^+) were stored for a week at 60°C oven. Before and after the storage, AC impedance of the cells was measured. AC impedance measurement was made at the fully charged state in the frequency range of 0.005 Hz-100 kHz with an AC amplitude of

10 mV. And then, the composite electrodes from dismantled the cells were compared to the state of the electrode degradation.

3. Results and Discussion

Fig. 1 shows the surface and cross sectional images of the normal Al current collector and the etched Al current collector. The thickness of the two current collectors is about 20 μm. The comparison for Fig. 1(a) and Fig. 1(b) reveals that the normal Al current collector has a clean and smooth surface but the etched Al current collector has the pores evenly throughout the surface. As seen from the cross sectional images, the normal Al current collector is densely packed without empty space (Fig. 1(c)). However, the etched Al current collector is etched to a thickness of about 4~5 μm up and down (Fig. 1(d)). It is likely that the large surface area due to the pore structures can improve the current collecting ability of the substrate.

Fig. 2 shows the XPS spectra for the two current collectors. The Al 2p photoelectron spectra show a presence of Al_2O_3 on the Al current collector surface. From these spectra, it can be seen that the surface of the two current collectors is covered with Al_2O_3. The Al_2O_3 layer on the etched Al current collector surface is thickly distributed compared to the normal Al current collector.

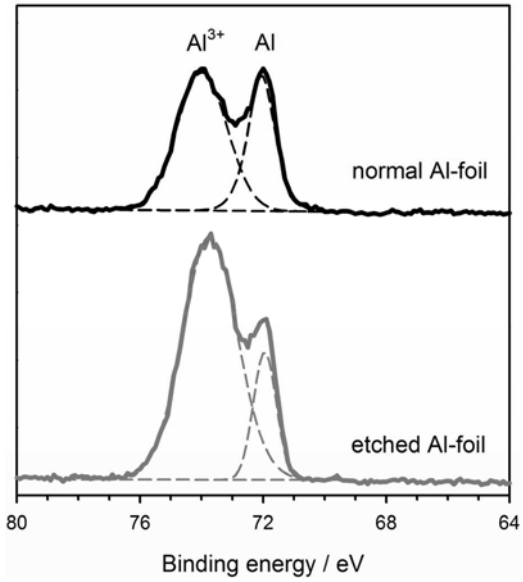

Fig. 2. XPS spectra of Al 2p for the normal Al-foil and the etched Al-foil. The fitted curves, by using the defined model peak shapes (30% Gaussian/Lorentzian algorithm), are indicated by the dotted lines.

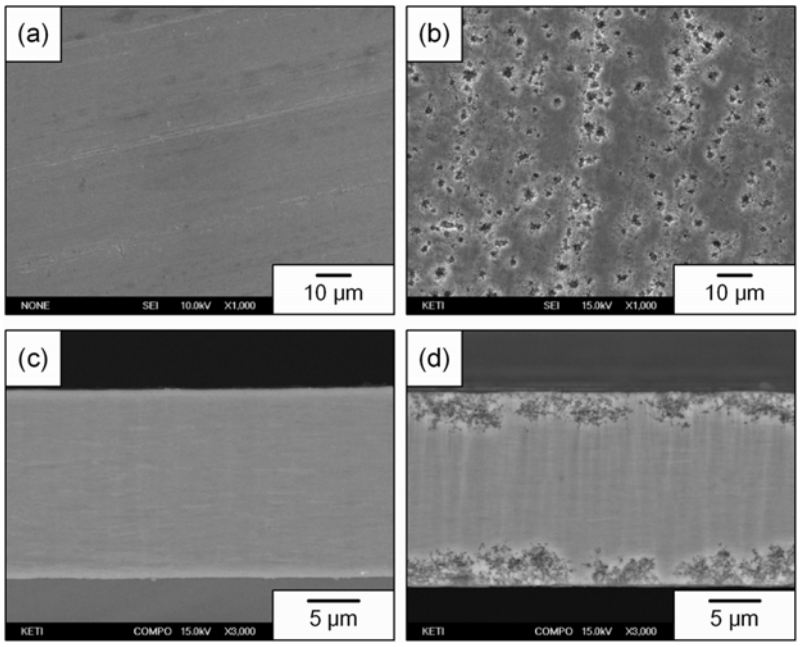

Fig. 1. FE-SEM images of the current collectors: the upper side (a) normal Al-foil, and (b) etched Al-foil; cross section (c) normal Al-foil, and (d) etched Al-foil.

As the etched Al current collector has larger surface area, the more Al_2O_3 exist on the surface. It was also reported that Al_2O_3 layer works to strengthen the connection of the electrode materials with the substrate surface.[14] The passive aluminum oxide layer on the current collector surface provides more suitable sites for the deposition of the electrode materials.

Fig. 3 shows the cross sectional FE-SEM images of the electrode layers after roll-pressing. In the electrode from the normal Al current collector, it is identified the narrow gap between the electrode materials and the current collector (Fig. 3(a)). On the other hand, the electrode from the etched Al current collector is hard to distinguish interface since the electrode materials can be filled uniformly in the inner pores of the etched Al current collector. It is thus very likely that the use of etched Al current collector can improve the adhesion properties of the electrode. To ascertain this, the peel strength between the electrode materials and the current collector was measured by the 180° peel test. As shown in Fig. 4, the peel strength of the electrode using the etched Al current collector is more than three times greater than using the normal Al current collector. The peel strength is more important than almost any other electrode property, because the electrochemical performances are not achievable if the peel strength is insufficient to endure repeated charge-discharge cycling.[15]

The rate capability of two electrodes is compared in Fig. 5. As the discharge *C*-rate increases, a larger capacity loss is observed with the electrode prepared on the normal Al current collector. In this electrode, only 30% of the capacity at 0.2 *C*-rate is retained at 10 *C*-rate, which is lower than that observed with the electrode prepared by the etched Al current collector (75%).

The reason why the electrode using the etched Al current collector shows a better rate capability can be accounted for by comparing the evolution of cell resistances. The cell resistances for discharging and charging

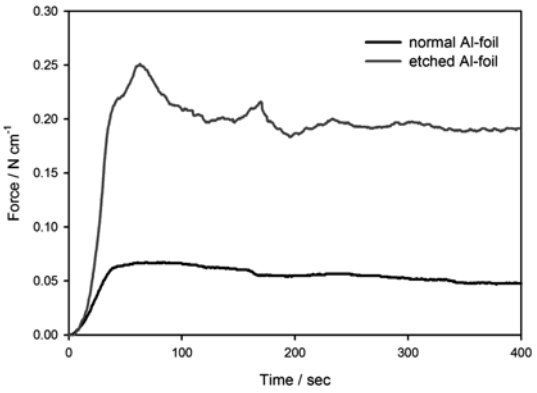

Fig. 4. Peel strength between the electrode materials and the current collector measured by the 180° peel test.

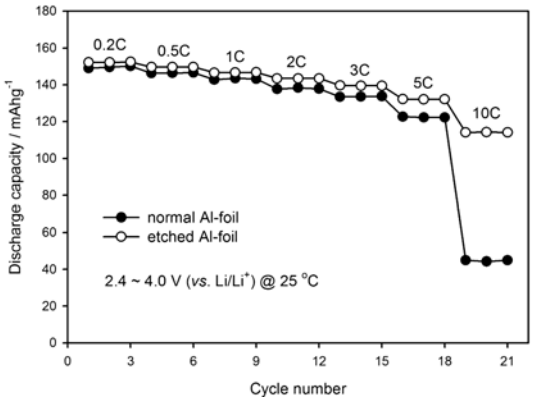

Fig. 5. Rate capability observed with Li/$LiFePO_4$ cells using the normal Al-foil and the etched Al-foil at 25°C. The *C*-rate is indicated in the inset.

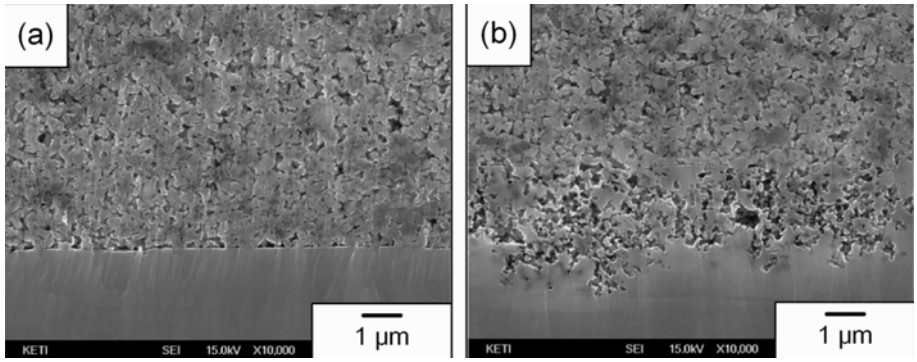

Fig. 3. Cross-sectional SEM images of the composite electrodes: (a) normal Al-foil and (b) etched Al-foil.

were monitored as a function of depth of discharge (DOD) (Fig. 6). The area-specific impedances (ASI) were determined using a ΔV/I calculation for each iteration employing the HPPC test protocol. Two features should be noted in Fig. 6. First, the discharge resistance (lithiation) becomes larger at the end of discharge due to the lacks of the available Li^+ storage sites. The second observation in Fig. 6 is that both the discharge and charge resistance are smaller in the electrode fabricated by using the etched Al current collector. Therefore, since the electrode from the etched Al current collector has larger adhesion strength between the electrode material and the substrate, the cell impedance is smaller.

To investigate the electrode degradation that may be caused by a high-temperature exposure, AC impedance spectra were taken before and after the storage at the charged state at 60°C for one week. The evolution of cell resistances is compared for two electrodes in Fig. 7. The cell resistances before storage are similar, whereas

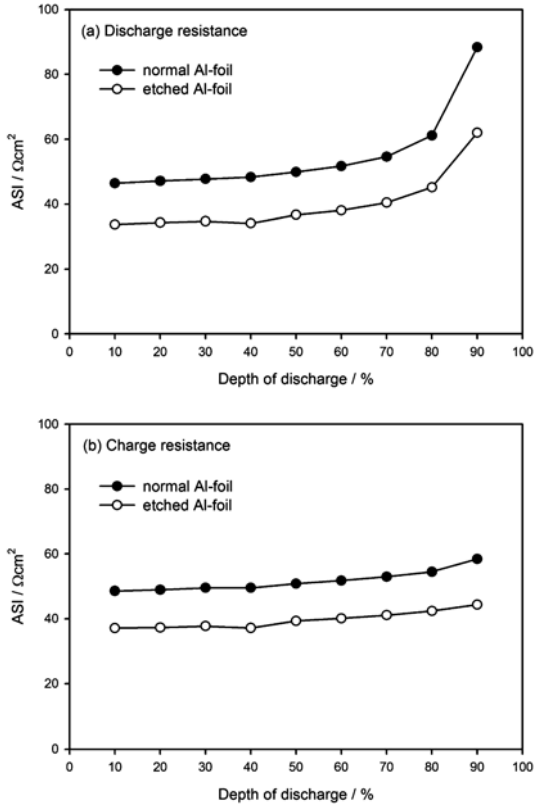

Fig. 6. Area-specific impedances (ASI) for discharging and charging that were traced as a function of depth of discharge (DOD).

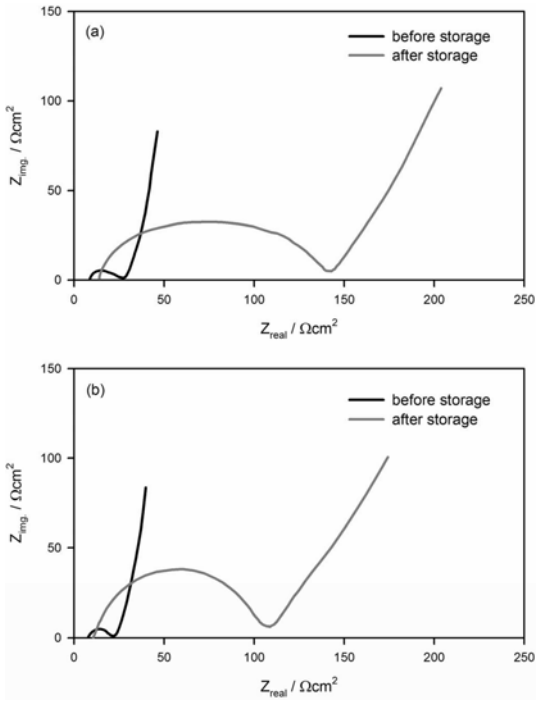

Fig. 7. AC impedances before and after storage for 1 week at 60°C that were obtained at the fully charged state.

after storage are larger differences. The electrode from the normal Al current collector shows a larger increase in the cell resistances as compared to that from the etched Al current collector. This difference results from the peel strength between the electrode materials and the current collectors. After storage, when the two cells are dismantled and investigated the states of the electrodes, the electrode from the normal Al current collector is peeled off the electrode material from the substrate (Fig. 8(a)). However, the electrode from the etched Al current collector remains intact (Fig. 8(b)).

Owing to these favorable features such as increasing the peel strength, both the contact resistance between the electrode material and the current collector, and the charge transfer resistance for lithiation/de-lithiation are smaller in the electrode made with the etched Al current collector. The smaller internal resistance leads to a better rate capability (Fig. 5).

4. Conclusions

A comparative study on the electrochemical performances was made for two $LiFePO_4$ positive electrodes

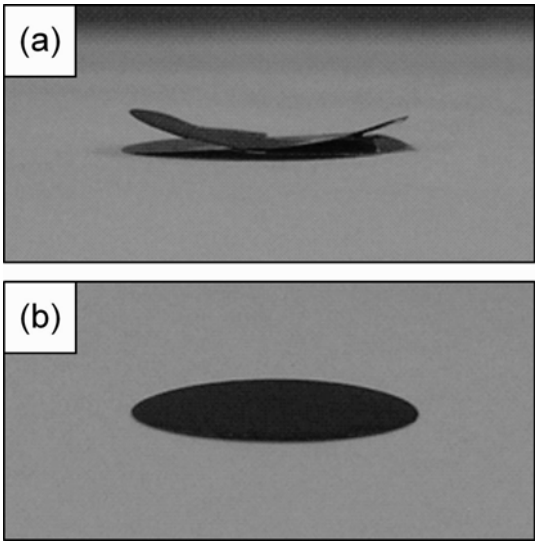

Fig. 8. The images of electrodes from dismantled cells after storage for 1 week at 60°C.

using normal and etched Al foils. The electrode performance was correlated with the contact area and adhesion stability between electrode material and current collector. The following points of value are summarized.

i) While the normal Al foil has a smooth surface, an etched Al foil has a rough surface with sub-micron pores. As these pores are filled by nano-sized $LiFePO_4$ positive electrode materials during the electrode fabrication process, the contact area between active materials and current collector increases and the more electronic pathways are provided.

ii) Excellent electrochemical performance is shown in the electrode using the etched Al current collector. Better rate capability and lower impedance are achieved by increase of electronic pathways. Cell degradation during the high temperature storage is also restricted by adhesion stability of the etched foil.

iii) The etched Al foil shows better adhesion strength than that of normal one. Moreover, the contact between electrode materials and etched Al foil is maintained after storage during one week at elevated temperature while the electrode is detached from the normal Al foil.

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References

1. A. K. Padhi, K. S. Nanjundaswamy, and J. B. Goodenough, 'Phospho-olivines as positive-electrode materials for rechargeable lithium batteries' *J. Electrochem. Soc.*, **144**, 1188 (1997).
2. A. Yamaha, S. C. Chung, and K. Hinokuma, 'Optimized $LiFePO_4$ for lithium battery cathodes' *J. Electrochem. Soc.*, **148**, A224, (2001).
3. V. Srinivasan, and J. Newman, 'Discharge model for the lithium iron-phosphate electrode' *J. Electrochem. Soc.*, **151**, A1517 (2004).
4. S. -Y. Chung, J. T. Bloking, and Y. -M. Chiang, 'Electronically conductive phospho-olivines as lithium storage electrodes' *Nat. Mat.*, **1**, 123 (2002).
5. H. Huang, S. -C. Yin, and L. F. Nazar, 'Approaching theoretical capacity of $LiFePO_4$ at room temperature at high rates' *Electrochem. Solid-State Lett.*, **4**, A170 (2001).
6. D. Choi, and P. N. Kumta, 'Surfactant based sol-gel approach to nanostructured $LiFePO_4$ for high rate Li-ion batteries' *J. Power Sources*, **163**, 1064 (2007).
7. N. Ravet, Y. Chouinard, J. F. Magnan, S. Besner, M. Gauthier, and M. Armand, 'Electroactivity of natural and synthetic triphylite' *J. Power Sources*, **97-98**, 503 (2001).
8. C. R. Sides, F. Croce, V. Y. Young, C. R. Martin, and B. Scrosati, 'A high-rate, nanocomposite $LiFePO_4$/Carbon cathode' *Electrochem. Solid-State Lett.*, **8**, A484 (2005).
9. Y. Lin, M. X. Gao, D. Zhu, Y. F. Liu, and H. G. Pan, 'Effects of carbon coating and iron phosphides on the electrochemical properties of $LiFePO_4$/C' *J. Power Sources*, **184**, 444 (2008).
10. P. S. Herle, B. Ellis, N. Coombs, and L. F. Nazar, 'Nano-network electronic conduction in iron and nickel olivine phosphates' *Nat. Mat.*, **3**, 147 (2004).
11. K. Striebel, J. Shim, A. Sierra, H. Yang, X. Song, R. Kostecki, and K. McCarthy, 'The development of low cost $LiFePO_4$-based high power lithium-ion batteries' *J. Power Sources*, **146**, 33 (2005).
12. M. Yao, K. Okuno, T. Iwaki, M. Kato, S. Tanase, K. Emura, and T. Sakai, '$LiFePO_4$-based electrode using micro-porous current collector for high power lithium ion battery' *J. Power Sources*, **173**, 545 (2007).
13. Idaho National Laboratory, "Battery test manual for plug-in hybrid electric vehicles", INL/EXT-07-12536, pp. 3-42, (2008).
14. A. Eftekhari, 'Aluminum oxide as a multi-function agent for improving battery performance of $LiMn_2O_4$ cathode' *Solid State Ionics*, **167**, 237 (2004).
15. J. -H. Lee, U. Paik, V. A. Hackley, and Y. -M. Choi, 'Effect of poly(acrylic acid) on adhesion strength and electrochemical performance of natural graphite negative electrode for lithium-ion batteries' *J. Power Sources*, **161**, 612 (2006).