



Manipulation of adipic acid application on the electrochemical properties of LiFePO₄ at high rate performance

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ABSTRACT

High performance nanocrystalline LiFePO₄ was successfully synthesized utilizing a solid-state method with adipic acid as the carbon source. Different molar ratios of adipic acid to total metal ions were analyzed, which included the mol ratios 0, 0.05, 0.1, and 0.2. Among the different concentrations tests, 0.1 mol adipic acid-treated LiFePO₄ exhibited superior performance in terms of capacity profile and a stable discharge behavior of ~150 mAh/g at room temperature. The thickness of the carbon coating layer was confirmed at approximately 5 nm by transmission electron microscopy. Rate capability studies were also performed from 1.0 to 37 C for 0.1 mol adipic acid-treated LiFePO₄. These studies clearly showed excellent capacity retention over 73 mAh/g at 37 C rate.

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1. Introduction

The application of lithium iron phosphate (LiFePO₄) as a potential cathode material for rechargeable lithium batteries were first demonstrated by Padhi et al. [1] in 1997. Since then, LiFePO₄ has offered several unique benefits when compared to conventional cathode materials such as LiCoO₂, LiNiO₂ and LiMn₂O₄. LiFePO₄ exhibits a flat discharge profile, good thermal stability, high theoretical capacity (170 mAh/g) and environmentally friendly properties [2]. However, a significant problem with the use of this material lies in its conductivity. This is due to the one-dimensional diffusion of Li⁺ ions along the *b* axis formed by edge-shared LiO₆ octahedra, compounded by poor electronic and ionic conductivity from the LiFePO₄–FePO₄ interface [3]. This leads to poor rate performance of the cell. Two methods have been employed to circumvent the poor conductivity issue. The first is to reduce the grain size of the cathode particles, which would shorten the diffusion path length for both electrons and Li⁺ ions. The second is the use of surface-modified LiFePO₄ with a conductive matrix made of carbon [4–6], copper [7,8] and silver [9], or doping with some guest species [10]. Of these methods, surface-modified LiFePO₄ with carbon has proved to be an excellent alternative in the search for improved

LiFePO₄ cathodes [11,12]. Numerous carbon source materials have been explored for coating LiFePO₄ and noteworthy among them are the carboxylic acids reported by Fey et al. [13].

Several methods have been proposed for the synthesis of olivine LiFePO₄, including microwave processing, solid-state, sol–gel, hydrothermal, spray pyrolysis, precipitation, mechano-chemical, and emulsion drying [14–20]. Of the synthetic methods, solid-state and solution-based routes are primarily appealing for large scale production [20]. For the sol–gel method, synthesis is carried out in two steps which are precursor preparation and powder crystallization. In addition, a final heating step is often carried out at high temperatures under an inert or reductive atmosphere to prevent iron oxidation [18]. The precursor is prepared in the liquid phase, by the subsequent evaporation of the solvent. During this process, care must be taken to prevent Fe²⁺ ions from being oxidized upon exposure to air. Therefore, the solution phase is less effective, although it offers uniform sized nanoparticles with a homogeneous coating. When compared with solution phase methods, the solid-state method provides an easier and more effective approach for mass production [14–20].

We recently reported on the synthesis of LiFePO₄ using adipic acid as a chelating agent by using the sol–gel method [21], and provided conclusive evidence of the enhanced and stable discharge profile at a high rate capability. Previously, we also reported on a new type of LiFePO₄ material using adipic acid as a carbon source that had been successfully synthesized by a solid-state method and

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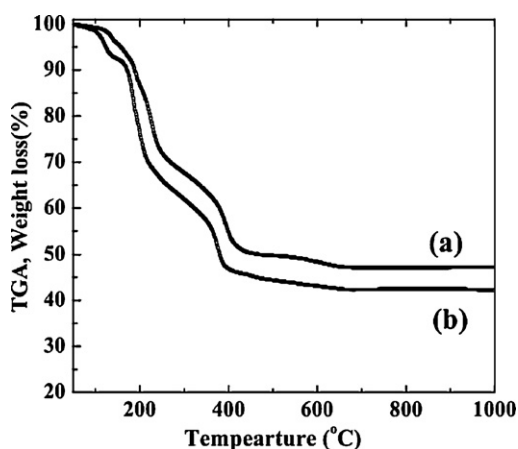


Fig. 1. Thermogravimetric and differential thermal analysis (TG-DTA) starting materials used for the synthesis of LiFePO_4 (a) Li_2CO_3 , $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, and $(\text{NH}_4)_2\text{HPO}_4$ and (b) Li_2CO_3 , $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{HPO}_4$, and $\text{C}_6\text{H}_{10}\text{O}_4$.

presented superior cycle performance under harsh conditions in communication [22]. In this study, we present the synthetic process and electrochemical properties of the LiFePO_4 material in more detail. Our results show the excellent battery performance results obtained to date of LiFePO_4 using adipic acid as a carbon source synthesized by a solid-state approach.

2. Experimental

The LiFePO_4 material was synthesized from Li_2CO_3 , $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{HPO}_4$, and $\text{C}_6\text{H}_{10}\text{O}_4$ (Sigma–Aldrich, USA) using a conventional solid-state method. Stoichiometric ratios of the Li:Fe:P source materials at various molar ratios of adipic acid to total metal ions (0, 0.05, 0.1, and 0.2) were used for the synthesis. The starting materials were finely ground in a mortar and precalcined at 400°C for 3 h to enable carbonate and oxalate decomposition. The product was finely ground again in a mortar and fired at 670°C for 5 h under an Ar atmosphere (99.9%) to achieve the resultant nanocrystalline LiFePO_4 . The same conditions and procedure were conducted for different molar ratios of adipic acid.

Thermal studies were carried out by means of thermogravimetric-differential thermal analysis (TG-DTA) using a thermal analyzer system (STA 1640, Stanton Redcroft Inc., UK) with a thin Pt plate used as the sample holder. The powder was heated at $5^\circ\text{C}/\text{min}$ and cooled at $10^\circ\text{C}/\text{min}$. Structural analysis was performed by powder X-ray diffraction (XRD, Rint 1000, Rigaku, Japan) using $\text{CuK}\alpha$ radiation. The carbon content of the synthesized LiFePO_4 particles was determined using an elemental analyzer (CHN Flash EA series, CE Instruments, Italy). The surface morphology of the resultant compound was observed using a field emission scanning electron microscope (FE-SEM, S-4700, Hitachi, Japan). Particle size distribution was carried out through a dynamic light scattering system (DLS-7000[AL], Otsuka electronics, Japan). The internal structure of the samples was observed by transmission electronic microscopy (TEM, TECNAI, Philips, Netherlands). Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were performed using a Bio-Logic electrochemical work station (SP-150, Biologic, France) with a three electrode cell configuration. In the three electrode configuration, metallic lithium served as the counter and reference electrodes. The composite cathode was fabricated with exactly 20 mg of active material, 3 mg of Ketjen black, and 3 mg of conductive binder (2 mg of Teflonized acetylene black (TAB) and 1 mg of graphite). It was pressed on a 200 mm^2 stainless steel mesh, serving as the current collector under a pressure of $300\text{ kg}/\text{cm}^2$ and dried at 130°C for 5 h. The cell was comprised of a cathode and a metallic lithium anode separated by a porous polypropylene film (Celgard 3401, USA). A 1 M LiPF_6 in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1, v/v, Techno Semichem Co., Ltd., Korea) mixture was used as the electrolyte. The charge/discharge current density was 0.1 C (1 C refers to a capacity of 170 mA g^{-1} in one hour) with a cut-off voltage of 2.8–4.0 V and various current densities (1–37 C) at room temperature.

3. Results and discussion

Thermogravimetric analysis (TGA) was used to ascertain the temperature conditions for the synthesis of the nanocrystalline LiFePO_4 material. Fig. 1 shows the TG trace performed on the LiFePO_4 precursor both with and without adipic acid (referred to as AA from here on), and is clearly separated by three main stages.

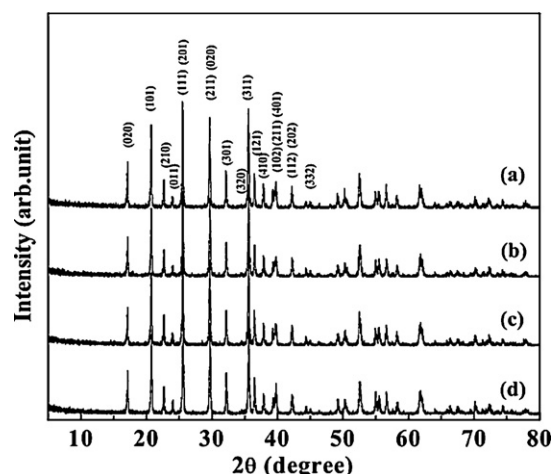


Fig. 2. X-ray diffraction patterns of LiFePO_4 obtained by different molar ratios of adipic acid to total metal ions: (a) without adipic acid; (b) 0.05 mol adipic acid; (c) 0.1 mol adipic acid and (d) 0.2 mol adipic acid.

The first stage comprising multiple endothermic events starts at $\sim 100^\circ\text{C}$ and ends at $\sim 300^\circ\text{C}$ for both cases. The initial weight losses observed are attributed to the dehydration and decomposition of acetate groups from the starting material, as well as to the melting of AA. The second melting event starts at $300\text{--}450^\circ\text{C}$ and can be recognized by decomposition of the remaining reactants with the carbonization of AA, which is the beginning of the crystallization of LiFePO_4 . The final stage containing the slow and gradual weight loss above $450\text{--}650^\circ\text{C}$ corresponds to decomposition of the remaining reactants and oxidation of carbon to produce either carbon monoxide or carbon dioxide [23–25]. The major difference between the two materials is that the weight loss of the LiFePO_4 precursor with AA is larger than that of the precursor without AA, which resulted from the acceleration of the chemical reaction owing to the decomposition of adipic acid used as the carbon source. The thermal analysis suggested that the precursor was heat-treated at temperatures above 650°C for the synthesis of a pure LiFePO_4 phase with high crystallinity.

The X-ray diffraction pattern of the LiFePO_4 compound prepared by the solid-state reaction method with different molar contents of AA is presented in Fig. 2. The occurrence of broad and well-defined Bragg peaks demonstrated the formation of size controlled and highly crystallized LiFePO_4 grains. The Miller indices (hkl) of these peaks were indexed as per the JCPDS Card No. 40-1499, corroborating the existence of an orthorhombic structure with a $Pnma$ space group. The lattice parameter values are presented in Table 1. The lattice parameters of the parent LiFePO_4 were consistent with those reported in the literature [1,14]. The carbon-coated LiFePO_4 materials showed a slightly lower lattice parameter value than the uncoated material due to the absence of impurity phases. Furthermore, the absence of a peak at $2\theta = 27$ and 41° indicated the phase purity of the synthesized material without impurities such as $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$, FeP, and Fe_2S [8,13,25,26]. The XRD pattern revealed that carbonization of AA not only provides the carbon coating, but also provides a reducing atmosphere that favors the formation of phase pure LiFePO_4 .

Surface morphology features of the particles were analyzed by scanning electron microscopy and each image is shown in Fig. 3. Smooth surfaces were observed for uncoated and 0.1 mol AA-coated LiFePO_4 , whereas flaky appearances were seen for 0.05 and 0.2 mol AA-coated LiFePO_4 materials. Uniform and smooth surface morphologies are a prerequisite for commercial cathode materials [27]. All the carbon-treated materials showed reduced particle sizes compared to uncoated LiFePO_4 , suggesting that formation of

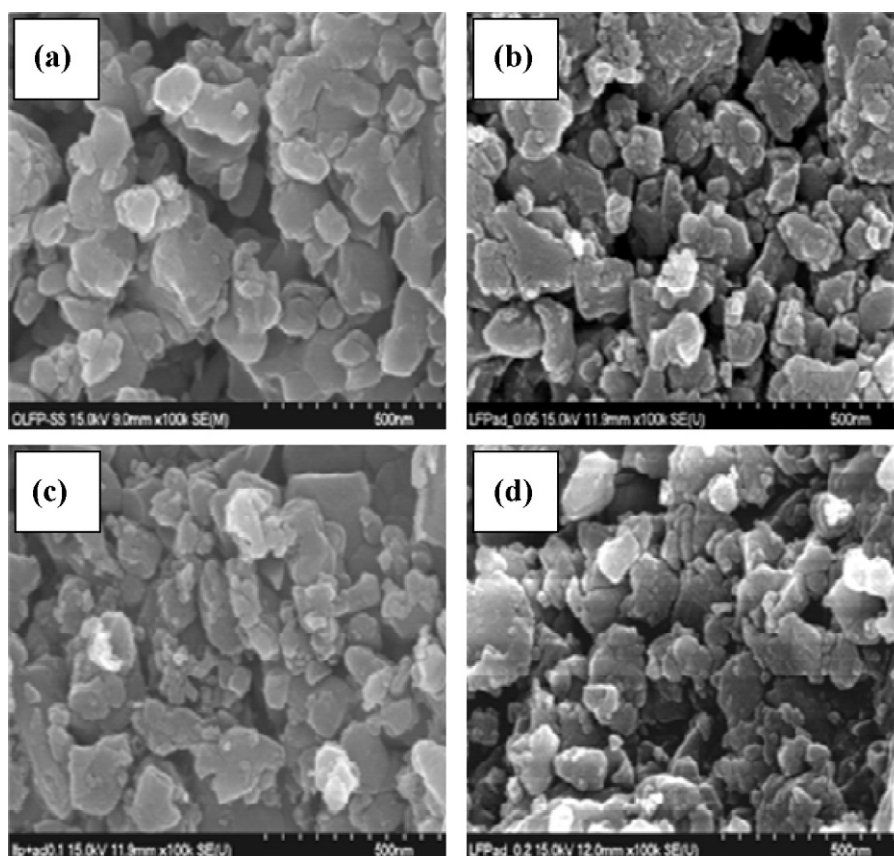


Fig. 3. SEM images of LiFePO_4 obtained by different molar ratios to total metal ions: (a) without adipic acid; (b) 0.05 mol adipic acid; (c) 0.1 mol adipic acid and (d) 0.2 mol adipic acid.

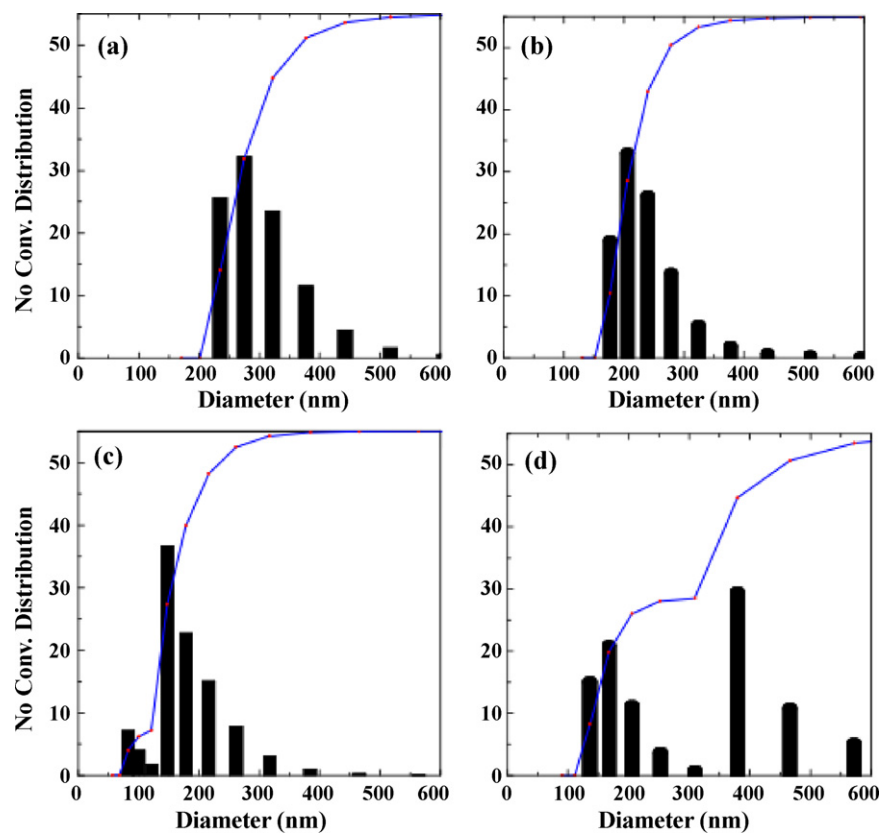


Fig. 4. Particle size distribution of LiFePO_4 obtained for different molar ratios to total metal ions by solid-state method: (a) without adipic acid; (b) 0.05 mol adipic acid; (c) 0.1 mol adipic acid and (d) 0.2 mol adipic acid.

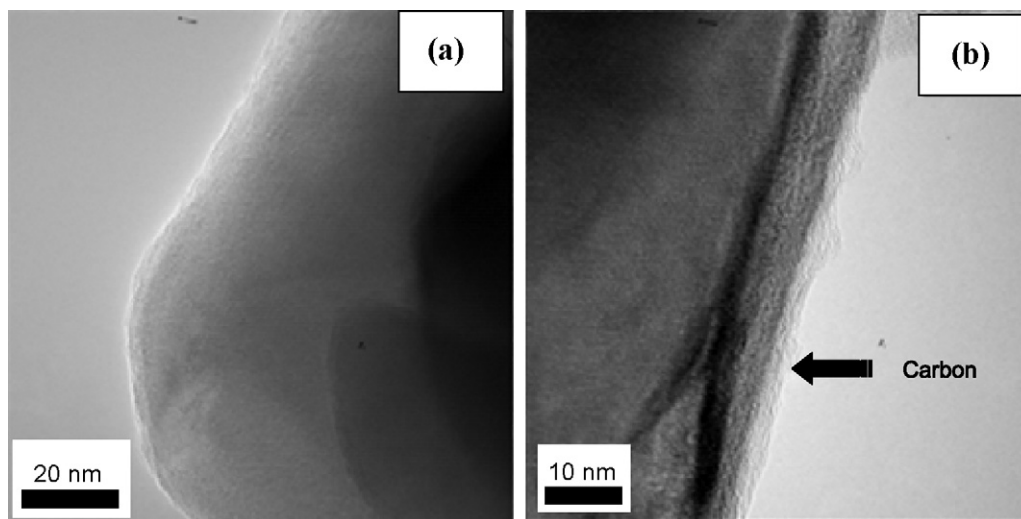


Fig. 5. TEM images of LiFePO₄ for (a) without adipic acid and (b) 0.1 mol adipic acid.

a carbon layer hinders particle growth at high temperatures [28]. Dynamic light scattering experiments were performed to study the distribution of the synthesized particles by the solid-state method and this is graphically illustrated in Fig. 4. For the parent LiFePO₄, the majority of the particles lie between 200 and 400 nm. The size of the particles was drastically reduced after the introduction of the carbon coating, with the major proportion of the particles between 150–300 nm, 100–200 nm, and 150–400 nm for 0.05, 0.1, and 0.2 mol AA-treated LiFePO₄, respectively. This might be due to coated carbon preventing the growth of LiFePO₄ particles during synthesis. This result is in agreement with Konorova and Taniguchi's report [29] on the suppression of particle size during the synthesis process. In the case of 0.2 mol adipic acid-treated LiFePO₄ comprises two separate range of particle distribution ~150–250 nm and ~400 nm region. Appearance of ~400 nm region is due to the presence of few larger size particles (based on the particles distribution) along with smaller ones that could be the reason for the two separate regions in the particle size distribution. The 0.1 mol AA-treated LiFePO₄ has a smaller particles size compared to other AA coating concentrations and this may be reflected in the electrochemical performance of the cell via the improved Li⁺ ion diffusion kinetics and high surface area.

Furthermore, elemental analysis was also performed to gauge carbon content in LiFePO₄ by the solid-state method. As shown in Table 1, carbon contents of 0.26, 1.02, 0.92, and 0.54 wt.% were observed for 0, 0.05, 0.1, and 0.2 AA contents against the total metal ions present in LiFePO₄, respectively. Very small amounts of carbon present in the untreated LiFePO₄ may be due to decomposition of the starting materials, such as Li₂CO₃ and FeC₂O₄·2H₂O. At the higher concentration of 0.2 mol the carbon content was found to be lower, which may be attributed to the fact that the carbon was highly oxidized and could form CO and CO₂ at high temperatures [23]. It was expected that a carbon content of between 0.9 and 1.0% weight was good for the electrochemical performance of the cell. If the carbon content in the LiFePO₄ was higher or lower than 1.0% weight, this lead to

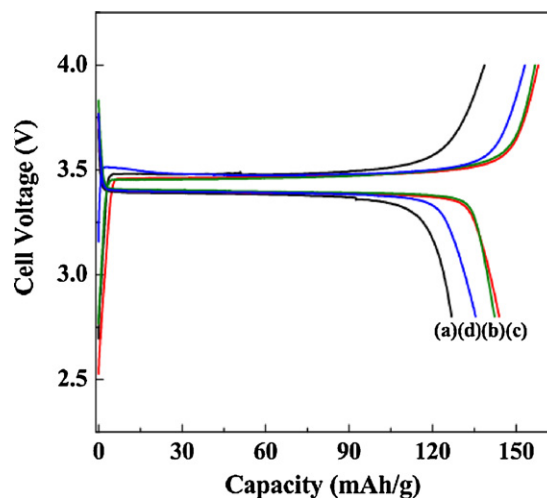


Fig. 6. The first charge/discharge curves of the Li/LiFePO₄ cell obtained for different molar ratios to total metal ions: (a) without adipic acid; (b) 0.05 mol adipic acid; (c) 0.1 mol adipic acid and (d) 0.2 mol adipic acid.

poor cell performance at a calcination temperature of 670 °C. This result is in agreement with Konorova and Taniguchi's study on carbon analysis [28].

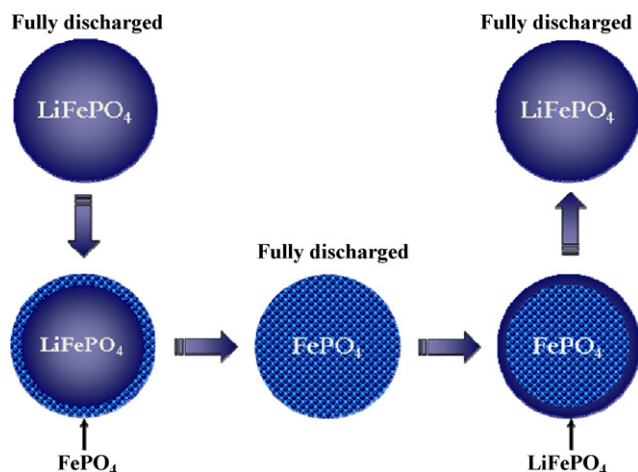
Fig. 5 shows transmission electron microscopy (TEM) images of pristine and 0.1 mol AA-treated LiFePO₄ particles. A clear difference was observed between the pristine and carbon-coated materials. From this, it is apparent that the 0.1 mol AA is well formed as the layer of carbon on the surface of the LiFePO₄ particles. The carbon is coated on the LiFePO₄ particles at a thickness of approximately 5 nm, suggesting that the carbon layer also plays a crucial role in particle growth of LiFePO₄ during the synthetic process [29].

The first charge/discharge curves of the Li/LiFePO₄ cells at 0.1 C with different levels of carbon treatment are presented in Fig. 6.

Table 1

Powder properties of LiFePO₄ materials obtained by different molar ratios of adipic acid to total metal ions.

Molar ratio of adipic acid	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α (°)	β (°)	γ (°)	<i>V</i> (Å) ³	Carbon content (wt.%)
0	10.347	6.019	4.699	90	90	90	2.923	0.26
0.05	10.332	6.010	4.663	90	90	90	2.916	1.02
0.1	10.339	6.011	4.663	90	90	90	2.919	0.92
0.2	10.329	6.009	4.638	90	90	90	2.913	0.54



Scheme 1. Dual phase nature of LiFePO₄.

The charge/discharge profiles of LiFePO₄ show long and flat voltage plateaus near the 3.4–3.5 V region, revealing the two-phase nature of the lithium extraction and insertion reaction between LiFePO₄ and FePO₄ [1,30]. The dual phase nature is schematically represented in Scheme 1. It is evident that 0.1 mol AA-treated LiFePO₄ exhibits the highest discharge capacity profile compared with the additional concentrations tested. The initial discharge capacity values of carbon-coated LiFePO₄ were 127, 142, 144, and 135 mAh/g for the 0, 0.05, 0.1, and 0.2 mol concentrations of AA, respectively. As shown in Fig. 7, the 0.1 mol AA-treated LiFePO₄ showed an increase in discharge capacity until the sixth cycle, a larger value than the 0.05 mol AA, even though it showed almost the same discharge capacity in the first cycle. Furthermore, a small voltage difference between charge and discharge plateaus of 0.1 and 0.05 mol AA-treated LiFePO₄ indicated improved kinetics compared to other concentrations. This was relevant after considering the low electrochemical diffusion rate of lithium ions in the solid-phase as well as its poor electronic conductivity [13,16].

Carbon-coated LiFePO₄ cells showed stable discharge behavior for observed cycles, whereas uncoated LiFePO₄ showed a continuous capacity fading due to sluggish kinetics and inherent conducting behavior. Of the carbon-coated materials, the 0.1 mol AA-treated LiFePO₄ delivered a superior performance with a discharge capacity of 150 mAh/g for 50 cycles. However, initial few

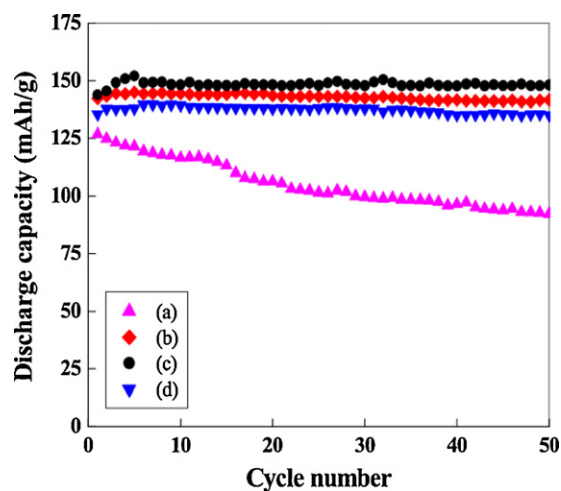


Fig. 7. Cycle performance of the Li/LiFePO₄ cells obtained by different molar ratios to total metal ions: (a) without adipic acid; (b) 0.05 mol adipic acid; (c) 0.1 mol adipic acid and (d) 0.2 mol adipic acid.

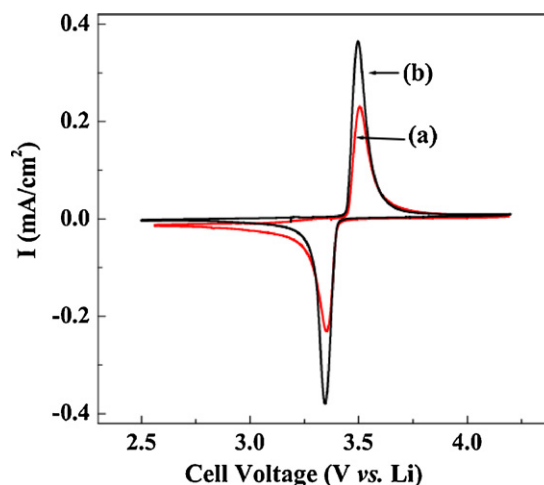


Fig. 8. Cyclic voltammograms of (a) without adipic acid and (b) 0.1 mol adipic acid. The metallic lithium can act as reference and counter electrodes between 2.4 and 4.2 V with the scan rate of 0.02 mV/s.

cycles are required for the complete participation of active material used to deliver such stability, which was the reason to increase in discharge capacity during first few cycles. In particular, similar stability was also observed for 0.2 mol AA-treated, but with marginally lower capacities than the 0.1 mol treated material. This may be due to the residual carbon tending to form an inactive layer on the surface of the active material, thus diluting the active particle distance and leading to the reduced discharge capacity of the LiFePO₄. Furthermore, the excess amount of carbon also accelerates the formation of Fe₂P from Fe and P and adversely affects cell cycling performance [20,29]. The 0.05 mol AA-carbon-coated LiFePO₄ also exhibited stable discharge behavior with a capacity significantly lower than the 0.1 mol AA-treated LiFePO₄. This decreased capacity may be attributed to the large particle size of LiFePO₄ compared to 0.1 mol AA-coated material, even though the residual carbon content was higher than that of 0.1 mol AA-coated LiFePO₄. Thus, an optimization of carbon coating is necessary to achieve higher and more stable discharge behaviors of LiFePO₄. As shown in these results, 0.1 mol AA concentrations are adequate to attain the desired properties of LiFePO₄ by solid-state synthesis.

Cyclic voltammograms of the pristine LiFePO₄ and 0.1 mol AA-treated LiFePO₄ electrodes recorded at a scan rate of 0.02 mV/s are presented in Fig. 8. Well-defined reduction and oxidation peaks of LiFePO₄ appear at 3.34 and 3.50 V, respectively, demonstrating that the Fe^{2+/3+} redox pairs contribute to the gain and loss of electrons in the LiFePO₄ crystal structure during the lithiation and delithiation process. In the 0.1 mol AA-treated LiFePO₄ electrode, the reduction and oxidation current is much higher than for uncoated LiFePO₄ and this demonstrates improved conducting properties as well as faster kinetics of the carbon-coated material. This also reveals that the addition of carbon to LiFePO₄ restrains its polarization. Furthermore, the same intensity values during extraction and insertion of Li⁺ ions corresponded to the excellent phase purity and reversibility of the material by adipic acid-intervened solid-state synthesis.

In order to study the effects of carbon coating on the electrochemical properties of LiFePO₄, a.c. impedance measurements were carried out for the pristine LiFePO₄ and 0.1 mol AA-treated LiFePO₄ cathodes. Fig. 9 shows the impedance spectra of the LiFePO₄ and 0.1 mol AA-treated LiFePO₄ electrodes. Both spectra showed a semicircle in the middle frequency region and a 45° inclined straight line in the low frequency region. The semicircle corresponds to the charge-transfer (CT) process, and the straight line is attributed to the diffusion of Li⁺ ions into the host material, also referred to as the alleged Warburg tail [31]. The CT resistance of

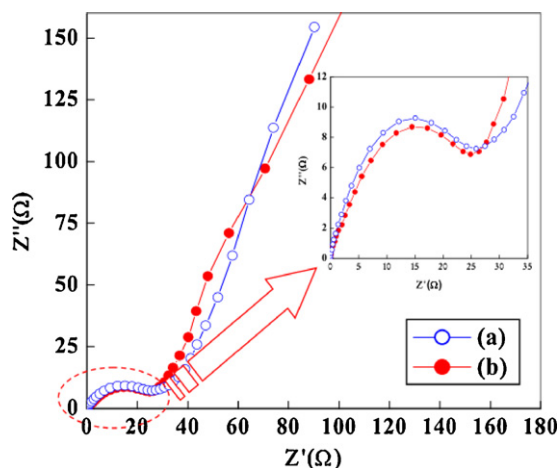


Fig. 9. Electrochemical impedance traces of (a) bare LiFePO₄ and (b) 0.1 mol adipic acid-treated LiFePO₄ at ambient temperature.

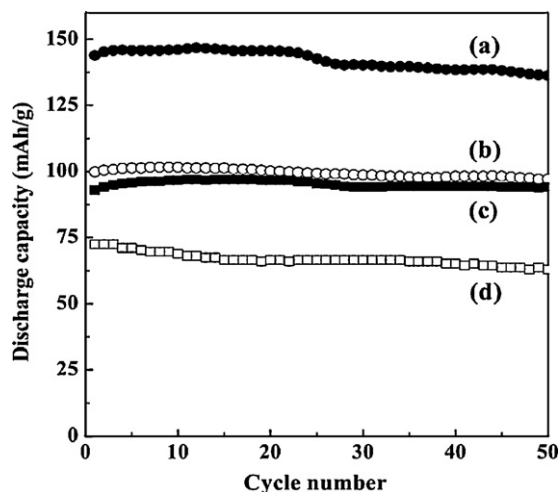


Fig. 10. Rate capability performance of the Li/LiFePO₄ cell at room temperature. The molar ratio of adipic acid to total metal ions is 0.1 and the current densities are (a) 1 C, (b) 8 C, (c) 11 C, and (d) 37 C.

the LiFePO₄ electrode was much larger than those treated with AA. Consequently, the improved battery performance of the LiFePO₄ electrode may be due to the decrease in CT resistance of the electrode.

Capacity retention is an important factor in determining the capability and structural stability of the prepared material. In order to study capacity retention, the 0.1 mol AA carbon-coated LiFePO₄ cell was further investigated. The rate capability and capacity retention of the Li/LiFePO₄ cell was analyzed at different current densities from 1 to 37 C at room temperature and this is illustrated in Fig. 10. The cell delivered a discharge capacity of 143 and 73 mAh/g for 1 C and the extremely high 37 C rates, respectively. This excellent rate capability performance may be ascribed to the superior phase purity and effective coating of carbon derived from adipic acid by the solid-state method used. The discharge capacity values were much higher than the reported values using solid-state synthesis [20]. Therefore, it was concluded that the synthesis of

carbon-coated LiFePO₄ by adipic acid using solid-state synthesis is simple, convenient and very easily reproduced on an industrial scale.

4. Conclusions

Nanocrystalline LiFePO₄ was successfully synthesized by a solid-state reaction method using various concentrations (0–0.2) of adipic acid proportional to total metal ions. Powder X-ray diffraction measurements demonstrated a well-developed LiFePO₄ phase and crystallinity of the synthesized materials. A carbon layer of approximately 5 nm was coated onto the synthesized particles from the carbonization of adipic acid at high temperatures, which was confirmed by TEM. The 0.1 mol adipic acid-treated LiFePO₄ exhibited superior performance over other concentrations of carbon coating. The cell presented an excellent cycle performance until 37 C.

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