

Environment-Friendly Cathodes Using Biopolymer Chitosan with Enhanced Electrochemical Behavior for Use in Lithium Ion Batteries

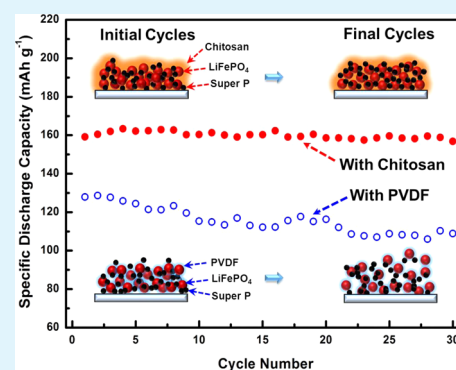
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S Supporting Information

ABSTRACT: The biopolymer chitosan has been investigated as a potential binder for the fabrication of LiFePO_4 cathode electrodes in lithium ion batteries. Chitosan is compared to the conventional binder, polyvinylidene fluoride (PVDF). Dispersion of the active material, LiFePO_4 , and conductive agent, Super P carbon black, is tested using a viscosity analysis. The enhanced structural and morphological properties of chitosan are compared to the PVDF binder using X-ray diffraction analysis (XRD) and field emission scanning electron microscopy (FE-SEM). Using an electrochemical impedance spectroscopy (EIS) analysis, the LiFePO_4 electrode with the chitosan binder is observed to have a high ionic conductivity and a smaller increase in charge transfer resistance based on time compared to the LiFePO_4 electrode with the PVDF binder. The electrode with the chitosan binder also attains a higher discharge capacity of 159.4 mAh g^{-1} with an excellent capacity retention ratio of 98.38% compared to the electrode with the PVDF binder, which had a discharge capacity of 127.9 mAh g^{-1} and a capacity retention ratio of 85.13%. Further, the cycling behavior of the chitosan-based electrode is supported by scrutinizing its charge–discharge behavior at specified intervals and by a plot of dQ/dV .

KEYWORDS: lithium ion batteries, cathode, binders, chitosan, ionic conductivity, capacity



1. INTRODUCTION

Lithium ion batteries are well established as a prominent option for electrical energy storage for high-power and high-energy applications such as transportation, entertainment, computing, and telecommunications equipment.^{1,2} A major challenge to the use of lithium ion batteries is cost and safety.^{3–5} Cost is generally tied to the raw materials, materials processing technology, and manufacturing and labor costs. The safety of the battery is also a matter of crucial importance.⁶ Safety issues have typically concentrated on the thermal stability and toxicity of the raw materials used.^{7,8}

Specifically for cathode active materials, LiFePO_4 , proposed by A. K. Padhi, has many advantages, such as low cost, environmental compatibility, and thermal stability⁹ in comparison to other conventional cathode materials, such as LiCoO_2 , LiNiO_2 , and LiMn_2O_4 . Also, with regard to the electrochemical behavior, LiFePO_4 has an appreciable theoretical capacity and a moderately flat voltage; i.e., the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple is conveniently located at 3.45 V versus Li/Li^+ , which is compatible with common organics as well as polymer electrolytes. Furthermore, LiFePO_4 has excellent cycling reversibility due to the fact that LiFePO_4 and FePO_4 are isostructural (space group $Pnma$) with only slight differences in cellular parameters. For instance, the volume decreases by 6.81% and the density increases by 2.59% when LiFePO_4 delithiates into FePO_4 .¹⁰ Furthermore, the use of LiFePO_4 as a cathode material can reduce the percentage of the cathode

cost from 10% to 50% of the total battery cost.¹¹ It is also perceived as a “green” material due to the environmentally friendly nature of the transition metals employed, namely Fe, which happens to be nontoxic, unlike nickel and cobalt, common components of lithium ion batteries.^{10,11} During fabrication of the LiFePO_4 cathode electrode, advantageous factors such as low cost and environmental compatibility are partially negated due to the addition of PVDF as a binder¹² and *N*-methyl pyrrolidone as solvent, which are highly expensive and toxic in nature.¹³ Very few efforts have been taken to replace the binder used in the fabrication of electrodes.^{14,15} One of the most remarkable efforts by Delphine Guy¹⁶ demonstrated that the electrochemical performance of the composite electrode may strongly depend on the selection of polymeric binder. A significant improvement in cycling capacity of LiFePO_4 due to a change in binder has been recently reported using poly(methyl methacrylate) (PMMA) and carboxymethyl chitosan mixed with styrene-butadiene rubber.^{17,18} With a change of binder, the following three issues should be considered in detail: (1) dispersion and stabilization of the active material and conductive agent in the electrode slurry during composite electrode preparation, which has a major effect on the structure of the electrode; (2) the electronic

Received: November 30, 2014

Accepted: March 30, 2015

Published: March 30, 2015

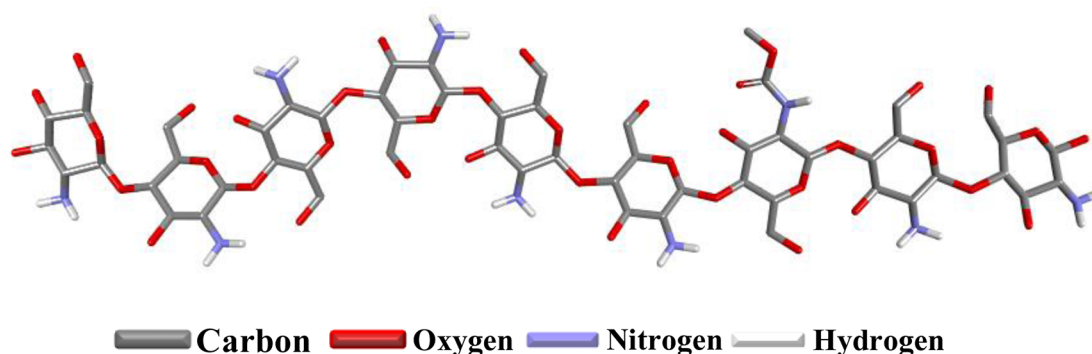


Figure 1. Chemical structure of chitosan.

and ionic conductivity of the composite electrode; and (3) mechanical properties, such as cohesion of the electrode and its adhesion with the current collector.^{19,20}

In concord with the above-mentioned issues, we replaced PVDF and NMP, which are used during the fabrication of the LiFePO_4 cathode electrode, with the biopolymer chitosan and water, respectively, to produce a “greener” electrode. This approach also has the potential to overcome drawbacks of the LiFePO_4 cathode electrode, including its lower intrinsic electronic conductivity, which prevents the full use of its theoretical capacity. Chitosan is a naturally occurring polysaccharide and is basic in nature, in comparison to the other naturally occurring polysaccharides such as cellulose, dextran, pectin, alginic acid, agar, agarose, and carragenans, which are characteristically neutral or acidic. Chitosan contains large quantities of amino and hydroxyl groups as shown in Figure 1, which determines its hydrophilic nature.²¹ Also, the presence of nitrogen in the structure is expected to increase the conductivity. Chitosan has been widely used in agriculture, water and waste treatment, food and beverages, cosmetics and toiletries, biopharmaceutics, and biomedical applications.²² It is also used in lithium ion batteries in a variety of areas, including as a template during the synthesis of active material, as a carbon coating precursor, as a binder for several anode materials, and as a gel polymer electrolyte.^{23–26}

2. RESULTS AND DISCUSSION

The viscosity of the prepared slurry is an important factor to determine the dispersion of solid particles during slurry preparation. Suspension of LiFePO_4 and Super P carbon black powders in the liquid used to prepare slurry or paste usually shows non-Newtonian behavior. The rheology of the final slurries prepared using both binders is shown in Figure 2, where the viscosity was observed to decrease in both cases with an increase in shear rate.

This phenomenon is denoted as a shear-thinning effect. The settling of suspended fine powders in the slurry was measured by the viscosity at low shear rate, where the viscosity is expected to be high to avoid settling of fine powders during slurry preparation.²⁵

In this case, slurry prepared using chitosan and water had a considerably viscous nature at low shear rate, even though it decreased suddenly compared to the slurry prepared using PVDF and NMP. At high shear rates, low viscosity is preferred²⁷ because a more uniform coating is expected with less viscous slurries, whereas the viscosity of the chitosan and water-based slurry was around 331.74 cP, which was slightly

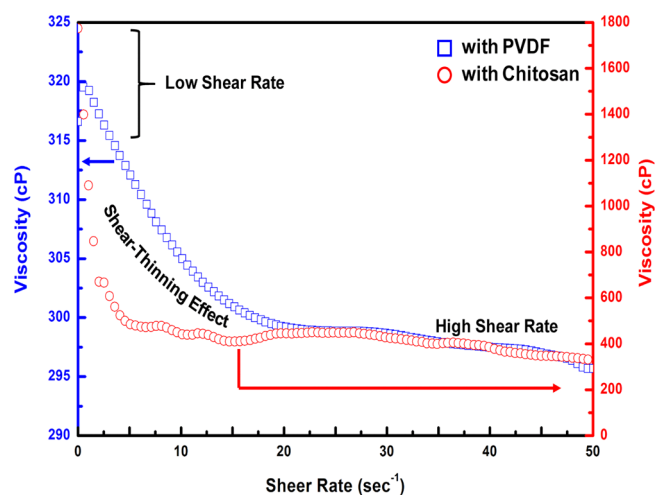


Figure 2. Viscosity of the slurry prepared using two different binders.

higher than that of the PVDF and NMP-based slurry around 295.7 cP.

In the case of slurry prepared using chitosan, acetic acid has been used in minor quantity to dissolve chitosan in deionized water and then LiFePO_4 and Super P is dispersed in it. Such prepared slurry is coated over the Al foil. The presence of acetic acid during electrode fabrication is anticipated to corrode the coated active material LiFePO_4 or the Al foil. Hence corrosion analysis was carried out by immersing the Al foil and the LiFePO_4 powders for 0.5 h in the solution containing appropriate amount of acetic acid used during the electrode fabrication. After the immersion period the Al foil and the LiFePO_4 powders are vacuum-dried at 60 °C overnight. The dried samples are examined using scanning electron microscope (SEM) and XRD analysis, respectively. The surface image of Al foil before and after immersing in appropriate amount of acetic acid solution shown in Figure S1 reveals no significant change on the surface of Al foil. Also the XRD patterns shown in Figure S1 confirm that there is no structural instability of LiFePO_4 powders after immersing in acetic acid solution.

The XRD patterns of the electrode prepared using PVDF and chitosan binders are shown in Figure 3. Both the substrates were observed to be crystalline in nature. The electrode prepared using the chitosan binder showed its characteristic peaks at 2θ angles of 17.90°, 23.9°, 25.57°, and 31.94° with (121), (220), (221), and (241) planes, respectively, in an orthorhombic system. The lattice constants showed a strong correlation with the existing JCPDS card number (39–1894; $a = 8.24$ Å; $b = 16.48$ Å; and $c = 10.39$ Å). It was also apparent

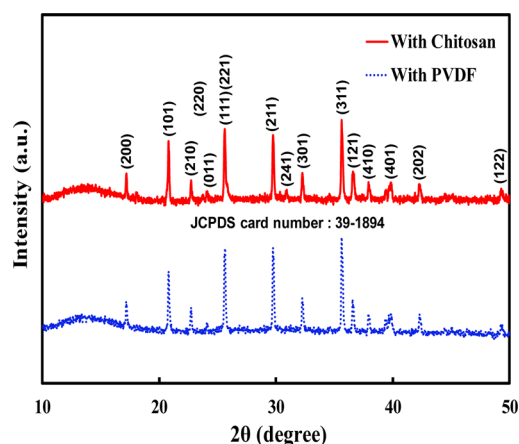


Figure 3. XRD patterns for LiFePO_4 electrodes prepared using different binders.

from the graph that the structure of the LiFePO_4 electrode prepared using chitosan and PVDF binder did not denature the crystalline structure of LiFePO_4 with regard to the literatures.^{28–30}

Surface morphologies of the electrodes prepared using PVDF (Figure 4a,b) and chitosan (Figure 4d,e) were obtained using FE-SEM at two different magnifications. The morphology obtained for the LiFePO_4 electrode prepared using PVDF binder was well matched with the literature.^{31,32} The LiFePO_4 electrode prepared using the chitosan binder alone enabled the formation of a uniform coating layer around the LiFePO_4 and Super P carbon black particles. The formed coating layer enabled a strong network between the LiFePO_4 particles, which

is expected to reduce the resistance between adjacent LiFePO_4 particles to improve the electron transfer efficiency and hence enhance the electronic conductivity.³³ The schematic view in Figure 4c and f represents the binder's interaction with the active material and conductive agent.

The compatibility of the substrate i.e., LiFePO_4 cathode electrode prepared using different binders, with the electrolyte is an essential parameter to guarantee acceptable performance in lithium ion batteries, especially cyclability and reliability. To investigate this crucial aspect and in an attempt to determine the prepared substrate/electrolyte interface over a prolonged time scale, a brief impedance analysis was conducted for the CR2032 coin-type cells that consisted of a cathode fabricated using synthesized LiFePO_4 sample with different binders, 1 M LiPF_6 in ethylene carbonate: diethylene carbonate (EC: DEC, 1:1 vol %) as the electrolyte, and a lithium as the anode. The assembled coin cells were stored and tested under open circuit conditions at room temperature. Figure 5a–c shows the temporal evolution of the impedance due to storage time. The spectra consisted of a semicircle in the high-frequency region, followed by a straight line in the low frequency region. In comparison to the cells that consisted of the chitosan binder (Figure 5a) and PVDF binder (Figure 5b), there was no significant change in the ohmic resistance R_s , whereas the cells that contained the chitosan binder had a resistance R_{ct} nearly ten times lower than the cells consisting of PVDF binder.

The reduced R_{ct} was attributed to the better compatibility of the LiFePO_4 electrode consisting of chitosan with the electrolyte; specifically, there was reductive decomposition of the electrolyte at the electrode/electrolyte interface. The reduction in R_{ct} indicated an increase in ionic conductivity.

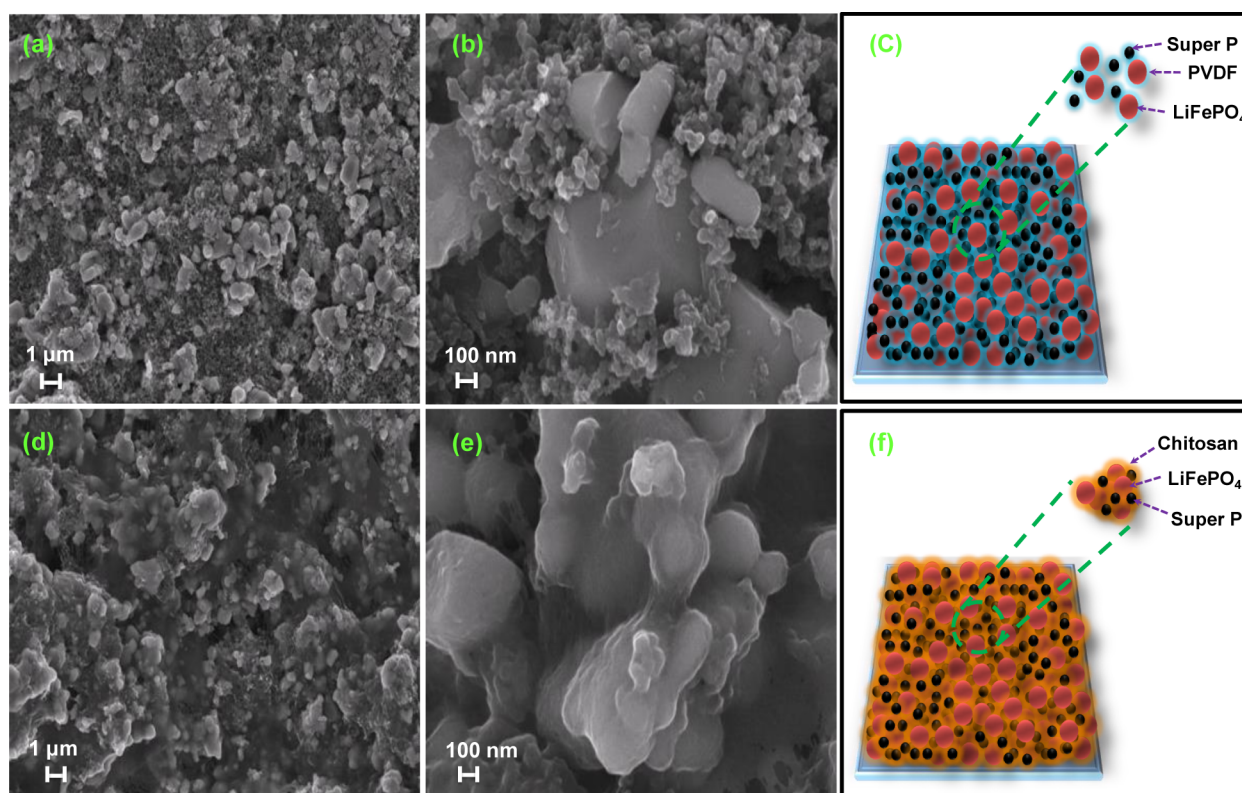


Figure 4. FE-SEM analysis of as-prepared LiFePO_4 electrodes with (a,b) PVDF and (d,e) chitosan binder. Schematic view of electrodes prepared with (c) PVDF and (f) chitosan binders.

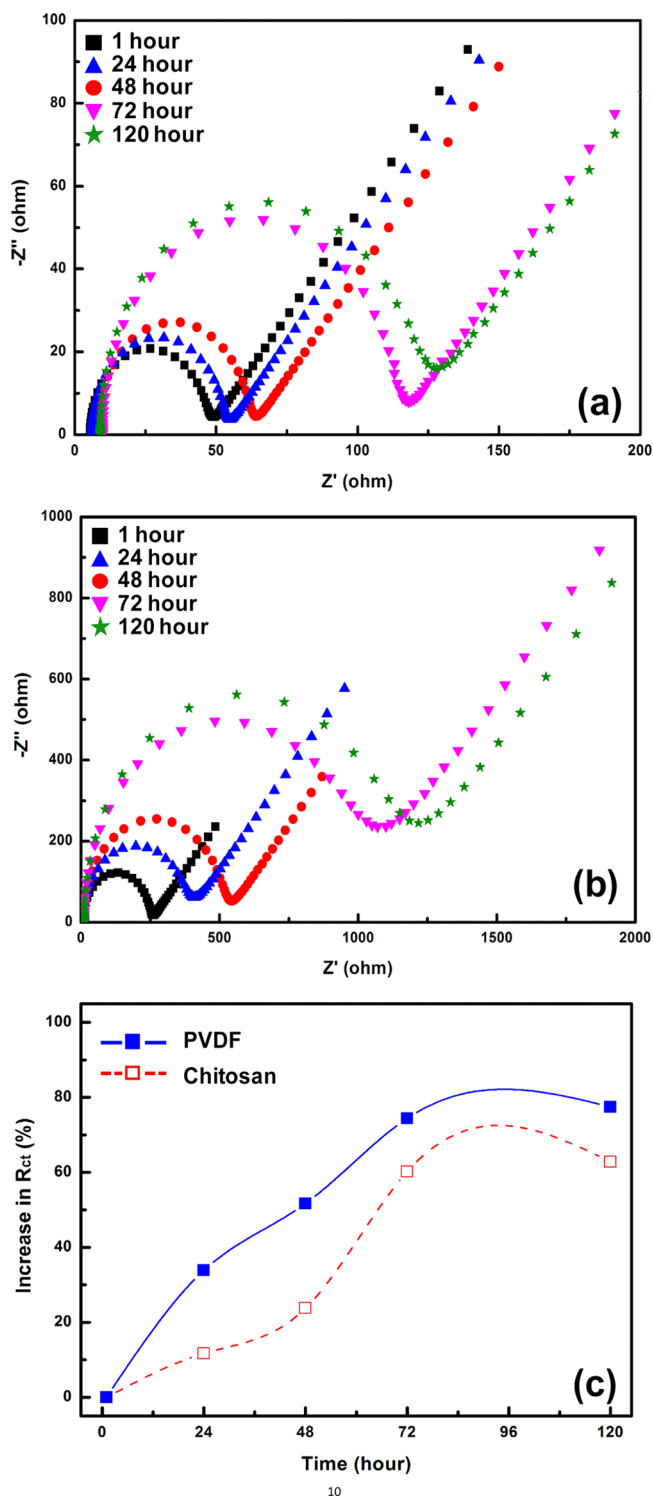


Figure 5. EIS obtained based on specified time intervals for LiFePO₄ electrodes prepared using (a) chitosan and (b) PVDF. (c) Percentage of increase in R_{ct} based on specified time intervals.

Figure 5c shows the percentage increase in R_{ct} based on the aging process. The increase in R_{ct} is based on the formation of a passivating film over the electrode due to prolonged storage. The controlled formation of the passivating film over the electrode consisting of the chitosan binder reduces the increase in R_{ct} and enhances the interfacial characteristics compare to the electrodes prepared using PVDF binder.³⁴

The cyclability of the synthesized LiFePO₄ sample fabricated as a cathode using chitosan and PVDF binder is examined via charge–discharge tests, and the results are shown in Figure 6.

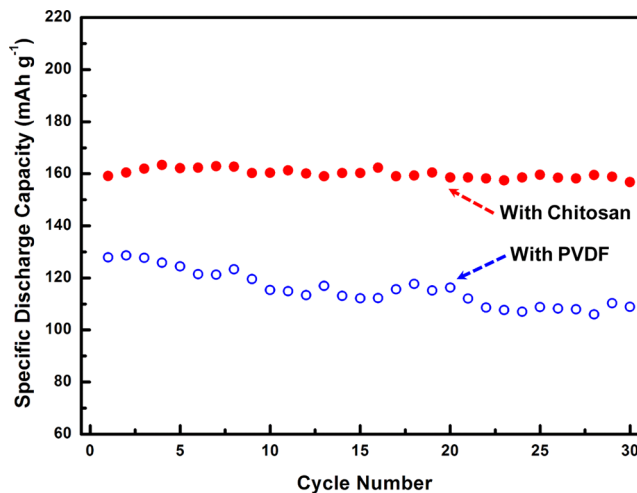


Figure 6. Cycling performance of LiFePO₄ electrodes prepared using different binders, at 0.1C between 2.7 and 4.3 V at room temperature.

Previous studies have shown that chitosan as a binder is chemically stable in the electrolyte used in this study. The LiFePO₄ electrode fabricated using the chitosan binder has shown tremendous cycling performance almost nearing the theoretical capacity of 170 mAh g⁻¹. Usage of the chitosan binder enhanced the electronic conductivity and reduced the R_{ct} , which aided in complete consumption of the active material. To confirm these assumptions the electronic conductivities of LiFePO₄ electrodes prepared using chitosan and PVDF binders were measured. The results confirm that the electronic conductivity of LiFePO₄ electrode prepared using chitosan binder is improved from 8.2×10^{-9} S cm⁻¹ of LiFePO₄ electrode prepared using a PVDF binder³⁵ to 2.89×10^{-7} S cm⁻¹, respectively. The initial capacity of 159.14 mAh g⁻¹, followed by the capacity retention ratio of 98.38% for 30 cycles at 0.1C was obtained for the electrodes with a chitosan binder, this may be due to the higher lithium-ion diffusion rate and improved electrical conductivity in the FePO₄ phase, which enables the complete conversion of LiFePO₄ to FePO₄ and back again, inducing better specific capacity with excellent capacity retention. The electrodes with PVDF binder possessed a poor initial capacity of 127.9 mAh g⁻¹ and a capacity retention ratio of 85.13%. In addition to examine the proposed binder under prolonged cycling condition the prepared coin cells were cycled at 1C rate for 100 cycles and the results are shown in Figure S2. After 100 cycles, cells with chitosan binder retained 90.13% of the initial capacity of 98.30 mAh g⁻¹, whereas cells with PVDF binder retained only 77.92% from the initial capacity of 68.53 mAh g⁻¹.

The obtained capacity for LiFePO₄ electrode using PVDF binder is also comparatively lower than the commercially available LiFePO₄ electrode. The reason for lower capacity and faster capacity fading may be attributed to hydrothermal synthesis condition of LiFePO₄ active material as reported by recent research articles.^{36,37} The drawbacks of hydrothermal synthesized LiFePO₄ cathode had been rectified by coating of carbon from different sources.^{38–41} The usage of nitrogen rich chitosan as a binder rectifies the major drawback of electronic conductivity. Also the presence of amino groups ($-\text{NH}_2$) in the

chitosan is responsible for donation of electrons, which will eventually lead to shifting of Fermi level to lowest unoccupied molecular orbital (LUMO). Due to the strong electron donating characteristics of amine group, the π -electron delocalization of chitosan is increased. It ensues decrease in the energy of π - π^* electron transition and thereby increases the electronic conductivity.^{42,43} The enhanced electronic conductivity helps in improving the specific capacity and capacity retention of the synthesized LiFePO_4 .

In support of the cycling behavior, the charge–discharge curves were further investigated at the 2nd, 15th, and 30th cycles, as shown in Figure 7a,b. Since all other contributing factors in the fabricated coin cell were constant, the improved capacity and capacity retention compared those with of PVDF binders were attributed to chitosan binders. Using chitosan binders, a discharge capacity of 159.14, 160.27, and 156.83 mAh g^{-1} was obtained for the above-mentioned cycle numbers, respectively.

During the charge and discharge process, the cell exhibited a flat voltage plateau at 3.48 and 3.38 V for the first cycle, and it was observed to be constant for the 15th and 30th cycles, where it possessed a polarization value around 100 mV as shown in Figure 7a. For cells containing PVDF binders, a deteriorating discharge capacity of 128.65, 112.19, and 108.91 mAh g^{-1} was observed for the specified cycle numbers, respectively. The voltage plateau obtained for these cells showed a significant increase with respect to an increase in cycle number, i.e., the polarization value, increased with an increase in cycle number, with a polarization value of 780 mV noted for the 30th cycle as shown in Figure 7b.^{44,45} The polarization values obtained were in good agreement with the results shown in Figure 6.

In further support of the cycling behavior, Figure 7c shows dQ/dV curves that originated from the charge–discharge behavior of cycle #3, between the potential range of 3 and 4.3 V of the LiFePO_4 electrodes prepared using PVDF and chitosan binders. Through the dQ/dV curves, the intensity of the anodic and cathodic peaks and their potential difference were determined to allow better understanding of the electrochemical properties. The high peak intensity and small potential difference are characteristics of good electrochemical performance. The cathodic and anodic peaks represent the potential difference ΔE ($E_{\text{oxidation}} - E_{\text{reduction}}$) between the oxidation and reduction processes, which correspond to lithium extraction and insertion, respectively.

The LiFePO_4 electrodes prepared using chitosan were observed with a high peak intensity and lower cathodic potential of 3.480 V compared to the LiFePO_4 electrodes prepared using PVDF binders, which were of low peak intensity and higher cathodic potential of 3.486 V. The potential difference of the chitosan-prepared electrode was 0.096, whereas that for the electrode prepared using PVDF was 0.107, indicating that the chitosan binder has high ionic conductivity, which leads to low electrochemical polarization.^{46,47}

Figure 8 exhibits the discharge capacity of the cells containing chitosan and PVDF binders at different C -rates. The rate test was increased gradually from 0.1C to 2C. The cells that contain the chitosan binder showed a higher discharge capacity under all different current rates, i.e., 161.10, 156.71, 137.82, 98.45, and 64.24 mAh g^{-1} , compared to the cells containing the PVDF binder, which showed a discharge capacity of 127.57, 124.17, 105.67, 69.51, and 47.83 mAh g^{-1} at 0.1, 0.2, 0.5, 1, and 2C rates, respectively. The rate capability

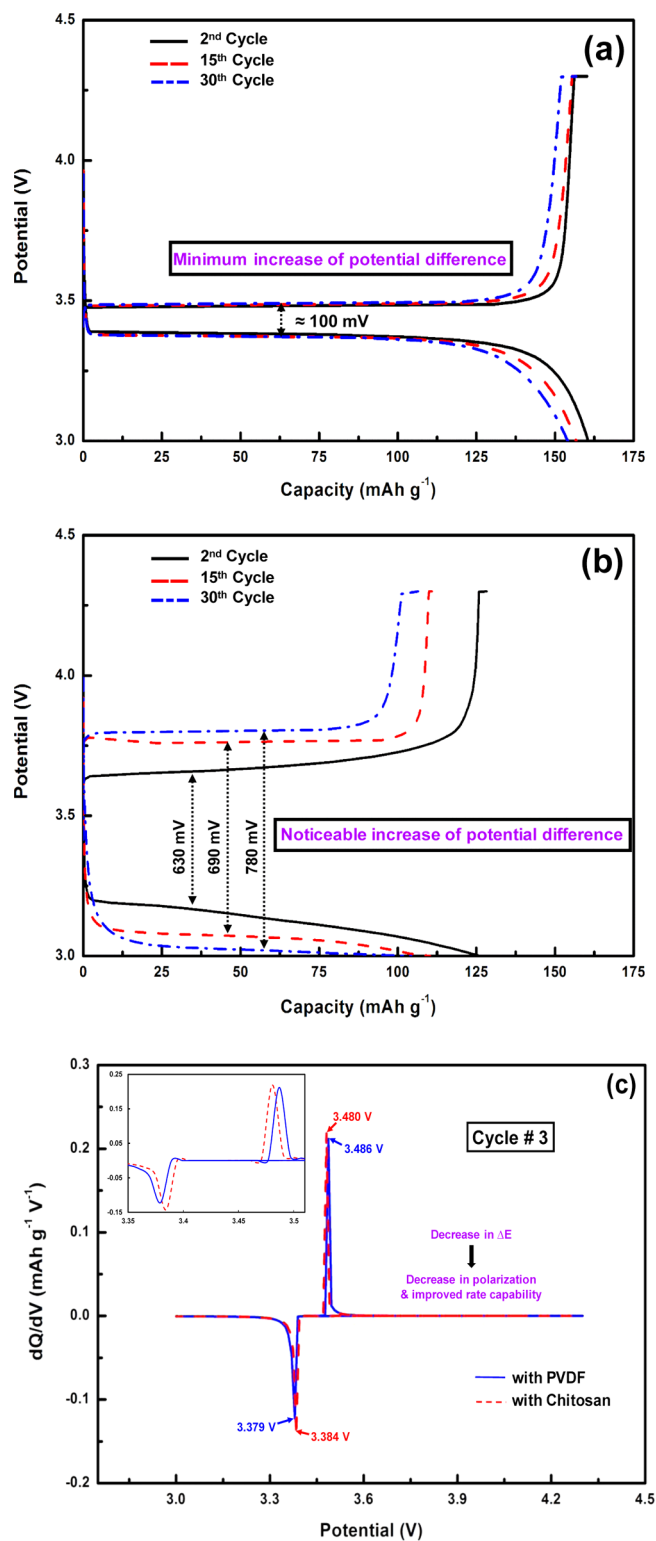


Figure 7. Charge–discharge profiles of LiFePO_4 cathodes with (a) chitosan and (b) PVDF binders at 0.1C between 2.7 and 4.3 V at room temperature. (c) dQ/dV curves for LiFePO_4 electrodes prepared using different binders. The inset image in (c) shows the magnified view of peak positions.

was determined by calculating the percentage of capacity retained at higher C -rate “2C” from the capacity obtained at lower C -rates “0.1C” i.e., $2C/0.1C$. For the electrodes with chitosan binder 39.87% of capacity was retained and for

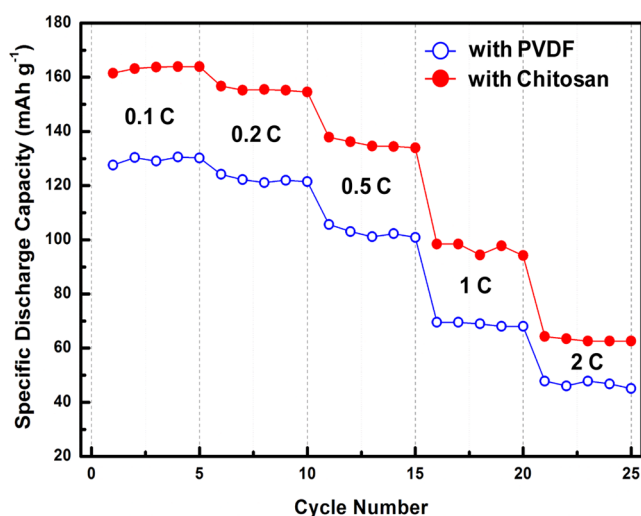


Figure 8. Rate performance of electrodes prepared using different binders at room temperature.

electrodes with PVDF binder 37.49% of capacity was retained. At the high rate, cells containing the chitosan binder may accelerate the diffusion of lithium ions between the electrode and the electrolyte, which leads to the improved rate capability as observed compared to the cells containing PVDF binder.⁴⁸

3. CONCLUSIONS

In summary, the usage of chitosan as a binding material during the fabrication of LiFePO_4 cathode electrodes was compared with commercially obtained PVDF binders. Three mandatory properties of the binders used in lithium ion batteries include dispersion and stabilization of the active material, electronic and ionic conductivity of the composite electrode, and adhesion with the current collector. These properties were demonstrated using an analysis of viscosity, and electrochemical impedance. Chitosan, through demonstration of its unique properties, shows tremendous potential to replace PVDF during the fabrication of cathode electrodes. With regard to the electrochemical analysis of the LiFePO_4 cathode electrode fabricated using chitosan binders, a higher discharge capacity was observed due to the enhancement of electronic conductivity and reduction of R_{ct} . Furthermore, the charge–discharge profile and dQ/dV curve supported the observation of enhanced electrochemical behavior of chitosan binders. This evidence suggests that chitosan can be utilized as a replacement for PVDF binders to allow production of less expensive and more environmentally friendly batteries.

4. EXPERIMENTAL SECTION

4.1. Material Synthesis. LiFePO_4 has been synthesized using the hydrothermal method. The starting materials $\text{LiOH}\cdot\text{H}_2\text{O}$, H_3PO_4 and $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ were taken in the molar ratio of 2.8:1:1, respectively, and added in the 80 mL of deionized water under continuous stirring. After that the reaction mixture was transferred into Teflon lined stainless steel autoclave and kept at 180 °C for 10 h. Once it reached the ambient temperature naturally the reaction mixture was taken out and washed with deionized water for multiple times until the washing water becomes colorless. The obtained precipitate was vacuum-dried at 60 °C for 12 h.

4.2. Substrate Preparation. The Synthesized LiFePO_4 and Super P carbon black was vacuum-dried for 6 h at 120 °C, respectively. Chitosan obtained from shells of shrimp was used as a binder. To prepare the cathode electrode, LiFePO_4 powder with Super P carbon

black and different binders, namely chitosan and PVDF in a weight ratio of 90:5:5, was mixed. Deionized water containing 0.5% acetic acid was used as a solvent for blending the electrode mixture for chitosan binders, while NMP was used as a blending solvent for the PVDF binder. For the preparation of the electrode, the binders were initially dissolved in their respective solvents, followed by the addition of LiFePO_4 and Super P carbon black. The mixture was thoroughly stirred for 12 h, cast onto Al foil using doctor blade method, and dried at 120 °C for 5 h. Then the dried electrodes were roll pressed for better adhesion between the electrode material and current collector. Finally, the roll-pressed electrodes were punched to the required size i.e., 14 mm in diameter - ϕ and dried again under vacuum at 100 °C for 4 h. Experimental procedures for the physical and electrochemical characterization of prepared substrate is provided in the Supporting Information.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental methods for physical and electrochemical characterization of prepared substrates and the corrosion analysis results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the IT R&D program of MOTIE (Ministry of Trade, Industry & Energy)/KEIT (Korea Evaluation Institute of Industrial Technology) [10041856].

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