Research Article

Synthesis and Characterization of Electrophoretically Deposited Nanostructured LiCoPO_4 for Rechargeable Lithium Ion Batteries

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Nanosized LiCoPO_4 (LCP) was prepared using a simple sol-gel method. For the first time, electrophoretic deposition process was employed to fabricate a LiCoPO_4 cathode material in order to improve the electrochemical performance. The prepared powder was deposited on titanium plate by electrophoretic deposition and their electrochemical properties were studied. The electrochemical properties were analyzed by using cyclic voltammogram studies, impedance studies, and charge/discharge tests. The thickness of the prepared cathode material was found to be 11-12 μm by using scanning electron microscope. The initial specific capacity and the charge transfer resistance (R_{ct}) of the prepared cathode was 103 mAh/g and 851 Ω , respectively. The charge/discharge profiles showed moderate columbic efficiency of 70%.

1. Introduction

Lithium-ion batteries exhibit good electrochemical performance compared to other types of batteries due to long storage life and environmentally friendly and low maintenance. They are the focus of attention as good energy storage devices and are nowadays commonly used in portable electronic devices such as laptops, mobile phones, camera, and so forth. For better performance, cathode materials with high specific energy density, high power density, and excellent thermal stability are necessary for lithium-ion batteries [1, 2].

LiCoO_2 is the commonly used cathode material. It has both high voltage and capacity but has its own disadvantages like high cost, toxic properties, and safety issues [3, 4]. So a quest for other cathode materials arises. Cathode materials having the general formula LiMPO_4 ($M = \text{Fe, Co, Mn, and Ni}$) are seeking attention nowadays [5–9]. They are having high theoretical capacity approximately 170 mAh/g. Their operating voltages are high. They are having a stable structure on charging and discharging, thermal stability, and flat voltage profile [10, 11].

Lithium cobalt phosphate (LiCoPO_4) has high energy density (750 Wh) which is comparable to lithium cobalt oxide (LiCoO_2) [12]. LiCoPO_4 is one material which has high voltage and capacity compared to LiCoO_2 and is predicted to have ~1.6 times the specific energy of LiCoO_2 [13–16]. It can operate at high voltage typically 5 V. It is cost effective and one of the promising cathode material. But their main disadvantages are their poor electronic and ionic conductivity and poor rate cyclability [17, 18]. Even though the theoretical capacity of LiCoPO_4 is 167 mAh/g, the obtained values are still lower due to the above reason. Reduction in particle size to nanometer size, doping with some metal ions, and adding carbon coating are the method to overcome these problems [19]. If we are able to overcome the low electronic and ionic conductivity of LCP, it would be the best alternative cathode material.

In the present work, LiCoPO_4 powders were synthesized using simple sol-gel method. The synthesized powders were successfully deposited on titanium plate electrophoretically which is reported for the first time. The work includes the study of electrochemical behavior of electrophoretically deposited LiCoPO_4 cathode materials and to see how this

FIGURE 1: XRD pattern of LiCoPO_4 .

method of deposition has its influence on the properties like specific capacity, impedance, charge/discharge profiles, and cycle stability.

2. Experimental Details

Lithium acetate, cobalt acetate, and orthophosphoric acid were used as starting materials and dissolved in 30 mL, 30 mL, and 40 mL of acetone, respectively. Then the three solutions were mixed thoroughly and kept at 80°C until the gel formation. Then, the gel was kept for overnight drying in the oven in order to get the powder material. After drying the gel completely, resultant powder was crushed well in the agate mortar. Then, the powder was kept for presintering at 400°C for 5 h under air followed by sintering at 750°C for 24 h under air to get the crystalline phase. The resultant product was ground well to get the single phase olivine LiCoPO_4 (LCP).

Electrophoretic deposition of LCP was done by taking platinum rod (inert electrode) as the anode and titanium plate as the (substrate) cathode. The solution was prepared by taking isopropanol as the solvent. 30 mg of LCP was added to 15 mL of isopropanol. The solution was sonicated for 30 minutes to get the powder well dispersed in the solvent. 2 mg of lithium chloride was added to charge the solution. The mixture was then stirred for 15 minutes. EPD process was done by giving a voltage of 60 V for 30 minutes to yield thin coating of LCP on titanium plate, followed by annealing at 70°C for 10 hrs.

XRD patterns were obtained by XRD X'pert PRO analytical with Cu $\text{K}\alpha$. The morphology of sample was studied by scanning electron microscope (SEM, model: JEOL JSM 6490LA). XPS (Kratos analytical, Shimadzu) was used to study the oxidation state and to see whether LCP has coated into titanium plate. The roughness of the samples was studied by Profilometer (Veeco Dektak 150). AUTOLAB (electrochemical workstation: Newport Model) was used to study the electrochemical properties. The electrochemical properties

like cyclic voltammogram and impedance were studied using a three-electrode system: the calomel electrode as reference electrode, platinum as counter electrode, and the LCP coated titanium plate as working electrode. The charge discharge profiles were studied by using two-electrode systems. The platinum rod was used as counter electrode and working electrode was the same as that for CV and impedance study. The electrolyte was 20 mL of propylene carbonate to which 2.12 g of lithium perchlorate was added.

3. Results and Discussion

3.1. Phase Analysis. The X-ray diffraction pattern of pure LCP is shown in Figure 1. The XRD pattern of pure LCP clearly shows the formation of single phase olivine. Lithium cobalt phosphate (LCP) with an orthorhombic structure with space group Pnma. (JCPDS file number: 32-552) [20]. The average grain size is 35 nm which was calculated from the Scherrer's formula.

3.2. Scanning Electron Microscopy. SEM image of pure LCP is shown in Figure 2(a). From the figure, we can clearly see that the particles are distributed in flake like structure nonuniformly. The average particle size was found to be about 200 nm. Figure 2(b) shows the SEM image of electrophoretically deposited LCP on titanium plate. The nanosized particles were found to get agglomerated to minimize the surface energy. The cross section of the deposited film is shown in Figure 2(c). The thickness of the film was found to be 11-12 μm .

3.3. XPS Studies. Figure 3 shows the XPS spectrum of LCP [21]. As seen from the graph the binding energy of lithium was 58 eV. The binding energy of phosphorus was 137 eV which was closed to the characteristic binding energy of phosphorus. As for oxygen the binding energy was found to be close to 535 which was in good agreement with the standard binding energy. In the case of cobalt the binding energy was found to be close to 785. But the high resolution spectrum (given in the inset) shows two distinct peaks which correspond to two different oxidation states: $\text{Co}2\text{p}_{3/2}$ which was located at 784.61 eV and $\text{Co}2\text{p}_{1/2}$ which was located at 800.66 eV which was in close agreement with the characteristic binding energies.

3.4. Electrochemical Measurements. The CV curves of pure LCP are shown in Figure 4. The selected potential window cut-off was from -5 to 3 V with the scan rate of 0.1 V/S. The oxidation and reduction peaks are located at -2.152 V and -2.628 V, respectively. The oxidation peak corresponds to the point at which lithium was extracted from LCP structure and reduction peak corresponds to the point at which lithium was reinserted into the LCP crystal structure. The specific capacity of the pure LCP cathode material was calculated to be 103 mAh/g. Specific capacity versus cycle number study is given in Figure 5. The specific capacity was 103 mAh/g in the first cycle. After that the value decreases and was comparatively stable from the 4th cycle to the 15th cycle

FIGURE 2: SEM image of (a) lithium cobalt phosphate powder, (b) electrophoretically deposited lithium cobalt phosphate film, and (c) cross section of deposited film.

FIGURE 3: XPS spectra of lithium cobalt phosphate powder (Inset shows the high resolution spectrum of Cobalt).

FIGURE 5: Graph showing specific capacity versus cycle number of LCP cathode material.

FIGURE 4: CV curve of LiCoPO_4 .

(45 mAh/g to 43 mAh/g). The system has comparable initial performance but it reduces and becomes stable at the fourth cycle. The lithium extraction takes place at a large rate at the beginning then the insertion was not happening at an equivalent rate which may result in a diminished value after the 4th cycle.

Figure 6 shows the impedance spectra of LCP and the frequency range given for impedance measurements were from 100 kHz to 1 mHz. For pure LCP, the curve consists of a depressed semicircle which does not touch the x -axis followed by a line which indicates Warburg resistance [22, 23]. Some scatterings were observed in the low frequency range. The value of charge transfer resistance from the curve is 851Ω which was fairly better compared to most of the other reported values. Lithium cobalt phosphate has high impedance generally. Techniques like carbon coating were done to minimize the impedance and to improve the conductivity. But here the formation of a thin layer composed of nanosized particle itself reduces the impedance to lower values. The columbic efficiency for the first cycle was found

FIGURE 6: Impedance spectra of LCP cathode material.

FIGURE 7: Columbic efficiency versus cycle number for LCP cathode material.

to be 70% in Figure 7. Columbic efficiency of the 3rd, 5th, 7th, 9th, and 10th cycle are 65%, 61%, 57%, 55%, and 53%, respectively.

4. Conclusion

LiCoPO_4 powder was successfully developed by a simple sol-gel method. The XRD results showed pure orthorhombic structure without any impurity. The grain size was found to be 35 nm. SEM image showed flake like structures having an approximate particle size of 200 nm. The SEM image of LiCoPO_4 deposited titanium plate showed agglomerated particles. LiCoPO_4 was successfully deposited onto the titanium plate for the first time by applying a voltage of 60 V for 45 minutes. Using XPS spectra the presence of LiCoPO_4 onto titanium plate was confirmed but a minor quantity of lithium chloride was also deposited. The thickness of

the LCP coating was found to be 11 μm . The cyclic voltammetry study showed that pure LCP was having a discharge capacity of 103 Ah/g. The R_{ct} value of pure LCP was found to be 851 Ω . The charge/discharge mechanism of LCP was found to be comparatively stable for LCP. LCP has moderate electrochemical performance initially but it sustains the performance throughout the next cycles. Electrophoretic deposition results in uniform LCP coating which is a novel method of cathode fabrication since the electrochemical performance is comparable with the previous results.

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