

Preparation and Characterization of Chlorine Doped $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ as High Rate Cathode Active Material for Lithium Secondary Batteries

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Monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3\text{Cl}_{0.01}$ was synthesized using the conventional solid state method and the X-ray diffraction pattern was indexed based on $P2_1/n$ space group. The sharp cyclic voltammetric curves clearly revealed three lithium extraction/insertion processes at approximately 3.64, 3.72, 4.13, and 4.58 V during the anodic scan and 3.96, 3.58, and 3.48 V during the cathodic scan. Charge/discharge studies showed reduced electrolyte decomposition contribution in the case of the chlorine doped $\text{Li}_3\text{V}_2(\text{PO}_4)_3\text{Cl}_{0.01}$ sample with an initial capacity of 176 mA h g⁻¹ at a 0.1 C current rate. The chlorine doped $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ sample showed an increased capacity retention with an increase in current rate, even at a very high C-rate (20 C), than the pristine and carbon coated samples. The pristine and carbon coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ samples showed a lower capacity retention of 71% and 84%, respectively, at a current rate of 0.1 C. In contrast, the chlorine doped $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ sample retained 87% of the initial capacity (176 mA h g⁻¹) at the same current rate but with a higher coulombic efficiency of 91%. The enhanced capacity retention for the chlorine doped $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ was attributed to the reduction in polarization and decreased charge transfer resistance of the electrode.

Keywords: Lithium Vanadium Phosphate, Cathode, Anion, Chlorine, Doping, Battery.

1. INTRODUCTION

Low cost, reliable, environmentally friendly batteries are urgently needed for deployment in applications such as electric vehicles, portable electronic devices, and backup power sources. Lithium batteries based on a combination of metallic lithium or lithiated carbon anode and a lithium intercalation host cathode have been, in principle, designed to meet these requirements.¹ Commercialized lithium batteries use LiCoO_2 as cathode materials, but the safety and high cost of cobalt were the major issues that restrained large scale utilization. Alternatively, transition metal phosphates such as LiMPO_4 (M = Ni, Co, Fe, Mn), $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, LiVPO_4F , and $\text{Li}_2\text{MPO}_4\text{F}$ (M = Co, Fe, Ni, Mn) have been proposed as future cathode materials because they have both high mobile Li ions for red-ox

reaction with a rigid phosphate framework and are electrochemically and thermally stable.^{2–16}

Owing to the high theoretical capacity (197 mA h g⁻¹) and high operating voltage (4 V vs. Li), $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ has been considered as a promising candidate for next generation lithium secondary batteries.¹⁷ The structural arrangement of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ ensured a three-dimensional pathway for Li diffusion and has been considered to be favorable for obtaining high discharge capacity together with cycle stability.¹⁷ $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ can be crystallized in two different forms, namely, rhombohedral and monoclinic. Both types of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ have $\text{V}_2(\text{PO}_4)_3$ units in common; however, the difference in 3D connectivity between these units was responsible for the different electrochemical properties exhibited.¹⁸ Monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ was of particular interest in this study, because of the complete removal of three lithium ions that ensured a pathway for achieving the theoretical capacity and good ionic mobility. The crystal

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structure of monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ consisted of VO_6 octahedron and PO_4 tetrahedron arranged into a 3D framework which enabled a three four-fold crystallographic position for lithium. The rapid lithium movement was governed by the arrangement of metal octahedron and phosphate tetrahedron accordingly so that each VO_6 octahedron was surrounded by six PO_4 tetrahedrons and each PO_4 tetrahedron was surrounded by four VO_6 octahedrons.¹⁹ The Li insertion/extraction in $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ follows three stages. The first stage, between 3.6 and 3.7 V, was the formation of the stable intermediate phase $\text{Li}_{2.5}\text{V}_2(\text{PO}_4)_3$, the second stage was the removal of lithium from the tetrahedral site in the voltage range of 3.7–4.1 V (at this stage, the full conversion of V^{3+} to V^{4+} is completed), and the final stage is represented by the conversion of V^{4+} to the V^{5+} redox couple which was attained at a voltage of 4.1–4.5 V.^{19,20} Hence, a charge cut-off voltage of 4.8 V versus Li was used to fully extract and re-insert the lithium ions from $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. Morcrette et al.²⁰ extensively studied three stages of lithium extraction in $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ using *in-situ* X-ray diffraction, and the results suggested extensive volume changes occurring during phase transitions; however, the structure of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ was highly reversible, even after the complete removal of all lithium ions.

Low intrinsic electrical conductivity was the main drawback for transition metal phosphates, affecting the rate capability and cycle stability of the active materials during the battery operation. Apart from carbon coating,²¹ anion substitution²² was also tested to improve the electrical conductivity. Anion substitution helped to improve not only the intrinsic conductivity of the materials, but also had additional effects such as suppression of phase transition during intercalation and de-intercalation reaction,¹⁹ improvement in rate capability and cycle stability,²³ and assistance in the growth of particles which affect the tap density of the electrode materials.^{24,25} While several reports have been presented of anion substitution in $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, until now no work has been carried out on the effect of anion substitution at high voltages above 4.2 V. The maximum capacity obtained using anion substitution was limited to less than 130 mA h g⁻¹ due to the non-removal of third lithium ion.^{22,26} Hence, in this study an attempt was made to improve the conductivity of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ by *in-situ* carbon coating using adipic acid as the carbon source and further improvement in cycle stability was promoted by a small amount of anion (Cl^-) substitution. An improvement in discharge capacity and retention was achieved using both carbon coating and anion substitution by following a simple solid state approach that could be easily adopted in the industry for large scale production.

2. EXPERIMENTAL DETAILS

Monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ was prepared by the conventional solid state approach using Li_2CO_3 (Wako, Japan),

V_2O_5 (Sigma–Aldrich, USA), $(\text{NH}_4)_2\text{HPO}_4$ (Sigma–Aldrich, USA), and adipic acid (Sigma–Aldrich, USA) as precursors. The starting materials were used as-received without any further treatment. The stoichiometric amount of precursors was mixed in an agate mortar for proper mixing. The optimized condition for synthesizing carbon coated monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ was as follows: pre-calcination at 300 °C for 4 h in air atmosphere followed by sintering at 900 °C for 8 h in Ar flow. The pre-calcination step was used for eliminating hydroxyl and ammonium moieties. The pre-calcined pellet was ground again, pelletized, and then used for the final sintering process to obtain phase pure $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. Anion substitution was carried out following the stoichiometry of $\text{Li}_3\text{V}_2(\text{PO}_4)_{(3-x)}\text{Cl}_x$ ($x = 0.01$ – 0.03) using NH_4Cl (Sigma–Aldrich, USA) as the source for chlorine. The preparation process was followed as that described above. A pristine sample without using adipic acid for the carbon source and NH_4Cl for chlorine substitution was also prepared for comparison following the same preparatory procedure. The samples prepared in this study were designated as LVP, C-LVP, and C-LVPC for the pristine, carbon coated, and carbon coated- $\text{Li}_3\text{V}_2(\text{PO}_4)_{2.99}\text{Cl}_{0.01}$ samples, respectively.

Structural confirmation of the synthesized samples was analyzed using X-ray diffraction studies (XRD, Rint 1000, Rigaku, Japan). Electrochemical characterizations of all the synthesized materials were performed using a CR2032 coin cell. The cell consisted of synthesized material as the cathode and metallic lithium as the anode, separated by a porous polypropylene separator (Celgard 3401, USA) with 1 M LiPF_6 as the electrolyte. The cathodes were prepared by mixing 20 mg of active material, 3 mg of Ketjen black (KB), and 3 mg of teflonized acetylene black (TAB) and were then pressed over a stainless steel current collector, followed by drying at 160 °C for 4 hrs before being used in the cell. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) studies were carried out using an electrochemical work station (SP-150, Biologic, France) at room temperature. The EIS spectra were measured in the frequency range of between 100 kHz and 100 MHz using applied current amplitude of 100 μA , while the CV was tested at a scan rate of 0.05 mV s⁻¹ between the operating voltage of 3 V and 4.8 V with lithium being both a counter and reference electrode. Galvanostatic charge/discharge with a battery tester (WBCS 3000, Won-A-Tech, Korea) was used to evaluate the charge/discharge behavior of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ samples.

3. RESULTS AND DISCUSSION

Highly crystalline phase pure $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ were prepared. The phase of the synthesized samples was confirmed using XRD studies and the results are shown in Figure 1. The reflection of the XRD pattern of all samples matched well with the monoclinic structure having a $P2_1/n$ space group and also with those reported in the literature (JCPDS

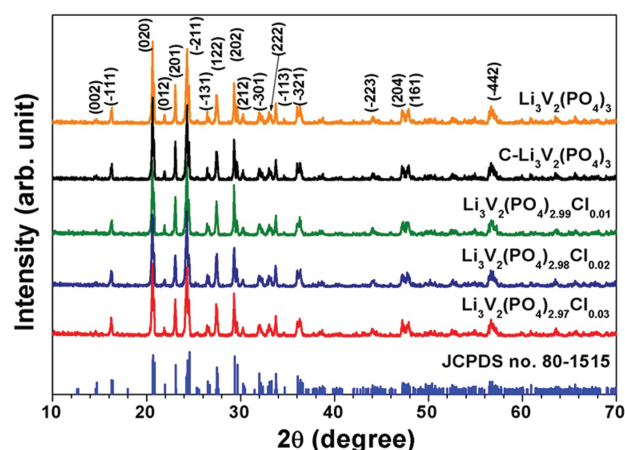


Figure 1. X-ray diffraction patterns of different $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ samples synthesized in this study.

80-1515).^{22–25} No peaks matched the characteristic peak positions of Li_3PO_4 , V_2O_3 , and V_2O_5 ; also, the absence of impurity peaks corresponding to chlorine or carbon attributed to the phase purity of the synthesized samples. Owing to the smaller amount of chlorine (1%–3%) and carbon (0.2 M), the phase purity was not affected. Since no peak for crystalline carbon occurred, the carbon must be in an amorphous form. All the powders synthesized were thus single phase materials. Therefore, the high performance electrode material was chosen based on the Li insertion property using a half cell configuration.

Charge–discharge studies were performed for all the samples synthesized between 3 and 4.8 V at a current density of 0.1 mA cm^{-2} . All the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ samples showed three stages of lithium extraction and insertion,^{19,20} which corresponded to a two phase reaction as shown in Figure 2. During charging, the first lithium ion was extracted in two steps, i.e., at $\sim 3.6 \text{ V}$ for the formation of intermediate phase $\text{Li}_{2.5}\text{V}_2(\text{PO}_4)_3$ followed by the ordered phase ($\text{Li}_2\text{V}_2(\text{PO}_4)_3$) formation at $\sim 3.7 \text{ V}$. The second stage extraction occurred at $\sim 4.1 \text{ V}$, which was responsible for the second lithium extraction and complete transformation

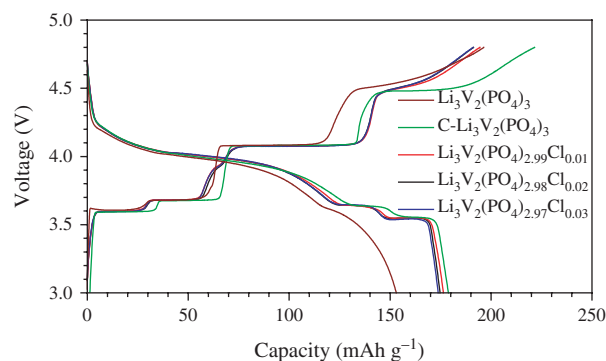


Figure 2. Galvanostatic charge–discharge studies of various $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ samples synthesized in this study between 3.0 and 4.8 V at 0.1 mA cm^{-2} (0.1 C).

of V^{3+} to V^{4+} . Finally, the third lithium ion extraction at $\sim 4.5 \text{ V}$ formed the third stage, in which all lithium ions were completely removed, resulting in $\text{Li}_0\text{V}_2(\text{PO}_4)_3$, where the $\text{V}^{4+/5+}$ conversion occurred. The reverse process of lithium insertion starting from $\text{Li}_0\text{V}_2(\text{PO}_4)_3$ to $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ occurred during discharge. The three stage lithium insertion occurred at $\sim 4.0 \text{ V}$, $\sim 3.6 \text{ V}$, and $\sim 3.5 \text{ V}$. The initial discharge capacity exhibited by LVP and C-LVP was 153 mA h g^{-1} ($\sim 2.33 \text{ Li atoms}$) and 179 mA h g^{-1} ($\sim 2.72 \text{ Li atoms}$), respectively. In the case of chlorine doped samples, a discharge capacity of 176, 175, and 174 mA h g^{-1} for $x = 0.01$, 0.02 , and 0.03 , respectively, was acquired. While the increase in chlorine content in the samples reduced the discharge capacity, the shape of the charge and discharge curves did not change. This indicated that the increase in chlorine content did not affect the crystal structure of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, although there could be a minor change in the coordination between the VO_6 and PO_4 arrangement due to the introduction of the anion in the crystal lattice. This would be result in a reduced discharge capacity among the chlorine doped samples. It is worth noting that the additional charge capacity (irreversible capacity loss) obtained for the carbon coated sample was reduced due to the presence of chlorine. A positive effect on cycle stability is thus expected. Since the best discharge capacity is obtained for the $x = 0.01$ sample, further studies were focused only on three samples: pristine LVP, C-LVP, and C-LVPC.

The coulombic efficiencies of the LVP, C-LVP, and C-LVPC samples were 78%, 81%, and 91%, respectively, for the initial cycle at 0.1 mA cm^{-2} (0.1 C , considering $1 \text{ C} = 100 \text{ mA g}^{-1}$). The increase in coulombic efficiency is related to the positive effect of chlorine in the crystal structure. The rate performances of LVP, C-LVP, and C-LVPC were carried out at different current rates as follows: 0.1 C , 0.5 C , 1 C , 5 C , 10 C , and 20 C and the results are shown in Figure 3(a). The capacity retention for the samples at each current rate was significant. However, the chlorine doped sample (C-LVPC) outperformed the other samples by maintaining a higher capacity at each current rate than the capacity exhibited by LVP and C-LVP. For comparison, the discharge capacity exhibited by the C-LVPC sample at 0.5 , 1 , 5 , 10 , and 20 C was 164, 155, 125, 106, and 72 mA h g^{-1} . The C-LVP sample showed 155, 144, 114, 91, and 60 mA h g^{-1} at the same current rates, whereas the discharge capacities of 141, 113, 68, 56, and 38 mA h g^{-1} were demonstrated by pristine materials. Thus, the chlorine doped sample is better for high rate energy storage. In general, the decrease in capacity with increase in current rate is correlated to the participation of only the surface of the particles; consequently, the effective surface area for electrochemical reaction is reduced and thus the capacity retained at a high rate is decreased.²⁷

Freshly prepared cells were used for cycling studies at 0.1 mA cm^{-2} to verify the long term cycle stability

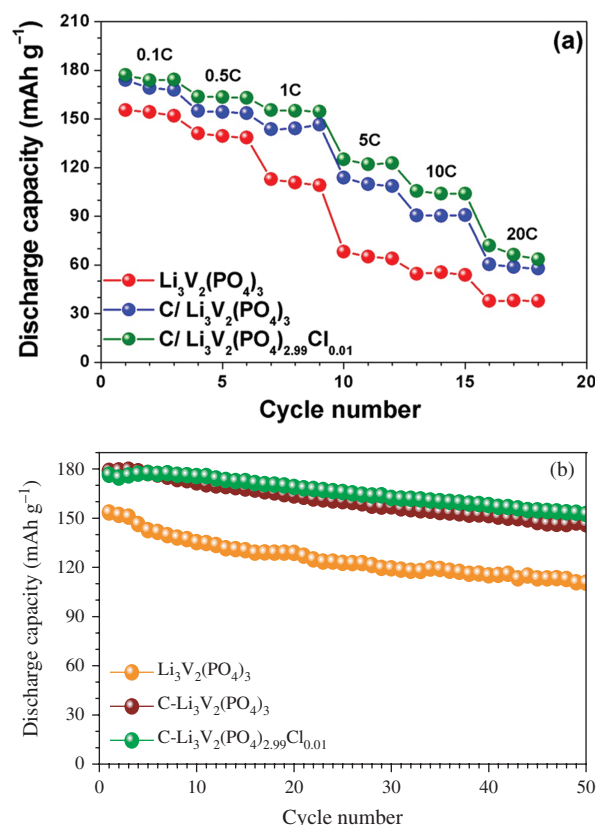


Figure 3. (a) Rate capability of LVP, C-LVP, and C-LVPC samples at different current rates cycled between 3 and 4.8 V. (b) Cycle stability of LVP, C-LVP, and C-LVPC samples at 0.1 C.

of the LVP, C-LVP, and C-LVPC samples. Figure 3(b) shows the discharge capacity versus cycle number curves of the above samples. The data clearly demonstrated the effect of chlorine on the long term cycle stability of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ samples. The pristine LVP sample exhibited 111 mA h g^{-1} after 50 cycles, while the carbon coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (C-LVP) showed 146 mA h g^{-1} , which accounted for a capacity retention of 71% and 84% when compared with the initial capacity. An appreciable discharge capacity of 153 mA h g^{-1} was demonstrated by the carbon coated-chlorine doped $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (C-LVPC) sample with a capacity retention of 87%. The marginal increase in capacity retention was obtained for a very small amount of chlorine (1%) in the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ crystals. The main advantage for doping chlorine was attributed to the increase in the coulombic efficiency (91% for C-LVPC) of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ sample, which is very important for applications such as commercial batteries. The high capacity retention after 50 cycles and high coulombic efficiency exhibited by the C-LVPC sample can be interpreted as an increase in the lithium diffusion property of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ sample. Moreover, the decrease in electrolyte decomposition at voltages above 4.5 V in the presence of chlorine was beneficial in retaining the metal ions in the crystal lattice.

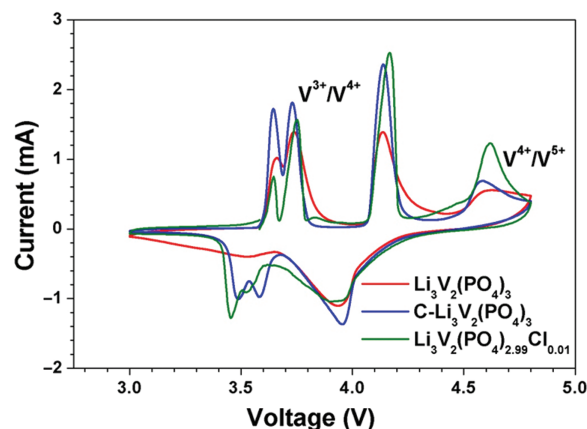


Figure 4. Cyclic voltammetric curves of LVP, C-LVP, and C-LVPC samples measured between 3 and 4.8 V at slow scan rate of 0.05 mV s^{-1} using Lithium as both counter and reference electrode.

The results obtained during galvanostatic charge/discharge studies were verified using cyclic voltammetry analysis within the same voltage range and at a slow scan rate of 0.05 mV s^{-1} . The insertion and extraction plateaus found in the charge/discharge curves were transformed to the potential peak position in the case of cyclic voltammetry. The slow scan rate used during cyclic voltammetry assisted in resolving sharp and definite peaks for all the samples as shown in Figure 4. The lithium extraction peaks were found at ~ 3.64 , ~ 3.72 , ~ 4.13 , and $\sim 4.58 \text{ V}$ during the anodic scan, while the insertion peaks during the corresponding cathodic scan were obtained at ~ 3.96 , ~ 3.58 , and $\sim 3.48 \text{ V}$. These voltage values were found to match the voltage plateaus reported in the charge/discharge studies.

In order to elucidate the conductivity of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ samples and to validate the effect of chlorine doping on electrochemical performance, electrochemical impedance spectroscopy was performed in freshly prepared cells containing LVP, C-LVP, and C-LVPC and the results are shown in Figure 5. In Figure 5, the impedance curves are characterized by a semicircle at the high-medium frequency region and by an inclined line (approximately 45°) at the low frequency region. The semicircle was interpreted as the charge transfer resistance (R_{ct}) of the active material and the inclined line indicated the lithium diffusion in the electrode. A solution resistance of $R_s = 3 \Omega$ was calculated from the high frequency intercept of the semicircle. As expected, the pristine LVP cell had the largest charge transfer resistance ($R_{\text{ct}} = 29 \Omega$). The introduction of carbon coating over the LVP particles resulted in the reduction of charge transfer resistance to a smaller extent and hence the R_{ct} of the C-LVP sample was 21Ω . When the chlorine of the $x = 0.01$ mole was mixed in the LVP along with the carbon coating, an overall $\sim 50\%$ reduction in R_{ct} ($\sim 14 \Omega$) was observed for the C-LVPC sample. This explained the improvement in electrochemical properties for the chlorine doped sample.

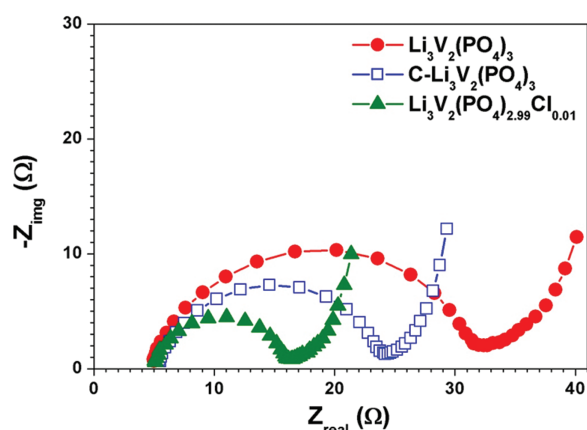


Figure 5. Electrochemical impedance spectroscopy results obtained for LVP, C-LVP and C-LVPC samples using freshly prepared cells at open circuit voltage between 100 kHz and 100 MHz.

4. CONCLUSION

The effect of chlorine doping on the electrochemical properties of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ was systematically studied. Although the initial discharge capacity obtained for C-LVP and C-LVPC is almost the same, the improvement in coulombic efficiency helped in the improvement of ionic conductivity and thereby resulted in better cycle stability. The cycle stability of the chlorine doped $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ sample was 87%, which is a comparable increase from 71% for the pristine LVP sample. The area under the curve obtained from the cyclic voltammetry curves correlated well with the capacity values obtained during the charge/discharge studies. Anion doping resulted in improved electronic conductivity because the anions induced a semi-conductivity effect in the crystal lattice. The reduced resistance observed from the electrochemical impedance spectroscopy studies was evaluated to have the positive effect of chlorine doping. Overall, carbon coating can help improve the resistance to some extent and the further improvement in conductivity can be achieved only by anion (Cl^-) doping, especially for cathodes that are operating at high voltages over 4.5 V.

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