ELECTROCHEMICAL STUDIES ON THE SYNTHESIS AND CHARACTERIZATION OF LITHIUM AND VANADIUM AND CHROMIUM PHOSPHATE COMPOUNDS

A. A. El-Aziz1, Atef Y. Shenouda1, M. M. S. Sanad1, H. F. Y. Khalil2 and M. M. B. El-Sabbah2

1Central Metallurgical R & D Institute (CMRDI), Tebbin, P. O. Box: 87 Helwan, Egypt.
2Chemistry Department Faculty of Science, Al-Azhar University, Nasr City, Egypt.

ABSTRACT

The use of monodiphosphate compounds as renewable sources of energy as positive (cathode) material for lithium-ion batteries (LIB) is considered a great target. Lithium vanadium chromium monodiphosphate (LVCPP) Li3V2.8Cr0.2(P2O7)3(PO4)2 and the Na-doped Li8.75Na0.25V2.8Cr0.2(P2O7)3(PO4)2 (LNVCPP) compounds have been prepared by using the sol-gel method. The prepared materials are characterized by XRD, FESEM, and EDX. The XRD data is indicated the presence of a single-phase of Li3V2.8Cr0.2(P2O7)3(PO4)2 and Li8.75Na0.25V2.8Cr0.2(P2O7)3(PO4)2 with trigonal structure. Both cycle performance and rate capability have shown improvement with moderate Na doping content. Li3V2.8Cr0.2(P2O7)3(PO4)2 and Li8.75Na0.25V2.8Cr0.2(P2O7)3(PO4)2 compounds presented the good electrochemical rate and cyclic ability. The cell is prepared with x=0.25 delivered a specific discharge capacity of 50 mAh g⁻¹ after 35 cycles in comparison with the other samples. The enhancement of the rate and cyclic capability may be attributed to the optimizing particle size, morphologies, and structural stability with the proper amount of Na-doping (x=0.25) in Li sites.

Keywords:
Lithium-ion battery, Cathode material, Sol-gel, and Li8.75Na0.25V2.8Cr0.2(P2O7)3(PO4)2.

1. INTRODUCTION

The demand in high energy density of lithium-ion batteries has enhanced small electronics devices during the past two decades[1]. In order to face the requirements of these lithium-ion battery technologies, many attempts were made to prepare electrode materials that can easily intercalate and transfer Li-ions at appropriate or suited potentials and a variety of oxides and polyaniionic materials have been reported [2–4]. After dealing with monoclinic LiV3(PO4)3 (LVP), which includes higher specific energy than lithium iron phosphate (LFP), vanadium oxy phosphates and vanadium phosphates are gaining substantial attention as a substitute positive material for lithium-ion batteries [2,5–8]. For example, monoclinic Li3V3(PO4)3 can deliver a theoretical capacity of 197 mAh g⁻¹ when the three Li ions are extracted at the average potential of about 4.1 V[9,10]. As recommended by Goodenough and his coworkers, the previous described material worked at a higher potential in comparison to their iron equivalent due to the inductive impact between the phosphate groups and vanadium[5]. This leads to increase the specific capacity. However, monoclinic LVP faces some problems from a great drop in structural instability and electronic conductivity with severe delithiation at high potentials[10]. This makes the extraction of the 3rd lithium ion unfeasible, consequently limiting the specific capacity to 131 mAh g⁻¹[11]. On further exploration, a new class of the novel layered monodiphosphate, Li9V3(P2O7)3(PO4)2 was used as potential positive materials for Li-ion batteries[12]. Li9V3(P2O7)3(PO4)2 has suitable layered structure and facile lithium diffusion. The theoretical capacity of Li9V3(P2O7)3(PO4)2 is 173.5 mAh g⁻¹ with six Li ions per formula extracted along the ab-plane or c-axis,-related to V⁵⁺/V⁴⁺ redox couples. Furthermore, allocated to the inductive effect of diphosphate radicals P2O7 and monophosphate radicals PO4 in the framework, Li9V3(P2O7)3(PO4)2 can display higher redox potential and good electrochemical stability during charge/discharge. This kind of material displays a
capacity of 110 mAh g⁻¹ and good cycle performance after 30 cycles over a broad operating voltage range of 2.0–4.6 V[13,14]. This new polyanionic compounds, with a twofold inner symmetry presents in the layered structure, provided rich and interesting crystal chemistry information on the electrochemical recrystallization during charge and discharge process. Although this material exhibited good capacity and reversibility after 30 cycles and may be expected to be used as another alternative cathode materials[12]. It is assumed that there are some unexplored places still exist at the doping of V site in Li₅V₃(P₂O₇)₃(PO₄)₂ systems, which influence on the structural and electrochemical properties. Inspired by these considerations, it has been sought to study the effect of part substitution of Cr in V site on the structural and electrochemical properties of the Li₅V₃(P₂O₇)₃(PO₄)₂ compounds. It is anticipated that Cr doping may allow the formation of more stable phase and improve the electrical or ionic conductivity, which would enhance the electrochemical properties, including improved specific capacity at a high rate and better or excellent cycle-life performance. The doped Li₅V₃−ₓCrₓ(P₅O₁₇)₃(PO₄)₂ compounds were synthesized by using the sol-gel method as reported for the 1st time [15]. The nine Li-ions occupy three different Li sites per molecular formula in Li₅V₃(P₂O₇)₃(PO₄)₂ as the following (Li₁(2b), Li₃(4d), and Li₅(12g)), and Li ions in site Li₁(2b) with the lowest formation enthalpy first extraction from the layered structure at ~3.7 V vs. Li [13,14,16–20]. If the Li ions in Li₁(2b) site are substituted by other steady alkali metal ions, the voltage plateau at ~3.7 V will be faded and only the voltage plateau at ~4.5 V left. If so, the charge and corresponding discharge voltage will be much improved. Taking into consideration there are six Li ions in Li₅(12g) site, which can carry out the oxidation of V⁴⁺ to V⁵⁺, thus the theoretical capacity is nearly unchanged after the substitution. Therefore, the energy density of Li₅V₃(P₂O₇)₃(PO₄)₂ can be enhanced due to the analysis of this material design. It was reported that Na ions were used to substitute the Li ions in Li₁(2b) site, since the atomic radius of Na-ion is close to that of Li-ion in all alkali metal ions[13]. Furthermore, the layered structure of Li₅V₃(P₂O₇)₃(PO₄)₂ could become unstable after extreme Li-ion extraction exactly like that of LiCoO₂ [21], and the vanadium (V⁴⁺/V⁵⁺) in Li-extracted vanadium based phosphates, such as Li₅V(P₂O₇)F₂, Li₁₆VP₂O₇ and Li₅V₃(P₂O₇)₃, are readily dissolved in the electrolyte [22–24]. LiₓNa₃V₃(P₂O₇)₃(PO₄)₂ and LiₓV₃(P₂O₇)₃(PO₄)₂ with layered structure may be more-appropriate as positive electrodes for rechargeable Li-batteries, and the Li intercalation behaviors of several phosphate cathode materials (such as Li₅V₃(P₂O₇)₃ and LiFePO₄) were investigated as well [25,26]. Therefore, the Li intercalation properties of Li₅V₃(P₂O₇)₃(PO₄)₂ were compared and presented with that of LiₓNa₃V₃(P₂O₇)₃(PO₄)₂ [27]. The aim of this work is the study of introduce of a small ratio of Na like Na₀.₂₅ that can be used to replace Li-ions. Therefore, preparation and characterization of the Li₅V₃ₓCr₀.₂(P₂O₇)₃(PO₄)₂ and Li₈.₇₅Na₀.₂₅V₃ₓCr₀.₂(P₂O₇)₃(PO₄)₂ compounds. According to the best of our knowledge, there is no work devoted Li₈.₇₅Na₀.₂₅V₃ₓCr₀.₂(P₂O₇)₃(PO₄)₂ vs. Li₅V₃ₓCr₀.₂(P₂O₇)₃(PO₄)₂ as materials obtained by sol-gel method.

2. EXPERIMENTAL

2.1. Synthesis and characterization

Li₅V₃ₓCr₀.₂(P₂O₇)₃(PO₄)₂ and Li₈.₇₅Na₀.₂₅V₃ₓCr₀.₂(P₂O₇)₃(PO₄)₂ samples for lithium-ion batteries were prepared by the sol-gel method. The solution for sol-gel method was obtained by dissolving stoichiometric ratios of lithium hydroxide (LiOH.H₂O, Sigma-Aldrich, >98.5%), sodium bicarbonate (NaHCO₃, Sigma-Aldrich,>99%), ammonium metavanadate (NH₄VO₃, Sigma-Aldrich,> 99%), chromium nitrate (Cr(NO₃)₃.9H₂O, Sigma Aldrich,>99%), and ammonium dihydrogen phosphate (NH₄H₂PO₄, Sigma-Aldrich,>99%) in distilled water and mixed well with citric acid in distilled water. The resulting precursor solution was evaporated at 80 °C under constant stirring to yield the gel. The gel was further heated until dryness and decomposition of the organic matter. After that the precursor powder was ground, then transferred into a tube.
furnace and heated at 400°C for 3 h under air atmosphere. After cooling to room temperature, the powder was ground again, and sintered at 800 °C for 7 h under flowing of mixed gas 95%Ar + 5%H₂. To reduce the crystallite size and particle size, ball milling of the as-synthesized LVCPP and LNVCPP was carried out for different time intervals.

X-ray diffraction (XRD) patterns for materials were collected on a Brucker axis D8 diffractometer with crystallographic data software Topas 2 using Cu-Kα (λ = 1.5406 nm) radiation operating at 40 kV and 30 mA. The angle scan rate was set at 2 °/min. The microstructure and morphology of the samples were characterized by Field emission electron microscope (FE-SEM QUANTAFEG 250). EDX was carried out by SEM, JEOL model JSM5040 and Inductive Coupled Plasma (ICP) with Perkin Elmer Optima 2000 DV.

2.2. Electrochemical measurements

The working electrodes (WE) for electrochemical measurements were manufactured by mixing the synthesized Li₈V₂.₈₆Cr₂.₂₈(P₂O₇)₃(PO₄)₂ and Li₈₇.₇₅Na₀.₂₅V₂.₈₆Cr₂.₂₈(P₂O₇)₃(PO₄)₂ active materials with carbon black and polyvinylidene difluoride (PVDF) in the ratio of 80:10:10 wt.% Typically, the slurry was prepared by mixing all the components in presence of N-methyl pyrrolidone (NMP) as a solvent. Then, the aluminum disk substrate (1 cm² area) was coated with this slurry to form the WE. The active material loading onto each electrode was approximately 5mg cm⁻². After being dried at 70 °C under vacuum overnight, the electrodes were transferred to an Ar-filled glove box with H₂O and O₂ content <1 ppm. The electrochemical measurements performed in coin cells where metallic Li (Sigma Aldrich, >99.9%) acted as a counter and a reference electrode. Celgard® C300 (microporous polypropylene) as a separator and 1 M LiPF₆ in EC: DMC (1:1, vol.%) were used as an electrolyte. The electrochemical capacity measurements were performed in the voltage range between 2 and 4.6 V and the electrochemical capacity of samples was evaluated using a Bitrode battery tester. Furthermore, electrochemical impedance spectroscopy measurements were applied using frequency range between 10² and 10⁶ Hz at amplitude of 10 mV using Potentiostat Model Parastat Princeton 4000.

3. RESULTS AND DISCUSSION

3.1. Material characterization

The XRD patterns of the Li₈V₂.₈₆Cr₂.₂₈(P₂O₇)₃(PO₄)₂ and Li₈₇.₇₅Na₀.₂₅V₂.₈₆Cr₂.₂₈(P₂O₇)₃(PO₄)₂ samples are shown in Fig.1. The two samples are found to be a single-phase with trigonal structure and no impurity phases can be detected under the resolution of our XRD instrument. Our results are in a good agreement with the reported one for LVCPP [28]. It is observed that a small amount substitution of Cr³⁺ for V³⁺ ions in a six-fold coordination environment, the whole diffraction peak positions almost kept consistently with Cr content. This can be explained in the light of the similarity between the ionic radii of Cr³⁺ and V³⁺ ions: rCr³⁺ = 0.615Å and rV³⁺ = 0.640 Å, respectively [15,29]. Also, the absence of diffraction peaks of impurities suggests that the final products are compounds of a single phase, indicating that doping a low amount of Na⁺ as compared by the amount of Li⁺ does not significantly affect the single structure of Li₈₇.₇₅Na₀.₂₅V₂.₈₆Cr₂.₂₈(P₂O₇)₃(PO₄)₂.

Also, the slightly change in peak position with the increase of Na content and the cell volumes of Na-doped Li₈₇.₇₅Na₀.₂₅V₂.₈₆Cr₂.₂₈(P₂O₇)₃(PO₄)₂ samples are somewhat larger than that of pristine one. Furthermore, the substitution of smaller radius of Li⁺ (r = 0.73 Å) by larger Na⁺ (r = 1.13 Å) may be responsible for the variation. Larger cell volume could supply the larger channel for transport of Li⁺ and facilitate rapid diffusion of Li⁺ in particles of the active materials, in favor of improving the electrochemical performance [27,30]. Furthermore, the crystallite size is calculated from Scherer equation[31]:

$$L = \frac{0.94λ}{β \cos θ}$$

(1)
Where; \( L \) is the crystallite size, \( \lambda \) is the wavelength of the target (1.5406 Å for Cu), \( \beta \) is full width half maximum (FWHM) and \( \theta \) is the chosen diffraction angle. The calculated crystallite size values are around 52 nm, while for \( x=0.25 \), the value is 40 nm. It is observed that 0.25 Na substitution to LCVPP gives a less crystallite size.

FESEM images of the samples are recorded in Fig. 2. The morphology of Li\(_9\)V\(_{2.8}\)Cr\(_{0.2}\) (P\(_2\)O\(_7\))\(_3\) (PO\(_4\))\(_2\) compound is dense agglomerated in the structure with a particle size of 400 to 600 nm. The addition of Na\(_x\) with \( x=0.25 \) to polyanion phosphate changes the dense aggregated crystal into a spherical small particle size of 300 to 400 nm as shown in Fig.2(b) along with the formation of nanowires. Therefore, it can be observed that the Na\(_{0.25}\) substitution for Li in Li\(_9\)V\(_{2.8}\)Cr\(_{0.2}\) (P\(_2\)O\(_7\))\(_3\) (PO\(_4\))\(_2\) material can reduce the grain size and facilitate the generation of Li\(_{8.75}\)Na\(_{0.25}\)V\(_{2.8}\)Cr\(_{0.2}\) (P\(_2\)O\(_7\))\(_3\) (PO\(_4\))\(_2\) micro wires and spheres. Similar results were reported by Kuang et. al. for Li\(_8\)Na\(_{1.0}\)-V\(_{2.8}\)Cr\(_{0.2}\) (P\(_2\)O\(_7\))\(_3\) (PO\(_4\))\(_2\) [27].

**Fig. 1** X-ray diffraction (XRD) patterns for Li\(_9-x\)Na\(_x\)V\(_{2.8}\)Cr\(_{0.2}\) (P\(_2\)O\(_7\))\(_3\) (PO\(_4\))\(_2\) (\( x=0.0 \) and 0.25).

**Fig. 2** FESEM images and EDX spectra of Li\(_9-x\)Na\(_x\)V\(_{2.8}\)Cr\(_{0.2}\) (P\(_2\)O\(_7\))\(_3\) (PO\(_4\))\(_2\) particles with different Na doping levels, \( x = 0.0 \) to 0.25 from (a) to (b), respectively.
The chemical composition of the samples is analyzed by energy dispersive x-ray spectra (EDX) as shown in Fig. 2 and inductive coupled plasma (ICP) analysis. The results are recorded in Tables 1 and 2. ICP has more accurate analysis than EDX for the stoichiometric ratios of the elements in the samples.

3.2. Electrochemical characterization

3.2.1. Electrochemical Impedance spectra

Electrochemical impedance spectra (EIS) measurements are done for the samples pellets of dimensions: radius (r) ~0.5 cm and thickness (t) ~0.2 cm to measure the bulk resistance of the materials as shown in Fig. 3. The resistance, resistivity, and conductivity of the material of the sample are listed in Table 3. It is observed that the lowest resistance and resistivity besides the highest conductivity are obtained for the pellet prepared from the Li$_{8.75}$Na$_{0.25}$VCrPP compound.

On the other hand, the electrochemical impedance spectra measurements are also carried out to have more information about the lithium-ion diffusion of Li$_{6}$V$_{2.8}$Cr$_{0.2}$ (P$_{2}$O$_{7}$)$_{3}$(PO$_{4}$)$_{2}$ and Li$_{9.5}$Na$_{0.25}$V$_{2.8}$Cr$_{0.2}$ (P$_{2}$O$_{7}$)$_{3}$ (PO$_{4}$)$_{2}$ for the cells. Fig. 4 shows the Nyquist plots of Li$_{6}$V$_{2.8}$Cr$_{0.2}$ (P$_{2}$O$_{7}$)$_{3}$(PO$_{4}$)$_{2}$ and Li$_{9.5}$Na$_{0.25}$V$_{2.8}$Cr$_{0.2}$ (P$_{2}$O$_{7}$)$_{3}$ (PO$_{4}$)$_{2}$ in the cells after one cycle at 0.2 C (theoretical capacity), when the cell materials are fully activated with keeping their open circuit voltages stable (around 3.0 V) after rest for several hours.

### Table 1. Element analysis of Li$_{6.8}$Na$_{2.8}$V$_{2.8}$Cr$_{0.2}$ (P$_{2}$O$_{7}$)$_{3}$(PO$_{4}$)$_{2}$ where x=0.0 and 0.25, materials by ICP.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Li%</th>
<th>Na%</th>
<th>V%</th>
<th>Cr%</th>
<th>P%</th>
<th>O%</th>
<th>Molecular formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$<em>{6}$V$</em>{2.8}$Cr$<em>{0.2}$ (P$</em>{2}$O$<em>{7}$)$</em>{3}$(PO$<em>{4}$)$</em>{2}$</td>
<td>6.8</td>
<td>0</td>
<td>16.2</td>
<td>1.06</td>
<td>26.3</td>
<td>49.64</td>
<td>Li$<em>{9.01}$V$</em>{2.90}$Cr$<em>{0.18}$ P$</em>{7.87}$O$_{26.79}$</td>
</tr>
<tr>
<td>Li$<em>{9.5}$Na$</em>{0.25}$V$<em>{2.8}$Cr$</em>{0.2}$ (P$<em>{2}$O$</em>{7}$)$<em>{3}$(PO$</em>{4}$)$_{2}$</td>
<td>6.56</td>
<td>0.62</td>
<td>15.6</td>
<td>1.18</td>
<td>26.54</td>
<td>48.98</td>
<td>Li$<em>{9.76}$Na$</em>{0.26}$V$<em>{2.66}$Cr$</em>{0.21}$ P$<em>{8.01}$O$</em>{28.65}$</td>
</tr>
</tbody>
</table>

* O % was calculated by subtraction from 100%

### Table 2. Element analysis of Li$_{6.8}$Na$_{2.8}$V$_{2.8}$Cr$_{0.2}$ (P$_{2}$O$_{7}$)$_{3}$(PO$_{4}$)$_{2}$, where x=0.0 and 0.25 materials by EDX.

** Li % was calculated by subtraction from 100%

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Li% **</th>
<th>Na%</th>
<th>V%</th>
<th>Cr%</th>
<th>P%</th>
<th>O %</th>
<th>Molecular formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$<em>{6}$V$</em>{2.8}$Cr$<em>{0.2}$ (P$</em>{2}$O$<em>{7}$)$</em>{3}$(PO$<em>{4}$)$</em>{2}$</td>
<td>6.787</td>
<td>0</td>
<td>12.04</td>
<td>0.96</td>
<td>26.62</td>
<td>53.593</td>
<td>Li$<em>{9.01}$V$</em>{2.75}$Cr$<em>{0.15}$ P$</em>{8.5}$O$_{11.15}$</td>
</tr>
<tr>
<td>Li$<em>{9.5}$Na$</em>{0.25}$V$<em>{2.8}$Cr$</em>{0.2}$ (P$<em>{2}$O$</em>{7}$)$<em>{3}$(PO$</em>{4}$)$_{2}$</td>
<td>6.203</td>
<td>1.57</td>
<td>17.34</td>
<td>1.26</td>
<td>27.12</td>
<td>46.507</td>
<td>Li$<em>{9.76}$Na$</em>{0.27}$V$<em>{2.62}$Cr$</em>{0.2}$ P$<em>{7.22}$O$</em>{28.99}$</td>
</tr>
</tbody>
</table>

** Li % was calculated by subtraction from 100%

### Table 3. The Resistance, resistivity, and conductivity of Li$_{6.8}$Na$_{2.8}$V$_{2.8}$Cr$_{0.2}$ (P$_{2}$O$_{7}$)$_{3}$(PO$_{4}$)$_{2}$, where x=0.0 and 0.25 materials.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Resistance(Ω)</th>
<th>Resistivity (Ω.cm)</th>
<th>Conductivity(S.cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$<em>{6}$V$</em>{2.8}$Cr$<em>{0.2}$ (P$</em>{2}$O$<em>{7}$)$</em>{3}$(PO$<em>{4}$)$</em>{2}$</td>
<td>8480</td>
<td>33284</td>
<td>3.00x10$^{-5}$</td>
</tr>
<tr>
<td>Li$<em>{9.5}$Na$</em>{0.25}$V$<em>{2.8}$Cr$</em>{0.2}$ (P$<em>{2}$O$</em>{7}$)$<em>{3}$(PO$</em>{4}$)$_{2}$</td>
<td>6560</td>
<td>25748</td>
<td>3.88x10$^{-5}$</td>
</tr>
</tbody>
</table>
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All the profiles exhibit a semicircle in the high frequency and a straight line in the low frequency. The high-frequency semicircle is related to the charge transfer process and the diameter of the semicircle is approximately equal to the charge transfer resistance \( R_{ct} \). The straight lines region at low frequencies represents the diffusion of the Li\(^+\) ion in the electrolyte-electrode interface layer towards the bulk electrode materials. The Li\(_{8.75}\)Na\(_{0.25}\)V\(_{2.8}\)Cr\(_{0.2}\)\((P_2O_7)\)\(_3\)(PO\(_4\))\(_2\) cells show the smallest \( R_{ct} \), as evidenced by the smallest diameter of semicircle as shown in Fig. 4. All the impedance parameters of the different cells are given in Table 4. The diffusion coefficient values of the lithium ions in the bulk electrode materials are calculated using Eqs. (2 and 3) \[32, 33\]:

\[
Z' = R_w + R_{ct} + \sigma_w \omega^{0.5} \tag{2}
\]

\[
D = 0.5\frac{RT}{An^2F^2\sigma_w C} \tag{3}
\]

Where \( D \) is the diffusion coefficient, \( \sigma_w \) Warburg factor can be obtained through the linear fitting of the \( Z' \) vs. \( \omega^{0.5} \) relationship within the low-frequency range, \( R \) is the gas constant, \( T \) is the absolute temperature, \( F \) is the Faraday’s constant, \( A \) is the area of the electrode surface, \( n \) is number of electron Li\(^+\)/Li, and \( C \) is the molar concentration of Li\(^+\) ions. It is indicated that Li\(_{8.75}\)Na\(_{0.25}\)V\(_{2.8}\)Cr\(_{0.2}\)\((P_2O_7)\)\(_3\)(PO\(_4\))\(_2\) has the lowest diffusion coefficient value of \( 7.14 \times 10^{-11} \) cm\(^2\)/s. Fig. 5 indicates the plot of \( Z' \) or \( Z \) versus the reciprocal square root of the lower angular frequencies, \( \omega^{0.5} \). The diffusion of the Li\(^+\) ions is so-called Warburg diffusion [32,33]. This relation is governed by Eq. (2). Thereby, it is observed that the Warburg impedance coefficient, \( \sigma_w \) is 442.49 \( \Omega \) \( \omega^{0.5} \) for Li\(_{8.75}\)Na\(_{0.25}\)V\(_{2.8}\)Cr\(_{0.2}\)\((P_2O_7)\)\(_3\)(PO\(_4\))\(_2\) which is the lowest value in comparison with the other samples, as shown in Fig. 5.

3.2.2. Potentiodynamic and galvanostatic measurements of the electrochemical cells

In order to investigate the electrochemical behavior of Li\(_9\)V\(_{2.8}\)Cr\(_{0.2}\)\((P_2O_7)\)\(_3\)(PO\(_4\))\(_2\) and Li\(_{8.75}\)Na\(_{0.25}\)V\(_{2.8}\)Cr\(_{0.2}\)\((P_2O_7)\)\(_3\)(PO\(_4\))\(_2\) cells, cyclic voltammetry (CV) is carried out in the potential range of 2.0–4.6 V vs. Li\(^+\) using a scanning rate
of 0.1 mV s\(^{-1}\) and the results are presented in Fig. 6. Three anodic peaks appeared during oxidation and are labeled as a\(_1\), a\(_2\) and a\(_3\), while two cathodic peaks are denoted as c\(_1\) and c\(_2\) occurred during reduction. The potentials for the CV peaks of Li\(_{8.75}\)Na\(_{0.25}\)V\(_{2.8}\)Cr\(_{0.2}\) (P\(_2\)O\(_7\))(PO\(_4\))\(_2\) composites are listed in Table 5. The Li\(_{8.75}\)Na\(_{0.25}\)V\(_{2.8}\)Cr\(_{0.2}\) (P\(_2\)O\(_7\))(PO\(_4\))\(_2\) cell exhibited three oxidation peaks for the following reactions:

\[
\text{Li}_8\text{V}_{2.8}\text{Cr}_{0.2}(\text{P}_2\text{O}_7)(\text{PO}_4)_2 \longrightarrow \text{Li}_8(\text{V}^{4+})_{2.8} \text{Cr}_{0.2}(\text{P}_2\text{O}_7)(\text{PO}_4)_2 + 3\text{Li}^+ + 3e^- \tag{4}
\]

\(E = 3.62\) V

Eq. (4) has a potential for de-insertion of 3 Li-atom for the first phase during the charging process. The obtained potential is in agreement with the reported one, 3.6 V [34]. Also, the oxidation of Cr\(^{3+}\) to Cr\(^{4+}\) gives a small peak at 3.7 V as follows:

\[
\text{Li}_8(\text{V}^{4+})_{2.8} \text{Cr}_{0.2}(\text{P}_2\text{O}_7)(\text{PO}_4)_2 \longrightarrow (\text{V}^{4+})_{2.8} \text{Cr}_{0.2}(\text{P}_2\text{O}_7)(\text{PO}_4)_2 + 0.2\text{Li}^+ + 0.2e^- \tag{5}
\]

\(E = 3.7\) V

The second phase of lithium deinsertion for another three atoms, takes place according to Eq. (6) beside the oxidation of V\(^{4+}\) to V\(^{5+}\). The peak observed at 4.1 V is in agreement with reported data [35]:

\[
\text{Li}_8(\text{V}^{4+})_{2.8} \text{Cr}_{0.2}(\text{P}_2\text{O}_7)(\text{PO}_4)_2 \longrightarrow \text{Li}_8(\text{V}^{5+})_{2.8} \text{Cr}_{0.2}(\text{P}_2\text{O}_7)(\text{PO}_4)_2 + 3\text{Li}^+ + 3e^- \tag{6}
\]

\(E = 4.1\) V

The reduction processes revealed three peaks at 4.49, 3.9 and 3.72 V as shown in Fig. 6. These peaks can be ascribed by the reduction of V\(^{5+}\)/V\(^{4+}\) and V\(^{4+}\)/V\(^{3+}\). Li\(_{8.75}\)Na\(_{0.25}\)V\(_{2.8}\)Cr\(_{0.2}\) (P\(_2\)O\(_7\))(PO\(_4\))\(_2\) has the smallest anodic and cathodic potential difference peaks, implying that Li\(_{8.75}\)Na\(_{0.25}\)V\(_{2.8}\)Cr\(_{0.2}\) (P\(_2\)O\(_7\))(PO\(_4\))\(_2\) has the best reversibility and electrochemical performance, in accordance of this compound.

\[
\begin{array}{|c|c|c|c|c|c|}
\hline
\text{Cells} & \text{Resistance of Electrolyte} & \text{Charge transfer resistance} & \text{Warburg impedance coefficient} & \text{Diffusion Coefficient} & \text{Current Electrode/Electrolyte interference} \\
& R_{e}(\Omega) & R_{ct}(\Omega) & \sigma_{W}(\Omega \cdot \text{cm}^2) & D(\text{cm}^2/\text{s}) & i^*(\text{A}) \\
\hline
\text{Li}_8\text{V}_{2.8}\text{Cr}_{0.2}(\text{P}_2\text{O}_7)(\text{PO}_4)_2 & 5.50 & 648.60 & 1216.52 & 9.45 \times 10^{-12} & 1.94 \times 10^{-6} & 3.95 \times 10^{-5} \\
\text{Li}_{8.75}\text{Na}_{0.25}\text{V}_{2.8}\text{Cr}_{0.2}(\text{P}_2\text{O}_7)(\text{PO}_4)_2 & 6.53 & 504.24 & 442.49 & 7.14 \times 10^{-11} & 1.99 \times 10^{-6} & 5.08 \times 10^{-5} \\
\hline
\end{array}
\]

Table 4. EIS parameters for different cells of Li\(_{8.75}\)Na\(_{0.25}\)V\(_{2.8}\)Cr\(_{0.2}\) (P\(_2\)O\(_7\))(PO\(_4\))\(_2\), where x = 0.0 and 0.25.

Table 5. Potentials for CV peaks of Li\(_{8.75}\)Na\(_{0.25}\)V\(_{2.8}\)Cr\(_{0.2}\) (P\(_2\)O\(_7\))(PO\(_4\))\(_2\), where x = 0.0 and 0.25.
Fig. 7 showed the specific charge-discharge capacity vs. voltage for the first cycle of the cells cycled at 0.05 C rate in the voltage range 2-4.8 V. There are three plateaus appeared in the charge at 3.65, 4 and 4.5 V and two plateaus appeared in the discharge process at 4.1 and 3.5 V, which are characterized the good electrochemical reactions between two phases and good agreement with the cyclic voltammetry analysis. It is observed that the 1st discharge capacity of Li$_{8.75}$Na$_{0.25}$V$_{2.8}$Cr$_{0.2}$ (P$_2$O$_7$)$_3$(PO$_4$)$_2$ gives 50 mAh g$^{-1}$. This cell delivers a greater capacity than the other cells.

Fig. 7. The voltage- capacity profile for Li$_{8.75}$Na$_{0.25}$V$_{2.8}$Cr$_{0.2}$ (P$_2$O$_7$)$_3$(PO$_4$)$_2$, x = 0.0 and 0.25) samples.

In order to investigate the effect of Na doping on the rate and cycle performance, Li$_9$V$_{2.8}$Cr$_{0.2}$ (P$_2$O$_7$)$_3$(PO$_4$)$_2$ and Li$_{8.75}$Na$_{0.25}$V$_{2.8}$Cr$_{0.2}$ (P$_2$O$_7$)$_3$(PO$_4$)$_2$ cells are cycled between 2 and 4.8 V potential windows at various current densities as shown in Fig. 8. The total of 35 cycles of charge and discharge are made in the charge/discharge curves for every cell, and the charging/discharging current rate is increased from C/20 (theoretical capacity divided by 20 hours, i.e. charging/discharging current =173.5 mAh/g/20h) to 2 C (theoretical capacity divided by 0.5 hours, i.e. charging/discharging current = 173.5 mAh/g/0.5h) after every 5 cycles. In the first 5 cycles at a lower current rate C/20, from the cycle no.6 at a C/15 rate to the cycle no.30 at 2 C, the discharge capacity of doped phase Li$_{8.75}$Na$_{0.25}$V$_{2.8}$Cr$_{0.2}$ (P$_2$O$_7$)$_3$(PO$_4$)$_2$ becomes higher than that of undoped one, and as the current rate further decreases, the rate capability is enhanced remarkably in comparison with the undoped one. The result indicates that the cycle-ability and rate performance of the lithium vanadium chromium polyphosphate can be enhanced by doping with Na. The improved electrochemical performance of the Na-doping sample is mainly related to the Li-ion transportation, good diffusion between the active materials and electrolyte and crystallite size of this compound.

Fig. 8. cycle life for specific discharge capacity performance of Li$_{9-x}$Na$_x$V$_{2.8}$Cr$_{0.2}$ (P$_2$O$_7$)$_3$(PO$_4$)$_2$, (x = 0.0 and 0.25) cells at various discharge rates in the voltage range of 2.0–4.8 V.

**CONCLUSION**

Li$_9$V$_{2.8}$Cr$_{0.2}$ (P$_2$O$_7$)$_3$(PO$_4$)$_2$ and Li$_{8.75}$Na$_{0.25}$V$_{2.8}$Cr$_{0.2}$ (P$_2$O$_7$)$_3$(PO$_4$)$_2$ have been successfully synthesized by the sol-gel method. The XRD results indicated that single-phase of Li$_9$V$_{2.8}$Cr$_{0.2}$ (P$_2$O$_7$)$_3$(PO$_4$)$_2$ and Li$_{8.75}$Na$_{0.25}$V$_{2.8}$Cr$_{0.2}$ (P$_2$O$_7$)$_3$(PO$_4$)$_2$ materials with trigonal structure can be obtained. The electrochemical properties of Li$_9$V$_{2.8}$Cr$_{0.2}$ (P$_2$O$_7$)$_3$(PO$_4$)$_2$ and Li$_{8.75}$Na$_{0.25}$V$_{2.8}$Cr$_{0.2}$ (P$_2$O$_7$)$_3$(PO$_4$)$_2$ phases have been investigated. Furthermore, the EIS parameters have the Na-doped sample with Na$_{0.25}$. Also, the CV of the cell compound has higher density content among the other cells. The doping of Li sites by the proper amount of Na$^+$ would be favorable for structural stability of Li$_9$Na$_x$V$_{2.8}$Cr$_{0.2}$ (P$_2$O$_7$)$_3$(PO$_4$)$_2$ where x=0.25 and thus can be counteracted the volume shrinking/swelling during the Li$^+$ reversible extraction/insertion resulting in the improvement of the cyclic ability. It is suggested that the partial substitution of Li with Na at x = 0.25 would be favorable for electrochemical performance and cyclic ability due to the enhancement of the structural stability of Li$_9$Na$_x$V$_{2.8}$Cr$_{0.2}$ (P$_2$O$_7$)$_3$(PO$_4$)$_2$.  

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where x=0.25, thereby optimizing the particle size and shape.

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الملخص العربي

الدراسات الكهروكيميائية على تحضير وتوصف مركبات فوسفات الليثيوم والفانديوم والكروم

يعتبر استخدام مركبات احادية وثنائية الفوسفات كمصادر للطاقة المتجددة كأقطاب موجبة في بطاريات اي و ليي وم هدفا عظيماً. تم تحضير مركبات الليثيوم فانديوم كروم احادي وثنائي الفوسفات المطعمة والغير مطعمة بصالوديوم بطريقة الـ sol-gel. تم عمل توصيف لهذه المركبات باستخدام حيود الأشعة السنية والمجهر الإلكتروني الاحترافي ومطيافيةUNCHT السينية. من خلال تحليل حيود الأشعة السينية تبين أن هذه المركبات تحتوي على طور واحد ذا هيكل ثلاثي. بعد اجراء عمليات الشحن والتفريغ للبطاري ات المحتوى علي اقطاب موجبة من هذه المركبات تبين علي مستوا 35 دورة شحن وتفريغ ومع تدوم في شدة التيار أن المركبات المطعمة بالصالوديوم بنسبة (0.25) ذات اداء أفضل من الغير المطعمة. المركبات المطعمة بالصالوديوم وصلت سعة تخزين الكهربائي 50mGh/g ويرجع ذلك الى ثبات الهيكل والقدرة علي تخزين الطاقة بشكل أفضل التي تتميز بها المركبات المطعمة بالصالوديوم عن نظيرتها الغير مطعمة.