Investigation of the Reversible Intercalation/Deintercalation of Al into the Novel Li₃VO₄@C Microsphere Composite Cathode Material for Aluminum-Ion Batteries

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Supporting Information

ABSTRACT: The Li₃VO₄@C microsphere composite was first reported as a novel cathode material for rechargeable aluminum-ion batteries (AIBs), which manifests the initial discharge capacity of 137 mAh g⁻¹ and remains at 48 mAh g⁻¹ after 100 cycles with almost 100% Coulombic efficiency. The detailed intercalation mechanism of Al into the orthorhombic Li₃VO₄ is investigated by ex situ X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) of Li₃VO₄@C electrodes and the nuclear magnetic resonance aluminum spectroscopy (²⁷Al NMR) of ionic liquid electrolytes in different discharge/charge states. First-principle calculations are also carried out to investigate the structural change as Al inserts into the framework of Li₃VO₄. It is revealed that the Al/Li₃VO₄@C battery goes through electrochemical dissolution and deposition of metallic aluminum in the anode, as well as the insertion and deinsertion of Al³⁺ cations in the cathode in the meantime. The rechargeable AIBs fabricated in this work are of low cost and high safety, which may make a step forward in the development of novel cathode materials based on the acidic ionic liquid electrolyte system.

KEYWORDS: aluminum-ion battery, ionic liquid, cathode, Li₃VO₄@C, mechanism

INTRODUCTION

Lithium-ion batteries (LIBs) have been deemed one of the most promising energy conversion and storage systems on account of its high operating voltage, high energy density, and long cycle life. Nevertheless, with the widespread promotion and application of LIBs all over the world in recent decades, lithium resources are faced with the risk of drying up, so the price of lithium metal is rising significantly year by year. Therefore, with the widespread promotion and application of LIBs all over the world in recent decades, lithium resources are faced with the risk of drying up, so the price of lithium metal is rising significantly year by year. However, commercial LIBs usually use carbonates like ethylene carbonate (EC), diethyl carbonate (DEC), and dimethyl carbonate (DMC) as electrolyte solvents, which as flammable and combustible organic solvents will bring potential safety hazards to LIBs. Therefore, it is imperative to find a substitute for LIBs to meet the requirements of high safety and large-scale energy storage systems.

Aluminum-ion batteries (AIBs) have recently attracted significant interest because aluminum is the most abundant metallic element and aluminum resources are evenly distributed in Earth’s crust. In addition, the AIBs with multivalent metal ions transmitting internally can provide a very high capacity (2.98 Ah/g and 8.05 Ah/cm³). Moreover, ionic liquids as electrolyte of AIBs can greatly improve the safety performance of the battery since its nonflammability and wide electrochemical window. Hence, it is reasonable to conclude that the AIBs will have a great application prospect and value in use for large-scale smart grid energy storage systems and car batteries that are at risk of collision and explosion. Up to now, the exploration of AIBs is still in early stage. As an important component of the rechargeable AIBs, Al-storage cathode materials have been most lately researched. There are several papers about the Al-ion battery cathode materials reported to date, involving the conversion electrodes such as FeS₂, Ni₃S₂, and electrodes based on intercalation reactions like graphite materials, Mo₆S₈, and Prussian blue analogues (PBAs). Owing to the strong electrostatic repulsion between Al³⁺ ions, it should be difficult for aluminum ions to intercalate into the frame structure of active materials. To sum up, a suitable intercalation electrode needs a large enough 2D or 3D framework and wide insertion/extraction channel to accommodate Al embedding back and forth quickly and a material structure which can remain stable in long cycling. Most recently, Li₃VO₄ has been massively reported as a promising anode material for LIBs due to its long cycle life and high reversible capacity. The framework of Li₃VO₄ can be counted as a hollow lanternlike 3D structure which consists of orderly corner-shared VO₄ and LiO₄ tetrahedrons, and there...
there are many empty sites in the hollow lanternlike 3D structure to accommodate ions inserting reversibly,9 which is shown in Figure 1g. The dynamic diameter of center space is 3.29 Å, much larger than the radius of Al\(^{3+}\) cations (0.59 Å) but smaller than the size of AlCl\(^{4-}\) (5.28 Å).13,20 Hence, Li\(_3\)VO\(_4\) can be a favorable intercalation electrode material for rechargeable AIBs, and predominantly Al\(^{3+}\) cations insert into the structure of Li\(_3\)VO\(_4\) upon discharging.

Herein, we report for the first time the fabrication of mesoporous Li\(_3\)VO\(_4\)@C hollow spheres composite as a novel cathode material for rechargeable AIBs. The initial discharge capacity of Al/Li\(_3\)VO\(_4\)@C battery is 137 mAh g\(^{-1}\) and remains at 48 mAh g\(^{-1}\) after 100 cycles with the Coulombic efficiency of near 100%. A pair of redox peaks in cyclic voltammogram show that Al reversibly intercalates/deintercalates into one kind of crystallographic sites of Li\(_3\)VO\(_4\), which is also supported by theoretical calculation. Meanwhile, ex situ X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) of Li\(_3\)VO\(_4\)@C electrodes and the nuclear magnetic resonance aluminum spectroscopy (\(^{27}\)Al NMR) of ionic liquid electrolyte in different states are carried out to evaluate the detailed intercalation mechanism of Al into the orthorhombic Li\(_3\)VO\(_4\). It may be reasonable to conclude that the battery undergoes electrochemical deposition and dissolution of metallic aluminum in the anode, as well as the insertion and deinsertion of Al\(^{3+}\) cations in the cathode. This work not only puts forward a novel cathode material for AIBs but also deepens the comprehension on the discharge–charge mechanism which is instructive to design new electrode materials for AIBs.

Figure 1. (a) XRD patterns and (b) Raman spectra of the as-prepared Li\(_3\)VO\(_4\)@C and Li\(_3\)VO\(_4\). (c, d) SEM images of Li\(_3\)VO\(_4\)@C composite. (e) TEM image and SAED pattern (inset) of Li\(_3\)VO\(_4\)@C composite. (f) HR-TEM image of Li\(_3\)VO\(_4\)@C. (g) Crystal structure of Li\(_3\)VO\(_4\) projected along a-axis. Color code: Li, green; V, dark blue; O, red.
RESULTS AND DISCUSSION

The sample composition and crystal structure of as-synthesized Li₃VO₄ and Li₃VO₄@C were measured by XRD, and the obtained patterns are given in Figure 1a. The diffraction lines of both samples perfectly match with the orthorhombic Li₃VO₄ (space group: Pnm2₁) with lattice parameters \( a = 5.45 \) Å, \( b = 6.33 \) Å, \( c = 4.95 \) Å and \( V = 170.54 \) Å³ (Powder Diffraction File (PDF) No. 38−1247, Joint Committee on Powder Diffraction Standards (JCPDS), 2004). No apparent impure diffraction lines can be observed from the XRD patterns, and the carbon layer coated on the Li₃VO₄ particles is likely to be amorphous since no diffraction peaks ascribed to crystalline carbon can be found in the XRD patterns. Figure 1b shows the Raman spectra of as-prepared samples. The peaks located from 200 to 500 cm⁻¹ and from 760 to 950 cm⁻¹ can be ascribed to the vibration of the Li₃VO₄ crystal lattice. Two broad peaks near 1358 and 1600 cm⁻¹ in the Raman spectra of Li₃VO₄@C are in accord with the disorder (D-band) and graphite (G-band) phases of carbon,²³ and there is no vibration peak of Li₃VO₄ can be detected in Li₃VO₄@C sample. The main reason may be that the superficial carbon layer is too thick to be penetrated by a laser wavelength of 532 nm. A laser wavelength of 638 nm or increasing laser intensity can detect the vibration of Li₃VO₄, as shown in Figure S4. High-resolution transmission electron microscopy (HR-TEM) of Li₃VO₄@C (Figure 1f) can also testify to this assumption.

Field-emission scanning electron microscopy (FESEM) and TEM were performed to obtain the morphology information on synthetic products. Figure S3a,b indicates the SEM images of pristine Li₃VO₄ particles, which are microspheres ranging from 0.5 to 10 μm in diameter with poriferous and hollow structures. Figure 1c,d are SEM images of Li₃VO₄@C composites, and it is easy to see from the smooth surface of spheres that there is a carbon layer coated on the Li₃VO₄ particles and that the diameters are between 0.5 to 5 μm which means the coated carbon layer can inhibit the growth of spheres. As shown in Figure 1e, the TEM image expressly

Figure 2. Electrochemical characterizations of Al/Li₃VO₄@C batteries. (a) Initial discharge/charge curves at a current density of 20 mA g⁻¹. (b) Galvanostatic discharge−charge profiles at a current density of 20 mA g⁻¹ from the second to the fourth cycle. (c) Cycle performance with Coulombic efficiency at a current density of 20 mA g⁻¹. All capacity calculations are based on the mass of Li₃VO₄@C. The mass of the active materials mainly ranges from 2.0 to 2.5 mg, and the area of electrodes is 1 cm². (d) Cyclic voltammogram (CV) of Li₃VO₄@C composite at the scan rate of 0.1 mV s⁻¹. (e) CV curves of Li₃VO₄@C composite at different scan rates ranging from 0.1 to 0.6 mV s⁻¹. (f) Fitted lines of \( i_p \) and \( v^{1/2} \) of reduction peak 1.
reveals the hollow structure of Li3VO4@C microspheres. The selected area electron diffraction (SAED) pattern (the inset of Figure 1e) of the Li3VO4@C particles demonstrates that Li3VO4 in the composites has a polycrystalline structure as the diffraction spots can be distinctly observed. From the HR-TEM image (Figure 1f) of the Li3VO4@C particle, it can be easily inferred that the thickness of the coated carbon layer is approximately 5 nm, and the carbon layer shows an amorphous and porous structure, which is also deduced by XRD pattern. The lattice fringe spacing of 0.41 nm is consistent with the (110) plane of orthorhombic Li3VO4 (PDF No. 38–1247, JCPDS, 2004). According to previous work from our group, the Li3VO4@C composites have a mainly mesoporous structure combined with a narrow pore size distribution of approximately 3.9 nm. Al can get through the porous carbon layer to participate in the insertion/extraction reaction with Li3VO4.

To investigate the electrochemical performance of as-prepared samples of ALBs, the galvanostatic discharge/charge measurements were executed in a voltage range of 0.05–0.95 V and at a current density of 20 mA g–1. Figure 2a indicates the initial cycle of discharge/charge curves. The initial discharge/charge capacity is 137 and 85 mAh g–1, respectively, with the Coulombic efficiency of 62%, which is similar to that of the LIBs (64%). Figure 2b shows the discharge/charge currents of the same battery from the second to the fourth cycle. What is the most noteworthy is that the completely overlapped discharge and charge platforms exist at 0.5 and 0.7 V, respectively, which conform to the insertion and extraction of Al in the framework of Li3VO4. The discharge/charge capacities for the second cycle are 98 and 74 mAh g–1 with a Coulombic efficiency of 76%. The irreversible capacity loss can be ascribed to the possibility that Al3+ ions are trapped in the framework of Li3VO4 and cannot be extracted to contribute charge capacities, which can be displayed intuitively in the XPS spectra of Al 2p after discharge and charge process (Figure S11). The similar phenomenon is also observed in other metallic oxide systems.

In the third and fourth cycles, the discharge capacities are reduced to 84 and 76 mAh g–1, respectively. The cycling performance along with corresponding Coulombic efficiency are revealed in Figure 2c at the current density of 20 mA g–1, from which it can be illustrated that the capacity decreases relatively slowly, and the electrode indicates a high reversible capacity of over 48 mAh g–1 after 100 cycles with Coulombic efficiency close to 100%. In short, the Li3VO4@C electrodes exhibit superb structure stability in electrochemical cycling. CV curves of Li3VO4@C and Li3VO4 electrodes are also performed between 0.05 and 0.95 V at a scan rate of 0.1 mV s–1 (Figures 2d and S10b) with aluminum foil as counter and reference electrodes. A distinct reduction peak (R) shows at 0.37 V, while an oxidation peak (O) arises around 0.81 V, which is in agreement with the discharge and charge plateaus, indicating that the reaction proceeds in one step, and a pair of current peaks can be assigned to Al reversibly intercalating/deintercalating into one kind of crystallographic sites of Li3VO4. The subsequent overlapped curves manifest the excellent electrochemical reversibility of Li3VO4@C electrode in aluminum-ion battery. Figure S10a,b also shows the electrochemical characterizations of pristine Li3VO4. The initial discharge/charge capacities at the current density of 20 mA g–1 are merely 106 and 37 mAh g–1, far below the Li3VO4@C electrode. The intensities of the peak current in the CV curves of Li3VO4 electrode are much weaker, and the potential shifts of the repeated cycling are much more distinct than that of Li3VO4@C electrode. The results mentioned above may attribute to the structural superiority of Li3VO4@C composite. According to our previous work,24 the carbon layer covering the spheres can not only promote the electronic conductivity of material but also regulate the size of sphere particles. Furthermore, the geometric structure of mesoporous hollow sphere can enlarge the contact area between electrolyte and active material and reduce the ion diffusion distance. The electrochemical effects of stainless-steel current collector26,27 and polyvinylene difluoride binder25,28,30 on Al/AlCl3–[EMIm]Cl/Li3VO4 battery system have been elaborated upon in Figures S5–S7.

In order to better research the electrochemical performance of electrode materials, CV analyses of Li3VO4@C and Li3VO4 at different scan rates were carried out, as indicated in Figures 2e and S10c, respectively. As the scan rate increases, the reduction peaks slowly shift toward lower potential, while the oxidation peaks shift toward higher potential, suggesting the enlarged polarization of battery which is also common in other battery systems.31 In Figure 2f, Li3VO4@C electrode manifests the better linear relationship (R2 = 0.9979) between the reduction peak current (iR) and the square root of scan rate (ν1/2), and Figure S8 demonstrates the linear relationship between log(iR) and log(ν) plots at different redox states, the obtained b values of peak 1 (reduction) and peak 2 (oxidation) are 0.5752 and 0.5479, respectively, approximately 0.5, which illustrates the electrochemical reactions in discharge/charge process are mainly ionic diffusion controlled.32,33 Therefore, the apparent ion diffusion coefficient can be approximately calculated on the basis of the Randles–Sevcik equation:

$$i_p = 0.4463nFAC \left( \frac{nFvD}{RT} \right)^{1/2}$$

where n equals the number of electrons transferred in the redox reaction which usually equals 3 in aluminum-ion batteries, F is Faraday constant (96 485 C mol–1), A is the effective surface area between the active material and the electrolyte (1 cm2), C stands for Al3+ concentration in the electrolyte (3.053 × 10–3 mol cm–3), ν is the scan rate, R is the gas constant (8.314 J K–1 mol–1), and T is the Kelvin temperature.25,34,35 According to the slope of iR–ν1/2 plots, the apparent diffusion coefficient of reduction peak 1 is calculated to be 1.928 × 10–12 cm2 s–1, which is approximately 8.6-fold that of Li3VO4 (2.233 × 10–13 cm2 s–1), showing the better electrode kinetics of Li3VO4@C. Therefore, it can be concluded that the Li3VO4@C composite improves the aluminum ion diffusion rate, which further accounts for better electrochemical performance of Li3VO4@C electrodes. In addition, galvanostatic intermittent titration technique (GITT) measurement was also carried out to investigate the aluminum ion diffusion coefficients of Li3VO4@C electrode in different discharge states; as demonstrated in Figure S9, the Al-ion diffusion coefficients of Li3VO4@C electrode lie in the range of 1.198 × 10–12–5.557 × 10–15 cm2 s–1, which is comparable with the apparent diffusion coefficients obtained from CV tests.

Judging from the discharge/charge mechanism of Li3VO4 in aluminum-ion active materials (xAl3+ + Li3VO4 + 3xe– → AlxLi1-xVO4), it is notable that the insertion of Al into the framework of Li3VO4 will be companied by the reduction of V5+, and the valence state of V in Li3VO4 can distinctly reflect x in AlxLi1-xVO4. Therefore, XPS spectra of Li3VO4@C electrodes in
different states were characterized to further investigate the electrochemical reaction process. As indicated in Figure 3a, for the fresh Li3VO4@C electrode, three successive peaks near 25.4, 24.6 (V\(^{\text{3+}}\)), and 23.7 eV (V\(^{\text{4+}}\)) agree well with V 2p\(_{1/2}\) and another three continuous peaks near 17.8 (V\(^{\text{5+}}\)), 17.1 (V\(^{\text{5+}}\)), and 16.5 eV are in correspondence with V 2p\(_{3/2}\). The existence of V\(^{\text{5+}}\) may be due to the partial reduction of V\(^{\text{5+}}\) to V\(^{\text{4+}}\) by the carbon source during the heat treatment process. For comparison, the fitted curves of the V 2p spectra for fully discharged and fully charged Li3VO4@C electrodes are indicated in Figure 3b,c, respectively. It is apparent that all the fitted peaks of fully discharged electrode reveal an apparent shift toward the low binding energy region. Simultaneously, the peak area of V\(^{\text{5+}}\) (516.7 eV) decreases, and the peak area of V\(^{\text{4+}}\) (517.3 eV) increases, indicating the reduction of V\(^{\text{5+}}\) to V\(^{\text{4+}}\) in the discharge process. After the Li3VO4@C electrode is initially charged to 0.95 V, all these fitted peaks move toward its original peak positions, and the peak area ratio of V\(^{\text{5+}}\) to V\(^{\text{4+}}\) is close to the original electrode, suggesting the oxidation of V\(^{\text{4+}}\) to V\(^{\text{5+}}\) in the charge process. On the basis of the results discussed above, it may be reasonable to conclude that Li3VO4@C can highly maintain the stability of structure in the intercalation/deintercalation of Al into the framework of Li3VO4. Figure S11 displays the XPS spectra of Al 2p in different states, which can visually show that the concentration of Al is augmented with the increasing of discharge depth and reduced with the increase of charge depth, which further indicates that Al can insert/extrude reversibly from the materials.

To get further insight into the structural reversibility of Li3VO4@C upon Al intercalation/deintercalation, the ex situ XRD measurements of electrodes at different insertion/deinsertion states were executed, as shown in Figure 3d. It is worth noting that the continuous three diffraction peaks at 21.65, 22.95, and 24.46° match well with the (110), (011), and (101) planes of orthorhombic Li3VO4 (PDF No. 38−1247, JCPDS, 2004). The peak intensities are slowly reduced with the increasing discharge depth, and the diffraction peaks shift to slightly lower degrees. It is easy to see from Figure 3e that the displacement distance toward the left is approximately 0.19 Å, showing the increasing of d space (about 0.03 Å calculated by Bragg equation), and the crystallinity of electrode materials is decreasing along with the insertion of Al into Li3VO4@C. In the subsequent charge process, the diffraction peak intensities are slowly aggravating, but they are slightly lower than that of the original electrode. The d-spacing distance basically has no change. Figure S12 clearly indicates that the crystallinity of electrode materials decreases and that the displacement distance still retains about 0.2° after 70 cycles. On the basis of the results, it is easy to conclude that the structure of Li3VO4@C will slightly distort irreversibly to accommodate the insertion of Al\(^{3+}\) in the initial cycle and remain stable in the subsequent cycles. However, such decrease in crystallinity of electrode materials is an accumulation process upon repeated Al intercalation and deintercalation during the discharge/charge cycling. Therefore, the gradual deterioration of crystallinity upon cycling may account for the capacity loss of Li3VO4@C electrode in the subsequent cycles. This phenomenon also occurs in LIBs with Li3VO4 as anode material.

First-principle calculations are available to further unravel the mechanism how aluminum ion intercalated into the Li3VO4\(_{\text{x}}\). As mentioned in CV curves, Al can reversibly intercalate/deintercalate into one kind of crystallographic site of Li3VO4\(_{\text{x}}\) which possesses two possible insertion sites to hold Al (shown in Figure 4a). Corresponding theoretical calculations were performed to elucidate which site is preferred. We optimized structures of Al-Li3VO4\(_{\text{x}}\) with Al in the a or b site, respectively. The results are shown in Table 1. The calculated lattice parameters of Li3VO4\(_{\text{x}}\) fit well with its experimental data, which means the calculation setting and the model are reliable. It is also obvious that the calculated free energy for Al intercalated into the a and b sites are −4.35 and −3.22 eV, respectively, suggesting that Al is more stable in the a site. The changes of all lattice parameters of Li3VO4\(_{\text{x}}\) when Al is inserted into the a site, are almost 0.1 Å as verified by XRD, indicating
that limited amount of Al inserted into a site does not result in overexpansion of the structure. The main reason may be that the attractive force between Al and O is much stronger than that of Li and O, and inserted Al will attract eight O atoms nearby, causing a certain volume shrinkage. However, the repulsive force between the inserted Al and V/Li will cause volume expansion; ultimately, the volume change is not obvious when a certain amount of Al intercalated into a site.

In consideration of the experimental amount of Al inserted into Li3VO4 being less than 1/2 (calculation based on capacities), the optimized model of Al1/3Li3VO4 is also shown in Table 1, indicating less structural changes than Al1/2Li3VO4.

The morphology and composition characterizations of Li3VO4@C electrodes before and after electrochemical tests have also been measured to investigate the changes of cathode materials. Figure 5 shows the TEM images and corresponding HRTEM images of the Li3VO4@C cathode materials in different discharge/charge states. It can be observed that the morphology of spheres is still well-maintained upon initial discharge/charge process; of note is that the microsphere morphology of Li3VO4@C after 100 cycles is also well-maintained (Figure S14), which confirmed the excellent structural stability of Li3VO4@C in long cycling. The relevant HRTEM images after initial discharge and charge are exhibited in Figure 5c,d, and the distinct lattice fringes illustrate that Li3VO4@C still retains crystallinity to a certain extent. Thereinto, the lattice fringe spacing of 0.24 and 0.36 nm in Figure 5c match well with the d-spacing of (002) plane and (101) plane of the orthorhombic Li3VO4, and 0.31 nm in Figure 5d agrees well with the d-spacing of (111) plane.9,36

Figure S13 indicates the correlative SAED patterns in different discharge/charge states. The blurry SAED rings in Figure S13d show the crystallinity of material decreases after discharged to 0.05 V, and the SAED ring patterns in Figure S13f can match well with those of (011) and (200) planes,45 which manifests the reinstatement of crystallinity in the charge process. Energy-dispersive X-ray spectroscopy (EDS) of the electrode after initial discharge process displayed in Figure S13g distinctly reveals the presence of C, V, O, and Al elements. Figure 6 exhibits the corresponding EDS mapping of Li3VO4@C electrode after discharged to 0.05 V, the C, O, V, and Al elements coexist and evenly distribute in the spheres.

To further explore the electrochemical reaction process taking place in Al/Li3VO4@C battery system, 27Al NMR spectra of the AlCl3/[EMIm]Cl ionic liquid electrolytes in different states were obtained to investigate the ionic compositions and the corresponding contents in discharge/charge process. As shown in Figure 7, one broad peak at 103.95 eV for AlCl3 [EMIm]Cl ionic liquid electrolytes, which is consistent with the previous results.46

Table 1. Lattice Parameters for Li3VO4 (Experimental and Calculated) and AlxLi3VO4

<table>
<thead>
<tr>
<th>structure</th>
<th>a, b, c (Å)</th>
<th>α, β, γ (deg)</th>
<th>ΔG (eV)</th>
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</thead>
<tbody>
<tr>
<td>Li3VO4</td>
<td>6.3259(12), 5.4460(8), 4.9460(9)</td>
<td>90.0, 90.0, 90.0</td>
<td></td>
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<tr>
<td>Li3VO4</td>
<td>6.38289, 5.50061, 5.03147</td>
<td>90.0, 90.0, 90.0</td>
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<tr>
<td>Li3Al1/2VO4 (a)</td>
<td>6.22159, 5.51365, 5.07447</td>
<td>91.4, 90.0, 90.0</td>
<td>−4.35</td>
</tr>
<tr>
<td>Li3Al1/2VO4 (b)</td>
<td>6.61605, 5.50503, 5.07852</td>
<td>89.9, 87.2, 88.7</td>
<td>−3.22</td>
</tr>
<tr>
<td>Li3Al1/3VO4 (a)</td>
<td>6.21805, 5.55101, 5.11558</td>
<td>90.4, 90.0, 90.0</td>
<td>−4.09</td>
</tr>
</tbody>
</table>
ppm and the comparatively small peak at 98.15 ppm for the electrolyte of AlCl3/[EMIm]Cl = 1.3:1 can be assigned to AlCl₄⁻ and Al₂Cl₇⁻, respectively, showing that both AlCl₄⁻ and Al₂Cl₇⁻ are major anions in the acidic ionic liquid electrolyte before and after electrochemical tests. The ratio of AlCl₄⁻ to Al₂Cl₇⁻ is calculated as approximately 6.98:1 in the original ionic liquid, but the ratio decreases to nearly 3.61:1 after initial discharge which reflects the AlCl₄⁻ anions in electrolyte reacting with Al³⁺ to form larger Al₂Cl₇⁻ anions.

Also, the ratio of AlCl₄⁻ to Al₂Cl₇⁻ in electrolyte increases to 5.45:1 as charged to 0.95 V, which represents the reverse reaction process. As described above, the discharge/charge reaction process of the Al/AlCl₃-[EMIm]Cl/Li₃VO₄@C battery system can be formulated as the following equations:

In the discharge process:
- **Cathode:**
  \[ \text{Li}_3\text{VO}_4 + x\text{Al}^{3+} + 3xe^- \rightarrow \text{Al}_x\text{Li}_3\text{VO}_4 \]  \( \text{(2)} \)
- **Anode:**
  \[ \text{Al} + 7\text{AlCl}_4^- - 3e^- \rightarrow 4\text{Al}_2\text{Cl}_7^- \]  \( \text{(3)} \)

In the charge process:
- **Cathode:**
  \[ \text{Al}_x\text{Li}_3\text{VO}_4 - 3xe^- \rightarrow \text{Li}_3\text{VO}_4 + x\text{Al}^{3+} \]  \( \text{(4)} \)
- **Anode:**
  \[ 4\text{Al}_2\text{Cl}_7^- + 3e^- \rightarrow \text{Al} + 7\text{AlCl}_4^- \]  \( \text{(5)} \)

Hence, the schematic illustration of the aluminum-ion battery during the discharge process is revealed in Figure 8.

### CONCLUSIONS

Li₃VO₄@C microsphere composite exhibits the ability to insert Al reversibly with acidic ionic liquid as electrolyte. The initial discharge capacity of Al/Li₃VO₄@C battery is 137 mAh g⁻¹ and remains at 48 mAh g⁻¹ after 100 cycles with the Coulombic efficiency close to 100% at the current density of 20 mA g⁻¹. Furthermore, the detailed intercalation mechanism of Al into the orthorhombic Li₃VO₄ was characterized by ex situ XRD and XPS spectra of Li₃VO₄@C electrodes and the ²⁷Al NMR spectra of ionic liquid electrolyte in different states. It is easy to conclude that the structure of Li₃VO₄@C will slightly distort irreversibly to accommodate the insertion of Al in the initial cycle and remain stable in the subsequent cycles. The first-principle calculations also elucidate Al mainly inserts into a site...
of Li₃VO₄, and there are scarcely any structural changes after intercalation. Even though the battery system in this work suffers from low capacity and low discharge plateau, such rechargeable AIBs are cost-saving, and still may make a step forward in the development of novel cathode materials based on acidic liquid electrolyte system.

**EXPERIMENTAL SECTION**

**Preparation of Composite.** The mesoporous Li₃VO₄@C hollow spheres were prepared by a spray-drying process and subsequent heat treatment in argon atmosphere. In a typical synthesis, 6 mmol of Li₂CO₃ (0.444 g), 2 mmol of V₂O₅ (0.364 g), and 0.9 g of glucose were added into 70 mL of distilled water. After magnetic stirring for 12 h, the whole preparation process was operated under an argon-atmosphere glovebox (M. Braun, Germany). The molar ratio of AlCl₃ to [EMIm][Cl] varied from 0.8 to 1.5. The ²⁷Al NMR spectra of room-temperature liquid electrolytes were recorded on the Bruker Avance II 400 spectrometer with 1.0 M Al(NO₃)₃ aqueous solution as the external chemical shift standard. In addition, as-synthesized liquid electrolytes were characterized by Fourier transform infrared spectrometer (Nicole iS5). Cyclic voltammetry (CV) was evaluated by soft package battery tester (Neware CT-3008W, Neware Battery Testing Instruments, PR China) at a scan rate of 0.1 mV/s. Al electrode was used as the counter and reference electrodes, while Au foil was used as the working electrode. Al electrode was treated by polishing with fine sand paper, followed by rinsing in acidic electrolyte for 5 min to remove the oxide layer on the surface of metallic aluminum.

**Electrochemical Measurements.** The electrochemical properties of the as-prepared mesoporous Li₃VO₄@C hollow spheres were measured in 1 cm × 1 cm soft package battery with metallic aluminum as anode material. The cathode material was a slurry consisting of 70 wt % active material (Li₃VO₄@C, ~100 mg), 20 wt % acetylene black, and 10 wt % polyvinylidene difluoride binder in N-methyl-2-pyrrolidinone (NMP). The slurry was coated on the stainless-steel substrate. The precursors were annealed at 550 °C for 5 h in argon atmosphere; Li₃VO₄@C hollow spheres were obtained. The pristine Li₃VO₄ was synthesized by a similar method in the absence of glucose.

**Synthesis of Ionic Liquid Electrolytes.** The ionic liquid electrolytes ([EMIm][AlCl₃]) were prepared by slowly dissolving anhydrous aluminum chloride (AlCl₃, 99%, Aladdin) in heat-treated 1-ethyl-3-methylimidazolium chloride ([EMIm][Cl], 98%, Aladdin). The obtained transparent light-yellow liquid was magnetically stirred at room temperature for several minutes, followed by standing for at least 12 h. The electrochemical properties of the as-prepared mesoporous Li₃VO₄@C hollow spheres were measured in 1 cm × 1 cm soft package battery with metallic aluminum as anode material. The cathode material was a slurry consisting of 70 wt % active material (Li₃VO₄@C, ~100 mg), 20 wt % acetylene black, and 10 wt % polyvinylidene difluoride binder in N-methyl-2-pyrrolidinone (NMP). The slurry was coated on the stainless-steel substrate and dried in vacuum oven at 60 °C overnight to remove residual NMP. The loading of active materials on the electrodes is around 2.0–2.5 mg/cm². The electrolyte used for aluminum-ion battery was the ionic liquid, electrochemical performance of Li₃VO₄, detailed characterization of ion diffusion coefficients from CV tests and GITT test, and electrochemical characterization of stainless steel and PVDF (PDF).

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b07503.

**Notes**

The authors declare no competing financial interest.

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