Highly conductive Ag is proven effective to improve the electrochemical performance of Li$_3$VO$_4$. Ag@Li$_3$VO$_4$ composite with unique architecture of Ag nanoparticles embedded homogeneously in Li$_3$VO$_4$ matrix is prepared by a facile intermediate solution method. The Ag@Li$_3$VO$_4$ delivers high initial discharge and charge capacities of 651 and 479 mAh g$^{-1}$ at a specific current of 0.15 A g$^{-1}$, maintaining of 498 and 492 mAh g$^{-1}$ after 150 cycles. Superior rate capability (364 mAh g$^{-1}$) can be achieved at 1.5 A g$^{-1}$, with more than 5 times improvement compared the one without Ag decoration. Herein, conducive but inert Ag is found facilitating fast Li$^+$ ion storage of the Li$_3$VO$_4$ owing to enhanced electronic conductivity, Li ion diffusion, and structure stability, distinctly improving cycle stability and rate performance.

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Ever-growing concern on energy crisis and environmental pollution drive the development of regenerative and clean energy, bringing high-performance electrochemical power sources into the spotlight of research.1–5 Owing to the outstanding merits in terms of long cycle life, high energy density, low self-discharge and high output voltage, lithium ion batteries have been intensively studied and widely used as power sources for diverse products such as portable electrics, electric vehicles and large energy storage equipment since its commercialization in 1991.4 However, the performance of lithium ion batteries has still fallen off the ever-increasing demand of power supply in our daily life.5

Definitely, electrode materials are crucial for the performance of lithium ion batteries. Many types of cathode materials have been proven viable for practical application in lithium ion batteries, while only a few sorts of anode material (i.e., graphite) has been successfully commercialized. According to charge/discharge mechanisms, anode materials can be segmented into three main categories:6,7 (1) intercalation/deintercalation material (i.e., graphite and Li$_4$Ti$_5$O$_12$); (2) the reduction/oxidation material (i.e., transition metal oxides); (3) alloying/dealloying material (i.e., Si and Sn). Considering the fact that only insertion type anode materials have been commercialized (reduction/oxidation and alloying/dealloying type anodes suffer from large volume variation upon lithiation/delithiation), developing high-performance insertion type anode materials are of especial significance for lithium ion batteries.

Apart from graphite and Li$_4$Ti$_5$O$_12$, insertion type Li$_3$VO$_4$ has become another promising anode material owing to its combined storage and rate capability of Li$_3$VO$_4$.8–11 One of the key obstacles Li$_3$VO$_4$ is its low electronic conductivity, which causes large polarization upon lithiation/delithiation and thus impedes full Li$^+$ ion storage and rate capability of Li$_3$VO$_4$.12 Carbonaceous materials are highly electric and been widely used to improve the electronic conductivity of composite material.13–15 For Li$_3$VO$_4$, combining it with carbonaceous materials (i.e., amorphous carbon, graphene, graphite, carbon nanotube) are also proven effective and widely adopted and to improve the performance.16–21 Ag with superb conductivity has been demonstrated to be an ideal electric component in composite electrode materials for lithium ion batteries.22–24 and the large density (vs. carbonaceous materials) is beneficial to improve the volume energy density of the composite. Combing with Ag is a highly promising approach to improve the performance of Li$_3$VO$_4$. However, to the best of our knowledge, no report on Li$_3$VO$_4$/Ag has been seen up to now. Here, we report, for the first time, distinctly improving the electrochemical performance of Li$_3$VO$_4$ via Ag decoration (Ag@Li$_3$VO$_4$). Even hybridization between nano-sized Ag and Li$_3$VO$_4$ facilitates the reaction kinetics of the Ag@Li$_3$VO$_4$ composite upon lithiation/delithiation, triggering overall exceptional performances.

**Experimental**

**Preparation process.—** Distinctive synthesis process of the Ag@Li$_3$VO$_4$ was carried out as follows. In a procedure, 1 mmol V$_2$O$_5$, 3 mmol Li$_2$CO$_3$ and 5 mmol hexamethylenetetramine were dissolved in 30 ml deionized water via stirring in a beaker. The solution was then transferred to an autoclave and reacted at 120 °C for 24 h to obtain homogeneous solution. In above experiment, 0.272 g Li$_3$VO$_4$ can be obtained theoretically. According to the mass of the Li$_3$VO$_4$, the required volume of AgNO$_3$ solution (0.1016 mol L$^{-1}$) for 3% and 5% Ag additive can be calculated to be 0.7 mL and 1.2 mL, respectively. After that, the AgNO$_3$ solution was added into the above solution drop by drop under oil bath at 75 °C for about 12 h. Finally, the obtained precipitates were annealed at 550 °C for 5 hours in nitrogen atmosphere.

**Structural, morphological and electrical characterization.—** The structure and morphology of the resulting products were characterized by X-ray powder diffraction (Rigaku Ultima IV Cu Kα radiation $\lambda = 1.5406$ Å), XPS spectrometer (Escalab MKII, Mg Kα exciting source, hv = 1253.6 eV) at pressure of $1.0 \times 10^{-4}$ Pa with resolution of 1.00 eV, field-emission scanning electron microscopy (FE-SEM JSM 7500F, JEOL) and transmission electron microscopy (TEM, Talos F200s, FEI). The electrical conductivity was measured via a powder conductivity measurement system (FT-300L, Rcio, China). Typically, 0.1 g powder sample was filled in a cylinder and compacted to thickness of ~1 mm.

**Electrochemical characterization.—** To prepare electrode, 80 wt% of active material, 10 wt% of acetylene black, and 10 wt%...
of polyvinylidene fluoride (dissolved in N-methylpyrrolidinone, 0.02 g mL\(^{-1}\)) were coated on copper foil and cut into disc with diameter of 14 mm. 2025 coin-type cells were assembled in an argon-filled dry box (MIKROUNA, Super 1220/750, H\(_2\)O < 1.0 ppm, O\(_2\) < 1.0 ppm), using Li foil as counter electrode, 1 M LiPF\(_6\) in ethylene carbonate and diethyl carbonate (volume ratio 1:1) as electrolyte, and celgard 2400 microporous polypropylene as separator membrane. The cells were tested in the voltage range between 0.02 and 3 V with a multichannel battery test system (LAND CT2001A). The Cyclic voltammetry (CV) measurement of the electrodes was carried out on a CHI660C electrochemical workstation at a scan rate of 0.2 mV s\(^{-1}\) between 0 and 3 V. Electrochemical impedance spectroscopy (EIS) measurements were performed on CHI660C electrochemical workstation in frequency region 0.01 Hz \(\sim\) 100 kHz by applying an AC signal of 5 mV.

## Results and Discussion

Figure 1a depicts XRD pattern of the as-prepared products. Sharp diffraction peaks located at 16.2°, 21.4°, 22.7°, 24.2°, 28.1°, 32.8°, 36.2°, 37.6°, 42.5°, 43.8°, 49.8°, 55.1°, 55.8°, 58.5°, 64.1°, 66.1°, 71.1°, and 77.3° can be clearly observed, corresponding to crystal faces of orthorhombic Li\(_3\)VO\(_4\) with lattice constants \(a = 6.319 \text{ Å}, b = 5.448 \text{ Å}\) and \(c = 4.940 \text{ Å}\) (JCPDS, no. 38–1247). However, diffraction peaks of silver were not detected due to the low content of Ag. Raman spectrum of the products is shown in Fig. 1b. Typical Raman peak corresponding to Li\(_3\)VO\(_4\) (822 cm\(^{-1}\)) can be clearly observed, and two characteristic peaks near 1357 cm\(^{-1}\) and 1568 cm\(^{-1}\) (the inset) correspond to D-band (in-plane vibrations of strong disorder carbon) and G-band (graphitic carbon) of carbon.8,25,26 The results suggest Ag@Li\(_3\)VO\(_4\) has been successfully prepared, and C signals may stem from the carbonization of residual hexamethylenetetramine in hydrothermal reaction.

The compositional information of the products was verified via XPS. Survey XPS spectrum in Fig 2a indicates the presence of C, Ag, N, V, and O in the composite. Ag 3d spectrum (Fig. 2b) exhibits two peaks at 367.7 and 373.6 eV, which correspond to the Ag 3d\(_{5/2}\) and Ag 3d\(_{3/2}\) of metallic Ag.27,28 XPS spectrum for V 2p in Fig. 2c can be divided into four peaks. Two peaks at 517.3 and 525 eV correspond to V 2p\(_{3/2}\) and V 2p\(_{1/2}\) of V\(^{3+}\) in Li\(_3\)VO\(_4\), and another two peaks at 516.7 and 523.9 eV can be ascribed to the V 2p\(_{3/2}\) and V 2p\(_{1/2}\) of...
V\textsuperscript{1+} spin-orbit levels. Coexistence of V\textsuperscript{4+} and V\textsuperscript{5+} in Li\textsubscript{3}VO\textsubscript{4} has also been observed in previous research, which suggests the presence of Ag and C do not affect the composition of Li\textsubscript{3}VO\textsubscript{4}.\textsuperscript{8,9} C 1s spectrum in Fig. 2d can be fitted into three peaks. One peak at 284.8 eV corresponds to the C-C bond in sp\textsuperscript{2} C, another peak at 285.7 eV is attributed to C-N or C\textequiv N bonds, and the third peak at 289.8 eV ascribes to O-C=O chemical bonds.\textsuperscript{8} O 1s spectrum (Fig. 2e) shows two peaks at 529.9 and 531.6 eV, correspond to V-O or Li-O bonds in the crystal structure and defects on the surface of Li\textsubscript{3}VO\textsubscript{4}\textsuperscript{8} N doping in C can also be confirmed. As shown in Fig. 2f, N 1s XPS spectrum can be divided into three peaks. Two peaks centered at 398.6 and 400.6 eV correspond to pyridinic and pyrrolic N, and another peak near 399.7 eV ascribes to C-N or C\textequiv N chemical bonds.\textsuperscript{8,20}

The microstructure of the Ag@Li\textsubscript{3}VO\textsubscript{4} is studied via SEM, backscattered electron (BSE), TEM and HRTEM. SEM image in Fig. 3a suggests the Ag@Li\textsubscript{3}VO\textsubscript{4} consists of numerous micro-particles ranging from hundreds of nanometers to several micrometers. Note these micro-particles are further composed of primary nano-particles (Fig. 3c). BSE image in Fig. 3b reveals clear two component of the Ag@Li\textsubscript{3}VO\textsubscript{4}, where numerous nanoparticles (~50 nm) embedded homogeneously in micro-particles. According to HRTEM image in Fig. 3d, these nano-particles are Ag (JCPDS, no. 04-0783) with interplanar spacing of 0.236 nm corresponding to the (111) planes, and these micro-particles are Li\textsubscript{3}VO\textsubscript{4} (JCPDS, no. 38-1247) with trilayer spacing of 0.236 nm corresponding to the (111) planes, embedded in Li\textsubscript{3}VO\textsubscript{4} micro-particles.

Table I. Summary of the electrochemical performance of Li\textsubscript{3}VO\textsubscript{4} electrodes.

| Material          | Current (mA/g) | Discharge capacity (mAh g\textsuperscript{-1}/cycle no.) | Ref. |
|-------------------|---------------|----------------------------------------------------------|------|
| Li\textsubscript{3}VO\textsubscript{4}/C | 0.2C          | 400/100                                                  | 13   |
| Li\textsubscript{3}VO\textsubscript{4}/CfGO | 0.25 C        | 410/5                                                   | 34   |
| Li\textsubscript{3}VO\textsubscript{4}/graphene | 0.25C        | 452/200                                                 | 35   |
| Li\textsubscript{3}VO\textsubscript{4}/C | IC            | 394/100                                                  | 33   |
| Li@Li\textsubscript{3}VO\textsubscript{4}/C | 0.8C          | 366/40                                                  | 36   |
| Li\textsubscript{3}VO\textsubscript{4}/NG | 156 mA/g      | 469/100                                                  | 21   |
| Li\textsubscript{3}VO\textsubscript{4}/Ni | 0.3C          | 379/100                                                  | 37   |
| Ag@Li\textsubscript{3}VO\textsubscript{4} | 150 mA/g      | 498/150                                                  | this work |

Galvanostatic charge/discharge test of the Ag@Li\textsubscript{3}VO\textsubscript{4} is performed between 0.02 and 3.0 V vs. Li\textsuperscript{−}/Li\textsuperscript{+}. Fig. 4a displays typical discharge and charge curves of the Ag@Li\textsubscript{3}VO\textsubscript{4} electrode at a specific current of 0.15 A g\textsuperscript{-1}. As seen, the first discharge exhibits different profile than that of the subsequent discharge curves, mainly corresponding to the formation of solid electrolyte interface (SEI).\textsuperscript{30–33} High reproducibility of subsequent charge and discharge curves indicates highly reversible delithiation and lithiation process. The cyclic voltammetric (CV) measurement was used to analyze the detailed electrochemical reaction of the Ag@Li\textsubscript{3}VO\textsubscript{4} electrode upon lithiation and delithiation. As shown in Fig. 4b, the profile for the 2nd and 3rd CV curves are similar, differing much from that of the 1st curve. In the 1st cathodic scan, two obvious reduction peaks at around 0.69 and 0.53 V correspond to the lithiation process that can be described as: \textsuperscript{x}Li\textsuperscript{+} + Li\textsubscript{3}VO\textsubscript{4} + xe\textsuperscript{−} \rightarrow Li\textsubscript{3+x}VO\textsubscript{4} (x≤3), accompanying by the formation of SEI.\textsuperscript{9,11} The slight shift of reduction peak to high potential region along with cycle number is due to activation of Li\textsubscript{3}VO\textsubscript{4}.\textsuperscript{30} The profiles for the initial three anodic scan are similar, showing an oxidation peak near 1.34 V, which is attributed to the delithiation process that can be described as: Li\textsubscript{3+x}VO\textsubscript{4} \rightarrow xLi\textsuperscript{+} + Li\textsubscript{3}VO\textsubscript{4} + xe\textsuperscript{−} (x≤3).\textsuperscript{9,11} The Ag@Li\textsubscript{3}VO\textsubscript{4} (3% Ag) exhibits exceptional cycling stability (Fig. 4c). It delivers initial discharge and charge capacities of 651 and 479 mAh g\textsuperscript{-1}, where the irreversible capacity loss may be mainly attributed to the formation of SEI film. Notably, after 150 cycles, the discharge and charge capacity maintain of 498 and 492 mAh g\textsuperscript{-1}, showing ignorable capacity attenuation compared with the initial charge capacity. The performance of our Ag@Li\textsubscript{3}VO\textsubscript{4} is distinctly improved compared with these of Li\textsubscript{3}VO\textsubscript{4}/carbon and Li\textsubscript{3}VO\textsubscript{4}/Ni reported in literature (shown in Table I).\textsuperscript{13,26–28}

In addition, the cycle stability of the Ag@Li\textsubscript{3}VO\textsubscript{4} increases distinct along with the increasing of Ag content, while the specific capacity of the Ag@Li\textsubscript{3}VO\textsubscript{4} decreases little when increasing Ag amount from 3% to 5%. This is mainly due to the electrochemical inert property of Ag, scarifying specific capacity. As shown in Fig. 4d, the charge and discharge curves of the Ag@Li\textsubscript{3}VO\textsubscript{4} (3% Ag) exhibit little polarization and good recovery along with the increasing of specific current. The Ag@Li\textsubscript{3}VO\textsubscript{4} with 3% Ag content exhibits the best rate capability (Fig. 4e). It delivers discharge capacity of 492, 434, 402, 378, and 364 mAh g\textsuperscript{-1} at 0.15, 0.3, 0.6, 0.75 and 1.5 A g\textsuperscript{-1}, respectively. Remarkably, a reversible capacity of 483 mA g\textsuperscript{-1} can be recovered once backing the specific current to 0.15 A g\textsuperscript{-1}.

Reaction kinetics of the Ag@Li\textsubscript{3}VO\textsubscript{4} electrodes in terms of electronic conductivity and lithium ion diffusion are studied to understand the exceptional performance. As shown in Fig. 5a, the intercept in high-frequency can be attributed to the contact resistance (Re) caused by SEI film and/or electrolyte, the medium-frequency semicircle correlates with the charge-transfer impedance (Rct) on electrode/electrolyte interface, and the inclined line in low-frequency corresponds to the Li\textsuperscript{+} ion diffusion process within electrodes. According to a R(C(RW)) equivalent circuit simulation, the electrode kinetic parameters can be obtained (Table II). As seen, Rct decreases distinctly after Ag decoration, showing the lowest value with optimal Ag content of 3%. Furthermore, powder conductivity measurement...
Figure 4. Electrochemical performance of the Ag@Li₃VO₄ (3% Ag). (a) The charge and discharge curves (b) Cyclic voltammograms at a scan rate of 0.2 mV s⁻¹. (c) Cycle performance comparison at a specific current of 0.15 A g⁻¹. (d) Representative charge and discharge curves at various current (see Fig. 4e) of Ag@Li₃VO₄ (3%). (e) Rate capability of Ag@Li₃VO₄ with various Ag content.

(Table III) also suggests the Ag@Li₃VO₄ with 3% Ag exhibits the highest electronic conductivity.

The lithium ion diffusion coefficient (D) of the Ag@Li₃VO₄ electrodes is also calculated according to the equation of

\[ D = \frac{R^2T^2}{2A^2n^4F^4C^2\sigma^2} \]

where R is the gas constant, T is the absolute temperature, A is the surface area of the cathode electrode, n is the number of electrons transferred per molecule, F is the Faraday constant, C is the Li⁺ concentration, and \( \sigma \) is the Warburg factor associated with \( Z’ (Z’\propto\omega^{-1/2}) \). The Ag@Li₃VO₄ with 3% Ag exhibits the highest D value. Both the electronic conductivity and lithium ion diffusion of the Ag@Li₃VO₄ correlate with the distribution between Ag and Li₃VO₄. As demonstrated, aggregation of Ag in the composite is inevitable along with the increasing amount of AgNO₃ in fabrication. The Ag@Li₃VO₄ (3% Ag) shows the highest electronic conductivity and lithium ion diffusion coefficient, profiting from the most homogeneous distribution between Ag and Li₃VO₄. As a result, the highest electronic conductivity and lithium ion diffusion, together, trigger the best performance of the Ag@Li₃VO₄ (3% Ag) electrode.

| Electrode          | Re(Ω) | Rct(Ω) |
|--------------------|-------|--------|
| Li₃VO₄             | 5.65  | 57.52  |
| Ag@Li₃VO₄ (3%)     | 3.057 | 17.22  |
| Ag@Li₃VO₄ (5%)     | 4.075 | 21.14  |

| Powder            | σ (S cm⁻¹)     |
|-------------------|----------------|
| Li₃VO₄            | 8.48 × 10⁻¹⁰   |
| Ag@Li₃VO₄ (3%)    | 9.66 × 10⁻⁹    |
| Ag@Li₃VO₄ (5%)    | 8.41 × 10⁻⁹    |
Figure 5. (a) EIS spectra and (b) Nyquist plots of the real parts of the complex impedance versus $\omega^{-1/2}$ for Ag@Li$_3$VO$_4$ electrodes.

Figure 6. Morphology variation of the Ag@Li$_3$VO$_4$ (3%) upon cycling. SEM (a), (c) and (b), (d) backscattered electron (BSE) images after (a), (b) 2 and (c), (d) 10 cycles.

Ag has been proven effective to improve the electrochemical performance of the Ag@Li$_3$VO$_4$ owing to enhanced electronic conductivity as well as improved lithium ion diffusion resulting from homogeneous hybridization between Ag and Li$_3$VO$_4$. To elaborate the inner mechanism of the cycle stability of the Ag@Li$_3$VO$_4$, the facile fabrication method combined with Ag decoration, carbon combination and N doping are of great interesting, which may be referential for the fabrication of other high-performance electrode materials.

Conclusions

Ag was firstly adopted to improve the electrochemical performance of the Ag@Li$_3$VO$_4$ with a specific current of 0.15 A g$^{-1}$, and the capacity shows little attenuation over 150 cycles. After 60 cycles at various specific current from 0.15 to 1.5 A g$^{-1}$, the Ag@Li$_3$VO$_4$ exhibits high capacity recovery of 483 mAh g$^{-1}$ when reverting specific current to 0.15 A g$^{-1}$. Apart from the superior performance of the Ag@Li$_3$VO$_4$, the facile fabrication method combined with Ag decoration, carbon combination and N doping are of great interesting, which may be referential for the fabrication of other high-performance electrode materials.

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ORCID

Dongliang Chao https://orcid.org/0000-0001-7793-0044
Xuelin Yang https://orcid.org/0000-0001-5626-701X
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