Electrostatic layer-by-layer self-assembly of 1D α -LiFeO₂ with enhanced rate capability and cycling performance

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ABSTRACT

α -LiFeO₂ is a promising cathode material for lithium-ion batteries due to its theoretically high specific capacity (282 mAh g⁻¹), abundant nature, low cost of raw materials and environmental friendliness. However, the intrinsic sluggish kinetics and poor electronic conductivity of α -LiFeO₂ prevent its practical use. In this work, we introduce a novel electrostatic layer-by-layer self-assembly method using PAH and PSS charged polyelectrolytes to grow in situ Ag nanoparticles on the surface of α -LiFeO₂ nanorods to improve the electronic and ionic conductivity in this material. The experimental results show that such tailored design effectively improves the cycling stability and provides the material with a superior rate capability. The Ag-1D α -LiFeO₂ material delivers a high discharge capacity of 162.6 mAh g⁻¹ at 0.5 C and a capacity retention of 89.6% after 50 cycles. The excellent electrochemical behavior may be ascribed to synergistic effects which combine the use of Ag NPs, which provide with improved electronic conductivities, and the large specific surface areas given by the 1D morphology of the nanorods, providing increased lithium and electron conduction pathways.

Introduction

Rechargeable lithium-ion batteries (LIBs) have become the predominant power device for portable electronic products, electric and hybrid vehicles and smart grid applications [1, 2]. However, with rapid technological developments and serious

environmental concerns, it is necessary to explore new cathode materials with high energy density, long cycle life, low toxicity and low production costs [2]. The commercialized LiCoO₂ cathode material provides stable cycling and rate performance, but the unethically sourced cobalt coupled with its toxic nature poses a problem for its future use [3]. Thus, alternative cathode materials are ought to be

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explored. α -LiFeO₂, with a disordered rock-salt structure, has been considered as a potential candidate to replace LiCoO₂ due to its high theoretical capacity (282 mAh g⁻¹), high elemental abundance, the low cost of the raw materials, environmental friendliness and safety during operation [4–9]. Unfortunately, α -LiFeO₂ suffers from an intrinsically poor electronic conductivity and slow lithium-ion diffusion kinetics. To this end, various strategies have been developed to improve the conductivity and lithium-ion diffusivity of α -LiFeO₂. Generally, nanostructured electrodes with one-dimensional (1D) morphology (e.g., nanorods, nanotubes and nanowires) have improved lithium storage performances due to their architecture, which facilitates electron transportation [10–14]. Furthermore, it has been demonstrated that modification with conductive additives can facilitate electron transport between the particles. Typically, researchers have used carbonaceous materials such as carbon from different organic sources and MWCNTs as conductive additives for α -LiFeO₂ [15–18]. A different approach has been to use metals such as silver and copper to decorate the surface of the electrode material to improve the electronic conductivity of the composite material [19–21]. Silver has been used as a conductive additive in cathode materials such as LiMn₂O₄/Ag, LiFePO₄/Ag, Co₃O₄/Ag and Si/Ag composites [22–27] given its high electrical conductivity (6.30×10^7 S m⁻¹). However, it is difficult to precisely control the uniformity and particle size of the additives when using traditional methods such as liquid precipitation, in situ synthesis and silver mirror reactions [28–30]. By contrast, layer-by-layer self-assembly (LBL) technology, which is a technique that lies on the deposition of alternating layers of oppositely charged materials is an efficient method that may provide with a uniform particle distribution [31, 32].

In this work, we demonstrate a novel, low-cost, simple and scalable method to prepare 1D α -LiFeO₂ modified with Ag NPs based on an electrostatic layer-by-layer self-assembly process using PAH and PSS polyelectrolytes. The results from structural and electrochemical analyses show that the Ag NPs were grown in situ on the surface of the α -LiFeO₂ nanorods. As a result, enhanced ionic and electronic conductivities which enabled improved electrochemical performance in terms of cycling capability and rate performance were observed. This design strategy

opens the pathway to the fabrication of new electrode designs with improved electrochemical properties.

Experiment section

Synthesis

Synthesis of α -LiFeO₂ nanorods

α -LiFeO₂ nanorods were prepared through a self-sacrificial template route using α -FeOOH nanorods [33]. The detailed experimental process for the synthesis of α -FeOOH nanorods is shown in the SI (Methods), and PXRD data can be found in Fig. S1. Then, 0.5 g α -FeOOH, 0.47 g LiOH·H₂O and 0.78 g LiNO₃ (Li/Fe = 4:1 molar ratio) were ground together with a mortar and pestle using a small amount of distilled water and anhydrous alcohol. After this, powders were dried at 80 °C for 12 h and then sintered at 400 °C for 6 h in a N₂ atmosphere using a heating rate of 3 °C min⁻¹. After naturally cooling down to room temperature, the product was washed with distilled water and ethanol and dried at 80 °C for 12 h. For comparison, α -LiFeO₂ particles were prepared by a traditional solid-state method using LiOH·H₂O and Fe₂O₃ (Li/Fe = 1.05:1 molar ratio) as precursors. The precursors were sintered at 800 °C for 8 h in a muffle furnace with a ramp of 3 °C/min and automatically cooled down to room temperature to obtain α -LiFeO₂. PXRD and SEM data can be found in Fig. S2 and Fig. S3, respectively.

Preparation of Ag-1D α -LiFeO₂ nanocomposite by electrostatic self-assembly

Typically, 0.25 g of as-synthesized 1D α -LiFeO₂ were stirred for 1 h in 120 ml of a 0.5 M NaCl solution and after that 0.3 g of PSS (sodium-4-styrene sulfonate) were added and stirred for another 0.5 h. Then, the sample was washed repeatedly with deionized water to remove the excess of PSS. The same procedure was carried out using 0.3 g of PAH (poly(allylamine hydrochloride)), and this was repeated with PSS. As a result, PSS/PAH/PSS-modified 1D α -LiFeO₂ was prepared. The modified 1D α -LiFeO₂ nanorods were placed into 50 mL water with 0.005 g AgNO₃ and 2.0 g polyvinyl pyrrolidone (PVP) and were stirred for 1 h. After this, 20 mL of a 0.025 M NaBH₄ solution were added dropwise into the layer-by-layer

modified sample. After stirred for 1 h, the resulting products were washed with distilled water and ethanol repeatedly and dried at 80 °C for 12 h. Figure 1 depicts a schematic of the electrostatic self-assembly process for the preparation of Ag-1D α -LiFeO₂.

Characterization

Structural characterization

Powder X-ray diffraction (PXRD) was performed using a Bruker DX-1000, equipped with a Cu K α radiation source ($\lambda_1 = 1.54056$ Å, $\lambda_2 = 1.54439$ Å) and a 2D detector.

Microstructural characterization

SEM (JEOL, JSM-6360LV) was performed using an accelerating voltage of 60 kV to determine the

microstructure of the as-prepared α -LiFeO₂ samples. TEM images were obtained using a JEOL, JEM-3010 at an accelerating voltage of 200 kV. TEM mapping images were obtained on an FEI Talos F200X with a field emission gun operating at 200 kV.

Zeta potential measurements

The zeta potentials of the Ag-1D α -LiFeO₂ suspension liquids were determined using a Zetasizer Nano ZS90 equipment.

X-ray Photoemission Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS, ESCALAB 250XI) was measured on an Ultra DLD using a monochromic Al X-ray source. The electronic conductivity is measured by a digital four-point probe tester (SX1934 (SZ-82)).

Figure 1 Schematic showing electrostatic layer-by-layer self-assembly of Ag-1D α -LiFeO₂ nanorods.

Electrochemical studies

The electrochemical performance of the 1D α -LiFeO₂ samples and pristine material was tested by using CR2025 coin-type cells, which were assembled in an Ar-filled glove box. Electrode slurries were made by mixing 85 wt% active material, 10% acetylene black (conductive additive) and 5% polyvinylidene difluoride (PVDF) (binder) with a mortar and pestle. The mixture was added into an N-methyl pyrrolidone solution that was stirred for 12 h. Then, the slurry was evenly coated onto aluminium foil with the help of a Doctor blade, and the films were dried at 80 °C for 30 min, followed by punching them into electrodes with a diameter of 12 mm. The electrodes were further dried at 100 °C for 12 h under vacuum before assembling them into coin cells. A loading of ca. 1.3 mg cm⁻² was achieved in the electrodes of this study. For coin cell assembly, lithium foil was used as the counter and reference electrode, a Celgard microporous polypropylene membrane was used as a separator, and 1 M lithium hexafluorophosphate (LiPF₆) dissolved in ethylene carbonate (EC) and diethyl carbonate (DEC) in a 1:1 volume ratio was used as the electrolyte. Galvanostatic measurements were performed on a Land CT2001A battery testing system at different current densities between 1.5 and 4.8 V (vs. Li⁺/Li). Electrochemical impedance spectroscopy (EIS) analysis was conducted on a CS-350 electrochemical workstation with a frequency range of 0.1 Hz to 100 kHz at an amplitude of 5 mV. Cyclic voltammetry (CV) was conducted at a scan rate of 0.1 mV s⁻¹ in the 1.5–4.8 V voltage range.

Results and discussion

Figure 1 describes the electrostatic self-assembly approach for the synthesis of Ag-1D α -LiFeO₂, where poly(allylamine hydrochloride) (PAH) and poly(sodium 4-styrenesulfonate) (PSS) were used as positively and negatively charged polyelectrolytes, respectively. The polyelectrolytes were used to homogeneously coat the 1D α -LiFeO₂ based on a self-assembly process. The PAH-PSS couple is characterized by a strong hydrophobic electrostatic interaction between the ammonium group [–NH₃⁺] of PAH and the sulfonate group [–SO₃⁻] of PSS, leading to a high charge density [31, 32]. A similar approach using poly(diallyl dimethylammonium chloride) (PDDA)

and poly(sodium-4-styrene sulfonate) (PSS) polyelectrolyte couples was used to coat a 3D carbon substrate with LiFePO₄ nanoparticles [34].

During the PSS/PAH/PSS dipping cycles, we observed changes in the surface charge of the 1D α -LiFeO₂ nanorods, going from negative (zeta potential = –7.91 mV) to positive (zeta potential = 9.0 mV) and then back to negative (zeta potential = –16.32 mV) (Fig. 2a), indicating the formation of opposite charges on the 1D α -LiFeO₂ sample. At this point, positively charged Ag⁺ ions (from a 5.8 × 10⁻⁴ M AgNO₃ solution) were adsorbed onto the surface of 1D α -LiFeO₂ nanorods due to the electrostatic attraction between these and PSS. A solution of NaBH₄ was then used to reduce in situ the Ag⁺ ions to Ag NPs onto the surface of 1D α -LiFeO₂ nanorods.

PXRD data of the 1D α -LiFeO₂ and Ag-1D α -LiFeO₂ samples are shown in Fig. 2c and d. Both samples show diffraction peaks that can be indexed to the layered structure of α -LiFeO₂ (Space group *Fm* $\bar{3}$ *m*, JCPDS No. 74–2284) and with lattice parameters in agreement with those reported in the literature [35]. The Ag-1D α -LiFeO₂ sample shows an additional peak at 38.4° 2 θ (marked in red), which matches to the most intense reflection of Ag (JCPDS No. 65–2871) [36] and thus confirms the presence of silver nanoparticles in the sample. No diffraction peaks from the α -FeOOH precursor were observed, indicating that these nanorods are fully converted into α -LiFeO₂. Furthermore, PXRD data confirm that the LBL process does not change the crystal structure of the α -LiFeO₂ nanorods, and thus, no side reactions occurred. Figure 2b shows the crystal structure of α -LiFeO₂.

Micrographs of the samples are shown in Fig. 3a–d. Figure 3a shows a typical SEM image of the as-synthesized α -FeOOH sample, which consists of nanorods with diameters up to ca. 150 nm and lengths of a few micrometers. The micrographs indicate that the morphology of the α -LiFeO₂ nanorods is retained after the thermal treatment on the α -FeOOH nanorods (Fig. 3b). Similarly, SEM images revealed that there are no changes in the diameter and morphology of the α -LiFeO₂ nanorods after the LBL process (Fig. 3c, d) and showed the presence of Ag nanoparticles of a few nanometers uniformly coated on the surface of the 1D- α -LiFeO₂.

TEM analysis further confirms the detailed microstructure of 1D α -LiFeO₂ and the distribution of

Figure 2 **a** Zeta potentials of 1D α -LiFeO₂ nanorods coated with PSS/PAH/PSS; **b** crystal structure of α -LiFeO₂, showing a disordered distribution of Li/Fe atoms in octahedral sites in a

cubic-close packing of oxygen atoms; **c** XRD data of 1D α -LiFeO₂; and **d** XRD data of Ag-1D α -LiFeO₂. *hkl* indexes are shown in **c** and **d**.

the crystalline Ag nanoparticles onto the surface of 1D α -LiFeO₂. Figure 4a shows a distinct α -LiFeO₂ nanorod with a diameter of ca. 150 nm, which is fully consistent with the SEM data (Fig. 3b). The HRTEM image in Fig. 4b shows well-resolved lattice fringes, illustrating the high crystalline nature of the 1D α -LiFeO₂ nanorods. The lattice fringe spacing of 0.24 nm is consistent with the (111) crystal planes of α -LiFeO₂ [15]. Figure 4c and d shows high-magnification images that reveal round NPs with diameters of ca. 5 nm attached to the surface of 1D α -LiFeO₂. The (111) crystal plane with an interplanar distance of 0.255 nm marked in Fig. 4e indicates the presence of silver nanoparticle [37]. The corresponding SAED pattern presented in Fig. 4f shows the diffraction rings formed from scattered dots, indexed from inside to outside as (111), (200), (220), (311), which are

in good agreement with the XRD results. Based on TEM evidence, it can be found the Ag NPs are in the nano-range and uniformly distributed on the surface of the 1D α -LiFeO₂ nanorods, suggesting a desirable architecture beneficial for fast electron transportation along the nanorods [30]. TEM-EDS mapping analysis shows a uniformly elemental distribution of O, Fe and Ag in the 1D- α -LiFeO₂ and Ag-1D α -LiFeO₂ nanorods (Fig. 5). Furthermore, the uniform coating of Ag nanoparticles is further confirmed in Ag-1D α -LiFeO₂, suggesting that Ag nanoparticles can be evenly coated onto 1D α -LiFeO₂ through a simple LBL approach.

X-ray photoelectron spectra (XPS) of the 1D α -LiFeO₂ and Ag-1D α -LiFeO₂ samples are shown in Fig. 6. According to the spectrum in Fig. 6a, Ag-1D α -LiFeO₂ consists of Li, O, Fe and Ag peaks, which is in

Figure 3 SEM images of: **a** as-prepared α -FeOOH; **b** 1D α -LiFeO₂; and **c, d** Ag-1D α -LiFeO₂ at different magnifications.

agreement with the formation and deposition of Ag NPs on the surface of 1D α -LiFeO₂. Figure 6b shows Fe 2p peaks for both samples locating at 711.04 and 724.56 eV, which are assigned to Fe 2p_{3/2} and Fe 2p_{1/2} spin-orbit peaks of α -LiFeO₂, respectively, thus confirming the Fe(III) oxidation state [38]. The two main peaks are accompanied by satellite peaks on their respective higher binding energy sides at about 719.8 and 733.4 eV [38]. No peak shift occurs to α -LiFeO₂ before and after the LBL process, indicating that the LBL process does not change the chemical state of Fe. The high-resolution XPS spectra of the Ag doublet (3d_{3/2} and 3d_{5/2}) in the Ag-1D α -LiFeO₂ nanocomposites are shown in Fig. 6c. The doublet is centered at 368.3 and 374.2 eV, which are higher than those of metallic Ag (0) (3d_{3/2} = 367.9 eV; 3d_{5/2} = 373.9 eV) [39], suggesting a successful reduction of Ag(I) ions to Ag (0) through the LBL process.

The electrochemical performance of the Ag-1D α -LiFeO₂ and 1D α -LiFeO₂ materials as positive for LIBs was evaluated in coin cells using lithium as the counter and reference electrode. Typical charge/discharge profiles in the voltage range 1.5–4.8 V at 0.5 C current rate are shown in Fig. 7a and b. The 1st cycle load profiles are similar on both samples. The voltage increases rapidly from the open-circuit voltage to

4.5 V, followed by a plateau (40 mAh g⁻¹) before reaching the cutoff voltage.

During the first discharge, the voltage decreases sharply to 2.75 V and then enters a semi-plateau region that extends to 1.75 V, followed by a plateau in the 1.75–1.5 V region. Subsequent charge/discharge curves were S-shaped, as observed in other α -LiFeO₂ materials [40]. Cyclic voltammetry was carried out to better understand the cycling behavior and redox processes occurring in the Ag-1D α -LiFeO₂ material using a sweep rate of 0.1 mV s⁻¹ between 1.5 and 4.8 V (vs. Li⁺/Li) (Fig. S4). We observed an anodic peak at 4.3 V during the first charge process which is consistent with the literature and the load curves (Fig. 7a) [41]. This peak disappears in the following cycles. Furthermore, the cathodic peak at 1.55 V decreased in intensity from the first to the second cycle. All the peaks maintained the same shape and current intensity after the first cycle. Based on this result, we assume that α -LiFeO₂ underwent a structural change during the first cycle and maintained the changed structure after the second cycle. Several works from other researchers [4, 5, 16, 40, 42, 43] have explained the mechanism of structural evolution during the first and consequent cycles. Sakurai et al. [4, 42] suggested that

Figure 4 TEM (a) and HRTEM (b) images of as-prepared 1D α -LiFeO₂. TEM (c, d) and HRTEM (e) images with corresponding SAED pattern (f) of the as-prepared Ag-1D α -LiFeO₂.

unstable Fe^{4+} forms during the first charging process and oxidizes the electrolyte to produce Fe^{3+} ions. It should be noted that not all the Fe^{3+} oxidizes to Fe^{4+} and thus the low capacity observed during the first cycle. Upon discharge and consequent cycles, the predominant redox reaction is that coming from the relatively more stable $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple. Furthermore, Morales et al. [43] have proposed a structural rearrangement upon lithium removal, where Fe^{4+} were displaced from octahedral 4a sites to tetrahedral 8c positions. The 1D α -LiFeO₂ sample exhibits a first cycle discharge capacity of

151.2 mAh g^{-1} and retains 73.7% of this capacity after 50 cycles. By contrast, a discharge capacity of 162.6 mAh g^{-1} was observed for the Ag-1D α -LiFeO₂ electrode, with a capacity retention of 89.6% after 50 cycles. Coulombic efficiencies close to 100% (except for the first cycle) were observed in both samples, indicating a superior reversible capacity (Fig. 7c). This initially low coulombic efficiency has been observed in other Li-Fe-O systems [6, 42, 44]. For reference, the electrochemical performance of the 1D α -LiFeO₂ and Ag-1D α -LiFeO₂ electrodes was tested against as-prepared pristine (P- α -LiFeO₂) using the

Figure 5 TEM mapping images of as-prepared 1D α -LiFeO₂ [TEM image (a); elemental mapping of O (b) and Fe (c)] and the Ag-1D α -LiFeO₂ nanorod (d, TEM image; elemental mapping of O (e), Fe (f) and Ag (g)).

same voltage window at 0.1 C (Fig. 7d). As summarized in Table 1, the capacity of P- α -LiFeO₂ fades from 176 to 109 mAh g⁻¹ after 50 cycles with only a 61.9% capacity retention, while this is 82.2% and 93.7% for 1D α -LiFeO₂ and Ag-1D α -LiFeO₂ electrodes, respectively.

The rate performance of the P- α -LiFeO₂, 1D α -LiFeO₂ and Ag-1D α -LiFeO₂ electrodes was tested and waterfall plots are shown in Fig. 7e. Samples were cycled at 0.1 C, 0.2 C, 0.5 C, 1 C and 2 C (five cycles each) between 1.5 and 4.8 V and then returned to 0.1 C. Overall, the discharge capacity decreases for all samples with increasing current. The Ag-1D α -LiFeO₂ sample delivers the highest of all current densities compared to the other two samples. Average discharge capacities of 193.5, 176.7, 147.9, 115 and 81.18 mAh g⁻¹ at 0.1, 0.2, 0.5, 1 and 2 C were observed for the Ag-1D α -LiFeO₂ electrode, which contrast to the average discharge capacities of 176.6 (0.1 C), 167.6 (0.2 C), 133.8 (0.5 C), 94.6 (1 C) and 70.5 mAh g⁻¹ (2 C) for 1D α -LiFeO₂ and 175.9 (0.1 C), 127.4 (0.2 C), 109.38 (0.5 C), 73.88 (1 C) and 44.2 mAh g⁻¹ (2 C) for the P- α -LiFeO₂ electrode (Fig. 7f). When the current density returns from 2 to 0.1 C, the average discharge capacities of the P- α -LiFeO₂, 1D α -LiFeO₂ and Ag-1D α -LiFeO₂ electrodes are restored to 97.6, 104.83 and 138 mAh g⁻¹, respectively. We attribute the enhanced rate

performance of the Ag-1D α -LiFeO₂ sample to the incorporation of Ag NPs on the surface of the nanorods, which allow for improved electronic and ionic conductivity in these materials. This is further confirmed by the impedance analysis (Fig. 8).

To further investigate the effects of Ag on the long cycling performance, 1D α -LiFeO₂ and Ag-1D α -LiFeO₂ were cycled 100 times at a 0.1 C rate (Fig. S5). Our data show that the capacity retention ratio of 1D α -LiFeO₂ and Ag-1D α -LiFeO₂ are 49% and 75.93%, respectively. We attribute this improvement in capacity retention to the improved electronic and ionic conductivity in Ag-1D α -LiFeO₂.

The Nyquist plots and equivalent circuit of the P- α -LiFeO₂, 1D α -LiFeO₂ and Ag-1D α -LiFeO₂ electrodes before and after cycling are shown in Fig. S6 and Fig. 8a. The semicircle dimensions of all cells increase after 50 cycles, suggesting an increased charge transfer resistance of the electrodes with cycling [45]. A broader semicircle was observed for the P- α -LiFeO₂ electrode before and after 50 cycles compared to the 1D α -LiFeO₂ and Ag-1D α -LiFeO₂ electrodes. This is also supported by the fitted parameters listed in Tables S1 and Table 2. The electronic conductivity of the 1D α -LiFeO₂ and Ag-1D α -LiFeO₂ electrodes was measured, and the results are shown in Table S2. These indicate that the homogeneous incorporation of the silver nanoparticles can decrease the resistance

Figure 6 a X-ray photoelectron spectroscopy (XPS) spectra of the pristine 1D α -LiFeO₂ and Ag-1D α -LiFeO₂ nanorods; XPS analysis of Fe 2p peaks (b); Ag 3d peaks (c); and O 2p peaks (d).

value in the α -LiFeO₂ nanorods, providing a long charge carrier transportation length. Furthermore, we calculated the lithium-ion diffusion coefficient of Ag-1D α -LiFeO₂ to be $8.24 \times 10^{-12} \text{ cm}^2 \text{ S}^{-1}$, which is about 6 times higher than that for 1D α -LiFeO₂ (1.3×10^{-12}). See supplementary information for more details.

Given the reduction of the charge transfer resistance value (R_{CT}) and the increase of exchange current density (i^0) after the modification of Ag nanoparticles, it can be concluded that 1D α -LiFeO₂ combined with acetylene black to enhance the surface electron conductivity of the electrode, provides more active sites for electron and lithium-ion transfer (Fig. 9). Moreover, the introduction of Ag NPs further enhances the electron conductivity and lithium-ion diffusion coefficient, thereby contributing to the high cycling stability and rate capability.

To understand the structural stability of the Ag-1D α -LiFeO₂ nanorods, the morphology of Ag-1D α -LiFeO₂ after 50 cycles was investigated by SEM analysis (Fig. S7). It was observed that the Ag nanoparticles still adhere tightly to the 1D α -LiFeO₂ nanorods even after 50 cycles at 0.5 C. This indicates enhanced structural stability achieved for the deposition of Ag nanoparticles on the 1D α -LiFeO₂ nanorods via LBL method.

Conclusion

In this work, we report a novel electrostatic layer-by-layer self-assembly method using PAH and PSS charged polyelectrolytes to grow in situ Ag nanoparticles on the surface of α -LiFeO₂ nanorods. When tested as a cathode material for LIBs, the Ag-modified 1D α -LiFeO₂ nanorods delivered a highly

Figure 7 Load curves using a 0.5 C rate in the voltage range (1.5–4.8 V) of Ag-1D α -LiFeO₂ (a) and 1D α -LiFeO₂ (b); specific capacity versus cycle number plots in the voltage range of 1.5–4.8 V at 0.5 C (c); and 0.1 C (d). Coulombic efficiencies are

shown in c and d; (e) Rate performance of the α -LiFeO₂ samples at 0.1 C, 0.2 C, 0.5 C, 1 C and 2 C (e); and f average specific capacity at various current densities.

reversible cycling capacity of 194.5 mAh g⁻¹ at 0.1 C after 50 cycles and show an excellent capacity at higher rates (144.8 mAh g⁻¹ at 0.5 C after 50 cycles) with a capacity retention of ca. 94% and 90%, respectively. By contrast, the unmodified 1D α -LiFeO₂ sample showed a capacity retention of ca. 82%

and 74% under identical conditions. Based on our data, the enhanced rate capability and improved cycling performance of Ag-1D α -LiFeO₂ can be ascribed to: (1) synergistic effects by combining Ag NPs with 1D microstructures, where the nanorod microstructure provides facilitated lithium and

Table 1 Electrochemical performance of 1D and pristine α -LiFeO₂ electrodes in the voltage range of 1.5–4.8 V at a constant current rate of 0.1 C

Sample	1st discharge capacity (mAh g ⁻¹)	50th discharge capacity (mAh g ⁻¹)	Capacity retention (%)
1D α -LiFeO ₂	206.6	169.8	82.2
Ag-1D α -LiFeO ₂	207.6	194.5	93.7
P- α -LiFeO ₂	176	109	61.9

Figure 8 **a** Nyquist curves at OCV and after 50 cycles of the 1D α -LiFeO₂ and Ag-1D α -LiFeO₂ nanorod electrodes (the inset shows the equivalent circuit), and **b** linear fitting curves of Z'' versus $\omega^{-1/2}$.**Table 2** Representative fitting data of the EIS data corresponding to Fig. 8a

R/sample	1D α -LiFeO ₂	Ag-1D α -LiFeO ₂
$(R_S + R_{SEI} + R_{CT})_0$ (Ω)	157.2	100.5
$(R_S + R_{SEI} + R_{CT})_{50}$ (Ω)	411.7	221.6

electron pathways given their large specific surface areas, and the evenly coated Ag NPs on the surface of these improve the electronic conductivity ($8.2 \times 10^{-9} \text{ S cm}^{-1}$) of the sample given their high electrical conductivity; (2) the large Li^+ diffusion coefficient of 8.24×10^{-12} and high exchange current density of $2.791 \times 10^{-4} \text{ mA cm}^{-2}$ observed; and (3) the excellent structural stability upon long cycling without undergoing severe agglomeration.

Figure 9 A schematic of the transport pathways of lithium-ions and electrons during the electrochemical reaction process.

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Compliance with ethical standards

Conflict of interest The authors declared that they have no conflict of interest.

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References

- Armand M, Tarascon JM (2008) Building better batteries. *Nature* 451:652–657
- Dunn B, Kamath H, Tarascon JM (2011) Electrical energy storage for the grid: a battery of choices. *Science* 334:928–934
- Whittingham MS (2004) Lithium batteries and cathode materials. *Chem Rev* 104:4271–4301
- Sakurai YJ, Arai H, Yamaki HJ (1998) Preparation of electrochemically active α -LiFeO₂ at low temperature. *Solid State Ion* 113:29–34
- Lee YS, Sato S, Sun YK, Kobayakawa K, Sato Y (2003) A new type of orthorhombic LiFeO₂ with advanced battery performance and its structural change during cycling. *J Power Sources* 119:285–289
- Kanno R, Shirane T, Inaba Y, Kawamoto Y (1997) Synthesis and electrochemical properties of lithium iron oxides with layer-related structures. *J Power Sources* 68:145–152
- Ado K, Tabuchi M, Kobayashi H, Kageyama H, Nakamura O (1997) Preparation of LiFeO₂ with α -NaFeO₂-type structure using a mixed-alkaline hydrothermal method. *J Electrochem Soc* 144:177–180
- Hu Y, Zhao H, Liu X (2018) A simple, quick and eco-friendly strategy of synthesis nanosized α -LiFeO₂ cathode with excellent electrochemical performance for lithium-ion batteries. *Materials* 11:1176
- Liu H, Ji P, Han X (2016) Rheological phase synthesis of nanosized α -LiFeO₂ with higher crystallinity degree for cathode material of lithium-ion batteries. *Mater Chem Phys* 183:152–157
- Bruce PG, Scrosati B, Tarascon JM (2008) Nanomaterials for rechargeable lithium batteries. *Angew Chem* 47:2930–2946
- Lu YX, Du SF, Wilckens RS (2018) Evolution of gas diffusion layer structures for aligned Pt nanowire electrodes in PEMFC applications. *Electrochim Acta* 279:99–107
- Liang K, He H, Ren Y, Wang H, Liao Y, Huang X (2019) Porous lithium titanate nanosheets as an advanced anode material for sodium ion batteries. *J Mater Sci* 55:4372–4381. <https://doi.org/10.1007/s10853-019-04290-1>
- Yang Z, Li Z, Li P, Gao C, Zhang H (2019) NiO/Ni nanocomposites embedded in 3D porous carbon with high performance for lithium-ion storage. *J Mater Sci* 55:1659–1672. <https://doi.org/10.1007/s10853-019-04075-6>
- Li P, Deng J, Li J, Zeng M, Wang L, Guo J (2019) Multi-functional hollow spheres as sulfur hosts for high-performance Li-S batteries. *J Mater Sci* 55:3964–3973. <https://doi.org/10.1007/s10853-019-04251-8>
- Rahman MM, Wang JZ, Hassan MF, Chou SL, Chen ZX, Liu HK (2011) Nanocrystalline porous α -LiFeO₂-C composite: an environmentally friendly cathode for the lithium-ion battery. *Energy Environ Sci* 4:952–957
- Rahman MM, Glushenkov AM, Chen ZQ, Dai XJ, Ramireddy T, Chen Y (2013) Clusters of α -LiFeO₂ nanoparticles incorporated into multi-walled carbon nanotubes: a lithium-ion battery cathode with enhanced lithium storage properties. *Phys Chem Chem Phys* 15:20371–20378
- Hu Y, Zhao H, Tan M, Liu J, Shu X, Zhang M, Liu S, Ran Q, Li H, Liu X (2019) Synthesis of α -LiFeO₂/graphene nanocomposite via layer by layer self-assembly strategy for lithium-ion batteries with excellent electrochemical performance. *J Mater Sci Technol*. <https://doi.org/10.1016/j.jmst.2019.04.044>

- [18] Guo SP, Ma Z, Li JC, Xue HG (2017) Facile preparation and promising lithium storage ability of α -LiFeO₂/porous carbon nanocomposite. *J Alloys Compd* 711:8–14
- [19] Kalantarian MM, Asgari S, Mustarelli P (2014) A theoretical approach to evaluate the rate capability of Li-ion battery cathode materials. *J Mater Chem A* 2:107–115
- [20] Li Y, Zhou X, Bai Y, Chen G, Wang Z, Li H, Wu F, Wu C (2017) Building an electronic bridge via Ag decoration to enhance kinetics of iron fluoride cathode in lithium-ion batteries. *ACS Appl Mater Interfaces* 9:19852–19860
- [21] Zhang H, Zong P, Chen M, Jin H, Bai Y, Li S, Ma F, Xu H, Lian K (2019) In situ synthesis of multilayer carbon matrix decorated with copper particles: enhancing the performance of Si as Anode for Li-ion batteries. *ACS Nano* 13:3054–3062
- [22] Lin XT, Wang PF, Li P, Yu HX, Qian SS, Shui M, Wang DJ, Long NB, Shu J (2015) Improved the lithium storage capability of BaLi₂Ti₆O₁₄ by electroless silver coating. *Electrochim Acta* 186:24–33
- [23] Kim SH, Choi SY (2015) Fabrication of Cu-coated TiO₂ nanotubes and enhanced electrochemical performance of lithium ion batteries. *J Electroanal Chem* 744:45–52
- [24] Zhou WJ, He BL, Li HL (2008) Synthesis, structure and electrochemistry of Ag-modified LiMn₂O₄ cathode materials for lithium-ion batteries. *Mater Res Bull* 43:2285–2294
- [25] Parka KS, Sona JT, Kim SJ, Chung HT, Lee CH, Kang KT, Kim HG (2004) Surface modification by silver coating for improving electrochemical properties of LiFePO₄. *Solid State Commun* 129:311–314
- [26] Hao Q, Yu Y, Zhao D, Xu C (2015) Composited Co₃O₄/Ag with flower-like nanosheets anchored on a porous substrate as a high-performance anode for Li-ion batteries. *J Mater Chem A* 3:15944–15950
- [27] Yin SS, Zhao D, Ji Q, Xia Y, Xia S, Wang X, Wang M, Ban J, Zhang Y, Metwalli E, Wang X, Xiao Y, Zuo X, Xie S, Fang K, Liang S, Zheng L, Qiu B, Yang Z, Lin Y, Chen L, Wang C, Liu Z, Zhu J, Muller-Buschbaum P, Cheng YJ (2018) Si/Ag/C nanohybrids with in situ incorporation of super-small silver nanoparticles: tiny amount, huge impact. *ACS Nano* 12:861–875
- [28] Li Y, Li W, Luo Y, Fang M, Yao X, Shui M, Shu J, Ren Y (2018) The enhanced electrochemical performance of Ag coating K_x Cu_{1-x} O_{1-γ} as high performance anode materials for lithium-ion batteries. *J Electroanal Chem* 818:114–123
- [29] Han X, Huang Y, Gao Q, Yu M, Chen X (2018) High thermal conductivity and mechanical properties of nanotube@Cu/Ag@graphite/aluminum composites. *Ind Eng Chem Res* 57:10365–10371
- [30] Cheong JY, Youn DY, Kim C, Jung JW, Ogata AF, Bae JG, Kim ID (2018) Ag-coated one-dimensional orthorhombic Nb₂O₅ fibers as high performance electrodes for lithium storage. *Electrochim Acta* 269:388–396
- [31] Xiang Y, Lu S, Jiang SP (2012) Layer-by-layer self-assembly in the development of electrochemical energy conversion and storage devices from fuel cells to supercapacitors. *Chem Soc Rev* 41:7291–7321
- [32] Richardson JJ, Bjornmalm M, Caruso F (2015) Technology-driven layer-by-layer assembly of nanofilms. *Science* 348:2491–2501
- [33] Zhai Y, Xu L, Qian Y (2016) Ce-doped α -FeOOH nanorods as high-performance anode material for energy storage. *J Power Sources* 327:423–431
- [34] Tian GY, Scheib F, Pfaffmann L, Fiedler A, Chakravadhanula VSK, Balachandran G, Zhao ZJ, Ehrenberg H (2018) Electrostatic self-assembly of LiFePO₄ cathodes on a three-dimensional substrate for lithium ion batteries. *Electrochim Acta* 283:1375–1383
- [35] Wang X, Gao LS, Zhou F, Zhang ZD, Ji MR, Tang CM, Shen T, Zheng HG (2004) Large-scale synthesis of α -LiFeO₂ nanorods by low-temperature molten salt synthesis (MSS) method. *J Cryst Growth* 265:220–223
- [36] Meng E, Zhang M, Hu Y, Gong F, Zhang LS, Li F (2018) Solid-state attachments of Ag nanoparticles onto the surfaces of LiFePO₄ cathode materials for Li storage with enhanced capabilities. *Electrochim Acta* 265:160–165
- [37] Sahoo PK, Kumar N, Thiagarajan S, Thakur D, Panda HS (2018) Freeze-casting of multifunctional cellular 3D-graphene/Ag nanocomposites: synergistically affect supercapacitor, catalytic, and antibacterial properties. *ACS Sustain Chem Eng* 6:7475–7487
- [38] Shilpa, Sharma A (2017) Template-free synthesis of hollow Li₂O–Fe₂O₃–Ag heterostructures for ultra-high performance Li-ion batteries. *J Mater Chem A* 5:14220–14229
- [39] Hao Q, Yu Y, Zhao DY, Xu CX (2015) Composited Co₃O₄/Ag with flower-like nanosheets anchored on a porous substrate as a highperformance anode for Li-ion batteries. *J Mater Chem A* 3:15944–15950
- [40] Wu SH, Liu HY (2007) Low temperature synthesis and electrochemical characteristics of LiFeO₂ cathodes. *J Power Sources* 174:789–794
- [41] Wang Y, Wang J, Liao H, Qian X, Zhu Y, Cheng S (2013) Synthesis and characterization of nanosized α -LiFeO₂ with increased electrochemical activity. *Int J Electrochem Sci* 8:8730–8739
- [42] Sakurai Y, Arai H, Okada S, Yamaki J (1997) Preparation of electrochemically active α -LiFeO₂ at low temperature, low temperature synthesis and electrochemical characteristics of LiFeO₂ cathodes. *J Power Sources* 68:711–715
- [43] Morales J, Santos-Peña J (2007) Highly electroactive nanosized α -LiFeO₂. *Electrochem Commun* 9:2116–2120

- [44] Kanno R, Shirane T, Kawamoto Y (1996) Synthesis, structure, and electrochemical properties of a new lithium iron oxide, LiFeO_2 , with a corrugated layer structure. *J Electrochem Soc* 8:2435–2441
- [45] Yu YL, Li G, Zhou S, Chen X, Lee HW, Yang WS (2017) Self-adaptive Si/reduced graphene oxide scrolls for high-performance Li-ion battery anodes. *Carbon* 120:397–404

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