Solvent mediated sodium storage enhancement in van der Waals layered materials

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ABSTRACT

Layered materials with weak van der Waals interactions between interlayers are able to provide adequate spaces for sodium ion intercalation and expressways for ion diffusion. Ether solvents are proved capable to facilitate the transport of ions and electrons transport in electrodes in virtue of their flexible one-dimensional chain structure. The combination of layered graphite and ether-based electrolytes even contributes to the revival of graphite as a promising anode material for sodium ion batteries via solvent co-intercalation. Lighted by these findings, in this work, we choose a quasi-layered vanadium sulfide (VS_4) as the electrode material and diglyme (DGM) as a multifunctional electrolyte solvent, to investigate the synergetic effects of solid material structure and electrolyte solvent on the electrochemical performances. Contrast to a drastically decay of capacity in electrolytes with ethylene carbonate/dimethyl carbonate, the capacity of VS_4/RGO composites in DGM could maintain a value of near 400 mAh·g^{-1} at a current density of 100 mA·g^{-1} over 30 cycles and a capacity about 300 mAh·g^{-1} at a quite high current density of 800 mA·g^{-1}. The performance enhancement could be ascribed to the solvent co-intercalation into the van der Waals gaps and the resulting facilitated ion diffusion in electrode, which was later proved by TEM characterization and EIS measurements. To further prove the role of DGM, the electrochemical performances of another typical layered material WS_2 in these two electrolytes were measured and DGM solvent was found to contribute to greatly promoted performances as well.

1. Introduction

Sodium ion batteries (SIBs) have been regarded as the most appealing alternative to lithium ion battery and become a hotspot for large scale storage applications owing to its low cost and abundant resource [1]. Currently, numerous efforts have been made to develop novel electrode materials following the tactics in lithium ion batteries (LIBs) [2–9]. However, the much larger ionic radius of sodium ions than that of lithium ions leads to poor reaction kinetics and sluggish ion transport at the electrode-electrolyte interface or inside the electrode, which makes it rather difficult to find ideal host materials for SIBs [10]. Taking graphite, a widely used anode materials, as an example, it is able to deliver a high capacity over 350 mAh·g^{-1} upon thousand cycles in LIBs. But it was once deemed as unfavorable for SIBs due to its relatively smaller interlayer spacing for sodium ion intercalation and thermodynamic instability of the Na-intercalated compounds [11]. Many efforts have been made to achieve sodium storage in graphite or few-layered graphene, a landmark breakthrough is the introduction of ether-based solvents that enables reversible sodium storage in graphite

via solvent co-intercalation accompanied by the formation of ternary compounds [12–15]. The co-intercalated ether solvents are able to enlarge the gap between graphite layers with well-retained layered structures and thus can facilitate fast sodium insertion/extraction. Here, the ideal layered structure of graphite are as well dedicate to solvent co-intercalation phenomenon, which provides adequate spaces for sodium ions and the solvents. From this viewpoint, some transitional metal sulfides, which hold quasi-layered or layered structure similar to graphite with weak van der Waals interaction between layers, are also found with good activity for sodium storage [16–20]. And these compounds are noted to possess even much larger interlayer distances for sodium ion insertion and possible solvent co-intercalation.

In addition to the activity of electrode materials towards sodium intercalation, the ion diffusion inside the electrode or electrode-electrolyte interface is another big concern. Present researches focus a lot on the structure engineering or compositional optimization to promote the sodium ion transport while less attention is paid to the electrolytes [21–25]. In fact, electrolyte is an important factor for sodium storage performances [26]. The solvent, as an essential part in electrolytes,

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greatly affects the behavior of the metal ions, solution structures and the ionic conductivity of the electrolyte [27]. Traditional carbonate-based solvents (ethylene carbonate (EC), dimethyl carbonate (DEC), etc.) have been predominately adopted in lithium/sodium ion batteries due to their high dielectric constants, wide chemical voltage windows and low volatilities. However, in view of their three-dimensional (3D) molecular structure, the solvated Na-carbonate group inevitably suffers from clumsy volume induced sluggish kinetics. Comparatively, the flexible 1D chain structure of ether molecular is expected to contribute to dramatically low spatial obstruction and accelerated intercalation kinetics [28]. DFT calculations also confirm that ether-based electrolyte can facilitate the transport of ions and electrons transport in electrodes [29]. Moreover, carbonate-based electrolytes are readily to react towards anionic groups or electrode intermediates upon cycling via a nucleophilic addition or substitution, while ether-based materials are much more inert towards those resultants and thus protect active materials from undesirable consumption [30–31]. Particularly, the introduction of ether solvents in Li-S or Na-S is proved capable to prohibit the reactions between the electrode charge/discharge intermediates and the electrolytes.

In this work, we choose quasi-layered VS_4 as the electrode material in consideration of its similar layer structure to graphite and diglyme (DGM) as a multifunctional electrolyte solvent, to investigate the synergetic effects of solid electrode structure and electrolyte solvent on the sodium storage performances. VS_4 demonstrates a loosely-stacked liner-chained framework connected via weak van der Waals force [32–34]. VS_4 possesses an interlayer distance of 0.583 nm that is larger enough for ion insertion and latent DGM co-intercalation. We first optimize the synthesis of VS_4/RGO composites via introducing polyvinyl pyrrolidone (PVP) as an effective surfactant to mitigate the restacking and self-aggregation of GO nanosheets. Then, the electrochemical performance in electrolyte with DGM and EC/DEC as the solvents is investigated in detail. The electrochemical results demonstrate much enhanced performances can be obtained in DGM electrolyte than in EC/DEC-based electrolytes. And similar promoted performances are also obtained for another typical layered material of WS_2 in DGM, which further prove the positive roles of ether-based solvents.

2. Experimental

2.1. Materials synthesis

All of the chemicals were analytical grade. 1.125 g (0.015 mol) of thioacetamide (TAA) and 0.55 g (0.0015 mol) of sodium orthavanadium ($Na_3VO_4\cdot12H_2O$) were dissolved in 15 mL of DI water, stirred until fully dissolved, then 20 ml commercial GO dispersion (2 mg/ml) with surfactant (cetrimonium bromide (CTAB) or PVP (Mw = 8000 or 1,300,000)) was added. Here, the ratio of V source to S source was set to be 1:10. In consideration of this far excess addition of sulfur source, the vanadium was assumed to be fully converted into the final dark VS_4 and thus, the amount of the RGO could be calculated to be 12.9 wt% to the total mass. For reference, pure RGO was obtained from the same reaction condition without the addition of vanadium source and sulfur source. The mixture was kept stirring for another 15 min at room temperature to utterly homogenize. Afterwards, the solution was transferred to a 50 ml Teflon lined stainless steel autoclave and kept at 160 °C for 24 h. After cooling naturally, the black gel product was dispersed, filtered and washed with DI water and freeze-dried for 24 h to obtain the final VS_4/RGO powder.

2.2. Structure and morphology characterization

The synthesized products were characterized using X-ray diffraction (XRD, PANalytical X'pert PRO-DY2198), scanning electron microscopy (SEM, FEI Sirion 200), transmission electron microscopy (TEM, FEI Tecnai G2 F30), confocal Raman spectroscopy (Raman, JobinYvon HR800) with a 532 nm excitation laser. Fourier transform infrared (FTIR) spectra were recorded in the range of 400 to 4000 cm^{-1} using a Bruker VERTEX 70 FTIR spectrometer.

2.3. Electrochemical measurements

The synthesized VS_4/RGO composite was manually mixed with polyvinylidene fluoride (PVDF) binder in *N*-Methyl pyrrolidone (NMP) and super C_{45} in a weight ratio of 80:10:10 to form slurry. The obtained slurries were coated uniformly onto copper foils and then dried in a vacuum oven at 80 °C for 12 h to remove the solvent before pressing. Finally, the electrode film was punched into disks of 10 mm in diameter for half-cell tests. CR2032-type coin cells were assembled inside an argon-filled glove box. Electrochemical measurements were performed using 2032 coin-type cells with thin sodium metal foil used as both the reference and counter electrodes. Celgard 3501 microporous film was chosen as the separator, 1 M sodium hexafluorophosphate ($NaPF_6$) in DGM was selected as the electrolyte. For comparison, 1 M $NaPF_6$ in EC/DEC was also used. Cyclic voltammetry (CV) studies were carried out at room temperature using CHI660e electrochemical workstation at different scan rate in the voltage window 0.01–2.2 V vs. Na^+/Na. Galvanostatic charge/discharge measurements were performed in a voltage range of 0.01–2.2 V vs. Na^+/Na at different current densities on the automatic battery testing system LAND CT2001A model. The dQ/dV tests were carried out on an automatic battery testing system of Hokuto Denko (HJ1001SD8).

3. Results and discussion

3.1. Synthesis and structural characterization of VS_4/RGO composites

The synthesis procedure of VS_4/RGO is schematically illustrated in Fig.1a. According to the XRD patterns presented in Fig. 1b, the addition of GO nanosheets plays a significant role in the formation of pure VS_4/RGO composites. GO nanosheets are reduced into RGO during the hydrothermal process at 160 °C. These RGO sheets together with the S^{2-} released from the TAA source both contribute to the reduction of vanadium ions. At the absence of GO sheets, two marked peaks originated from V_2O_5 impurities are observed at the absence of GO, which can be ascribed to the incomplete reduction of vanadium ions. Besides, GO nanosheet could be regarded as an ideal template or support for the nucleation and growth of VS_4 and conduces to the uniform distribution and the reduction in particle size of the products (Fig. 1c–d). These results have close relationships to the strong hydrophilicity of GO nanosheets and its electrostatic effect among VO_4^{3-} and S^{2-}, which are originated from the surface oxygenated functional groups of GO nanosheets [32].

However, the severe restacking and self-aggregation of GO cannot be neglected as shown in Fig. 1d. Therefore, PVP and CTAB as two of the most widely used surfactant are introduced to the reaction solution to address these issues on account of their chemical interaction towards GO [35]. Most of RGO nanosheets themselves were still accumulated together in solution with CTAB, while tiny cotton-like VS_4 particles were formed and tightly absorbed to the surface of RGO nanosheets once PVP is added. Besides, less aggregation was observed with gradually increased amount of PVP addition. PVP has already been proved to be an important inhibitor in limiting the growth of primary crystals, for example, during the synthesis of ZnS nanoparticles, [29] Ag nanowires [36], etc. PVP is comprised of hydrophobic vinyl and hydrophilic carbonyl groups that lead to the formation of polarized micelles [37–38]. During the nucleation process of VS_4 crystals, the carbonyl groups of PVP molecules are readily absorbed onto the solid particle surface, which can lower the surface energy and prohibit the aggregation and growth of these small particles via steric hindrance effect, leading to the amorphization and miniaturization of the VS_4 nanoparticles.