PEDOT-PSS coated ZnO/C hierarchical porous nanorods as ultralong-life anode material for lithium ion batteries

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Abstract

ZnO/C hierarchical porous nanorods were synthesized through one-pot wet-chemical reaction followed by thermal calcination. It was found that ZnO/C porous nanorods are composed of numerous nanograins, exhibiting a hierarchical micro/nanostructure. *In-situ* synchrotron high energy X-ray diffraction study revealed that ZnO/C hierarchical porous nanorods involve a two-step reversible lithiation mechanism during charge/discharge; and part of ZnO and Zn remain at the end of the first discharge and charge process, respectively, leading to a low coulombic efficiency in the initial few cycles. The electrochemical test demonstrated that the reversible capacity and the rate performance of ZnO/C hierarchical porous nanorods anode have been greatly improved by PEDOT-PSS coating, which could maintain a reversible capacity of 623.94 mAh g⁻¹ after 1500 cycles at 1 C. Its excellent high rate capability and long cycle stability were attributed to the high electronic conductivity of PEDOT-PSS coating layer and the hierarchical structures of ZnO/C porous nanorods.

Introduction

Zinc oxide (ZnO) has attracted a great deal of attention due to its wide application in many energy-related fields such as photo-electronics [1], sensors [2], solar cells [3-5] and photo-catalyst [6]. Recently, ZnO has also been considered as a promising anode material for the next generation lithium ion batteries owing to its high theoretical capacity of 978 mAh g^{-1} that is almost three times that of commercially used graphite anode (372 mAh g^{-1}), natural abundance, low cost and environmental friendliness [7-24]. Moreover, ZnO presents higher lithium-ion diffusion coefficient than other transition metal oxides [25]. ZnO can be also easily synthesized through a variety of methods such as hydrothermal reaction [26, 27], atomic layer deposition [10], magnetron sputtering [28, 29] and thermal decomposition [16, 17]. However, it was found that ZnO suffers from severe capacity degradation and inferior rate performance, which are both attributed to the low electronic conductivity of ZnO and the severe volumetric changes during charge/discharge [30]. A recent study by *in-situ* transmission electron microscopy (TEM) revealed that the lithium embrittlement of ZnO is much worse than that of SnO_2 , leading to the electrochemically driven solid-state amorphization and pulverization of ZnO [31]. Meanwhile, the lithiation mechanism of ZnO anode material in lithium ion batteries is still not very clear, preventing the application of ZnO as a battery electrode [32].

In order to overcome these issues, construction of nano-structured materials [13, 30, 33-35], metal doping [18] and decoration with highly conductive matrix [7-12, 36] such as graphene have been attempted to improve the electrochemical performance of ZnO anode. Very recently, MOF-derived ZnO@ZnO quantum dots/C core-shell nanorods array on a carbon cloth anode was synthesized and showed remarkable cycling performance [17]. Bresser et al. reported that the rate performance of ZnO anode could be greatly improved by transition metal (Fe or Co) doping at the atomic level [18]. Sun et al. synthesized a ZnO/graphene composite via atomic layer deposition, which can fine tune the size of ZnO quantum dots from 2 nm to 7 nm and size effect on the electrochemical performance was observed [10]. While Su et al.

reported that there are two kinds of reaction mode for ZnO electrode in terms of different reaction rates by in-situ transmission electron microscopy (TEM) [32]. Large Zn nanocrystals grew quickly in the violent reaction mode, preventing the formation of LiZn alloy and impairing the reversible capacity, which may be related to the electron transport and lithium-ion diffusion of various electrode materials at different rates. All these findings indicate that the rational design of ZnO nanostructures is of great importance to achieve an excellent lithium storage performance.

In this work, we have for the first time designed a PEDOT-PSS coated ZnO/C hierarchical porous nanorods nanocomposite as anode of lithium ion batteries, in which ZnO/C hierarchical porous nanorods are composed of numerous nanograins and was synthesized through one-pot wet chemical reaction followed by thermal calcination. PEDOT-PSS layer was then coated on the surface of ZnO/C porous nanorods by ball milling to further enhance its electronic conductivity. In this design, the hierarchical structures of ZnO/C porous nanorods helps accommodate the volumetric changes during charge/discharge, and the porous structures also facilitate the transportation of electrolytes and lithium ions. Furthermore, the graphitized carbon and the highly conductive PEDOT-PSS coating layer could greatly accelerate the electron transport. Benefitting from the above merits, PEDOT-PSS coated ZnO/C porous nanorods nanocomposite demonstrates high reversible capacity with excellent cycle stability and rate capability, which can maintain a reversible capacity as high as 623.94 mAh g⁻¹ after 1500 cycles at 1 C (1 C= 978 mA g⁻¹). Moreover, *in-situ* synchrotron high energy X-ray diffraction (HEXRD) was utilized to investigate the lithiation mechanism of ZnO anode, and revealed that unlike SnO₂ anode and other transition metal oxide (Co₃O₄, Fe₂O₃...) anode, ZnO/C hierarchical porous nanorods involve a two-step reversible lithiation mechanism, and part of ZnO and Zn remained at the end of the first discharge and charge process, leading to the low coulombic efficiency in the initial few cycles that are commonly reported in ZnO anode materials.

Experimental Section

Materials synthesis

ZnO/C hierarchical porous nanorods were synthesized according to the previous reported work with modification [37]. In a typical synthesis, anhydrous zinc acetate (4.0 g) was added to ethylene glycol (90 ml) and the mixture was stirred for 30 minutes under the protection of nitrogen. The above mixture was then stirred for another 90 minutes at 155 °C with reflux. After that, the obtained white slurry was collected by filtration followed by calcination at 600 °C for 2 h under argon atmosphere. PEDOT-PSS (Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)) solution (3%-4% in water) was purchased from sigma-Aldrich and used without any treatment. For the typical synthesis of PEDOT-PSS coated ZnO/C porous nanorods nanocomposite, 200 mg ZnO/C hierarchical porous nanorods were mixed with 790.0 mg PEDOT-PSS solution and balled milling for 1 h followed by drying in a vacuum oven at 100 °C overnight.

Structure characterization

The morphologies and structures of the as-synthesized materials were characterized by field emission scanning electron microscopy (HITACHI S-4700-II) and high resolution transmission electron microscopy (TEM, Philips CM30T, JEOL2100). The phase structure was collected by Powder X-ray diffraction (Miniflex, Rigaku Corp., Cu K α radiation). Raman experiment was performed using a Renishaw inVia microscope spectrometer.

Electrochemical measurement

The slurry was prepared by spreading a mixture of 79wt. % active material, 14wt. % carbon black and 7wt. % polyacrylic acid binder (9.8wt. %) onto a copper foil current collector. The as-prepared electrode was dried at 75 °C in a vacuum oven for 24 h. The electrochemical performances of the ZnO-based electrode were characterized by assembling them into coin cells (type CR2032) in an argon-filled glove box under conditions that the content of moisture and oxygen were both below 0.5 ppm. The anode was separated from lithium counter electrode by a separator (Celgard 2325). The electrolytes were carbonated electrolytes (GEN II) which is composed of LiPF₆ (1.2 M) dissolved in ethylene carbonate (EC) and ethyl methyl carbonate (EMC) (3:7

vol%), and a fluorinated carbonate-based electrolytes (named FC electrolyte) that was received from an industrial partner. The cells were charged and discharged in MACCOR system with a voltage range of 0.02-3.0 V (vs. Li/Li⁺). The capacities were calculated based on the active mass of ZnO/C composite and PEDOT-PSS/ZnO/C composite in the electrodes, respectively. The loading density was controlled at about 1.5-2.0 mg cm⁻².

***In-situ* synchrotron HEXRD study**

The *in-situ* synchrotron HEXRD measurements were carried out at Beamline 11-ID-C of the (Advanced Photon Sources, Argonne National Lab). The X-ray wavelength was 0.11798 Å. *In-situ* synchrotron HEXRD patterns were collected with custom-designed coin cells cycled with a MACCOR cycler at 0.08 C between 0.02 and 3 V. During the charging and discharging, the XRD patterns were collected for 1 min, with 10 min intervals, using a Perkin-Elmer 2D X-ray detector. 2D images were converted into a 1D plot of 2θ versus intensity by using the FIT2D program calibrated against a CeO₂ standard.

Results and discussions

The crystal structure of the as-synthesized ZnO/C hierarchical porous nanorods was characterized by X-ray diffraction. The Rietveld refinement of the XRD pattern (**Figure 1a**) shows that all the diffraction peaks of ZnO/C hierarchical porous nanorods can be well assigned to ZnO phase that belongs to a *P63mc* space group (PDF #89-0510, **Figure 1b**) with $a = b = 3.2477(2)$ Å and $c = 5.2061(1)$ Å. In addition, the pattern presents relatively sharp peaks, indicating good crystalline structure of the as-synthesized material. During the high temperature calcination process, the ethylene glycol was decomposed into carbon under the inert atmosphere. The property of the carbon was confirmed by Raman spectra (**Figure 1c**). Two broad peaks attributing to the typical disordered band (D band) (1337 cm⁻¹) and graphene band (G band) (1585 cm⁻¹) of carbon were observed. Moreover, the intensity ratio of the D band to the G band (I_D/I_G), standard of the graphitization degree, was calculated. The I_D/I_G value of ZnO/C porous nanorods is 0.867, which is lower than those of carbon black [38],

mesoporous carbon [39], and reduced graphene oxide [40], suggesting an increased graphitization and better electronic conductivity of carbon in the ZnO/C hierarchical porous nanorods.

The morphology, microstructure and crystallinity of ZnO/C hierarchical porous nanorods were characterized by scanning electron microscopy (SEM) and TEM. **Figure 2a** reveals its low magnification SEM image, which illustrates one dimensional rods with a diameter of 100-200 nm and length of several micrometers. It can be also clearly observed that the as-synthesized ZnO/C hierarchical porous nanorods are composed of numerous nanograins, exhibiting a hierarchical micro/nanostructure, which can be further confirmed by the SEM image in **Figure 2b** and the TEM image in **Figure 2c**. The primary particle size of these nanograins is determined to be about 10 nm from the high magnification TEM image in **Figure 2d**. Such a small particle size can effectively accommodate the mechanical stress during charge/discharge [41]. As these nanograins formed unique hierarchical nanorods, it can also prevent the aggregation of nanograins during repeated charge/discharge process [42]. The TEM images also illustrate that these nanograins are interconnected and formed a porous nanostructure. The formation of the pores should be attributed to the release of CO₂ during the decomposition of ethylene glycol. Such a structure could enable an efficient transportation of electrolytes and lithium ions as well as accommodate the volumetric changes during electrochemical cycling. N₂ adsorption/desorption curve and pore size distribution of ZnO hierarchical porous nanorods (see **Figure S1a** and **Figure S1b**) show it has a specific surface area of 87.0 m² g⁻¹ and a pore volume of 0.236 cm³ g⁻¹ with a wide pore size distribution. **Figure 2e** shows the HRTEM image of ZnO/C hierarchical porous nanorods, two sets of clear lattice fringes with interplanar distances of 0.259 nm and 0.244 nm were observed, which are in perfect agreement with the d-spacing of (002) and (101) planes of ZnO, respectively. The polycrystalline property of ZnO/C hierarchical porous nanorods is confirmed by the selected area electron diffraction (SAED) pattern in **Figure 2f**, which presents a typical polycrystalline ring pattern.

The understanding of lithiation/de-lithiation mechanism of ZnO anode is very

important for the improvement of its electrochemical performance. As a metal oxide anode, there are several possible mechanisms proposed for ZnO anode and their corresponding theoretical capacities are all estimated:

For mechanism 1, it is similar to the lithiation mechanism of SnO_2 anode [43, 44], which can therefore obtain a theoretical capacity of only 330 mAh g^{-1} (denoted as TC1). However, the TC1 is much lower than most of the reversible capacities for ZnO anode that have been reported. Therefore, such a mechanism is less likely. For mechanism 2, ZnO undergoes a conversion reaction mechanism that has been commonly reported in the transition metal oxide anodes such as Co_3O_4 and Mn_3O_4 [45-47]. Such a mechanism can therefore offer a theoretical capacity of around 658.5 mAh g^{-1} (denoted as TC2). This mechanism is kind of possible since most of the reversible capacities reported are in this range. While for mechanism 3, the ZnO anode presents a two-step reversible lithiation mechanism during the electrochemical cycling, involving the initial reduction of zinc oxide to metallic zinc accompanied by the formation of amorphous Li_2O , and further alloying of Li with Zn to form LiZn alloy, offering an overall theoretical capacity of 978 mAh g^{-1} (denoted as TC3) [18]. Such a mechanism was mostly reported but was generally inferred by ex-situ measurements [14, 48]. The distinct difference between mechanism 2 and mechanism 3 are the alloying process between Li and Zn to form LiZn. Once the formation of LiZn alloy could be confirmed, the mechanism of ZnO anode can be hence determined. In order to understand the lithiation mechanism and further improve the electrochemical performance of ZnO/C hierarchical porous nanorods, *in-situ* synchrotron HEXRD was conducted using custom-designed coin cell to tracking the structure changes and phase evolution of ZnO/C hierarchical porous nanorods during the charge/discharge process. High energy X-rays, which can penetrate the Cu current

collector and Li foil, make the measurements possible.

Figure 3a shows the contour plot of *in-situ* synchrotron HEXRD patterns collected during the 1st charge/discharge cycle at a rate of 0.08 C. The red color represents high intensity, and the blue color means low intensity. The blue rectangle area appeared corresponding to test time about 3.5-5.5 h was caused by the beam loss from a power supply during *in-situ* measurements. This interrupt did not affect the following *in-situ* measurements, which can be inferred from the quasi-linear changes of XRD signals during the 1st discharging. It can be seen that bulk phase consumption and new phase formation both occurred during the 1st charge/discharge process, and the major phase evolution appeared at 2θ range of $2-3^\circ$ and $4-5^\circ$. In order to trace subtle changes that are not visually clear in **Figure 3a**, **Figure 3b** and **Figure 3c** shows the enlarged 2θ range of $2.25-2.75^\circ$ and $3.9-5.2^\circ$, respectively. The signals appeared at $2\theta = 2.40^\circ, 2.60^\circ, 2.70^\circ, 4.16^\circ, 4.6^\circ$ and 4.9° are attributed to ZnO phase (PDF #89-0510). When the cell started to be discharged, the intensities of ZnO signal were gradually decreased, which was owing to the continuous reduction of ZnO during discharging. However, we did not observe simultaneously increase of Zn and Li_2O signals during this process, indicating that they may be formed in an amorphous state. When the cell was discharged to about 0.25 V, the signal of ZnO has almost disappeared. While we also do not observe the signal of LiZn when the cell was further discharged from 0.25 V to 0.02 V, indicating that there may be no formation of LiZn or LiZn also form in an amorphous state, which direct determine the lithiation mechanism of ZnO/C hierarchical porous nanorods. Such a debate could be settled based on the emergence of crystallized Zn phase ($2\theta = 5.1^\circ$) when the cell was recharged. If the ZnO/C porous nanorods undergo the conversion reaction (mechanism 2), there should be no appearance of Zn phase during the charging process. In other word, ZnO/C porous nanorods undergo two-step reversible lithiation mechanism (mechanism 3), and the emergence of crystallized Zn phase was due to the transformation of amorphous LiZn to crystallized Zn. However, it's obviously observed that the intensity for the ZnO signals cannot be completely recovered when the cell was charged back to 3.0 V; indicating that part of ZnO may be reformed in an

amorphous state or part of Zn remain at the end of charge process and therefore cannot be converted back to ZnO. In order to show the phase changes more clearly and clarify the lithiation mechanism, the HEXRD patterns of ZnO/C hierarchical porous nanorods collected at different charge/discharge states are shown in **Figure 4**.

Figure 4a and **Figure 4b** shows the HEXRD patterns collected at different charge/discharge states of ZnO/C hierarchical porous nanorods in the 1st cycle. It should be noted that the strong peaks at 3.25° and 3.735° are both assigned to the Cu (PDF #03-1015) current collector, and the peaks of the Li (PDF #15-0401) counter electrode in the coin cell appeared at 2.726°, 3.846° and 4.715°. The HEXRD pattern collected before charge/discharge can be well assigned to the ZnO phase (marked by star). As shown, there are no obvious changes when the cell was discharged from open circuit potential (3.03 V) to 0.684 V, indicating that there is no or very little reduction of ZnO above 0.684 V and the capacity in this region is mainly contributed by the decomposition of electrolytes to form the well-known solid electrolyte interphase (SEI) layer. When the cell was further discharged, the intensities for the XRD peaks belong to ZnO were gradually decreased from 0.684 V to 0.225 V and then remained unchanged from 0.225 V and 0.02 V, indicating that there are part of un-reacted ZnO remain at the end of the 1st discharge. Meanwhile, we do not observe XRD peaks of Zn and Li₂O during this process (0.684-0.225 V), which suggests that they are formed in an amorphous state. When the cell was discharged below 0.225 V, amorphous LiZn should be formed as there are also no XRD peaks belong to LiZn. During the 1st charge process, the intensities for the XRD peaks of Zn (marked by #) increased and remain unchanged below 0.756 V, which is attributed to the de-alloying process of amorphous LiZn. Here we speculated that amorphous Zn should be also generated and then converted back to amorphous ZnO during the 1st charge as the XRD intensities for crystallized Zn and the ZnO kept nearly the same while about 500 mAh g⁻¹ was obtained when the cell was charged from 0.756 V to 3.0 V (**Figure 4c**). The formation of amorphous transition metallic phase and Li₂O have been also reported in the mechanism study of metal oxide anodes by *in-situ* X-ray technique [18, 45, 49, 50], which may be due to their amorphous structure property, or the particle

size of the related phase is smaller than the X-ray coherence length. **Figure 4c** shows the proposed schematic for the phase evolution of ZnO/C porous nanorods in the 1st cycle. It can be divided into SEI region (I), ZnO reduction region (II) and alloy region (III) during discharge, which could contribute a capacity of about 240 mAh g⁻¹, 800 mAh g⁻¹ and 300 mAh g⁻¹, respectively. While de-alloy region (IV) and ZnO re-formation region (V) account for the whole charge process, offering a reversible capacity of about 300 mAh g⁻¹ and 500 mAh g⁻¹, respectively. The results show that the alloy and de-alloy process are highly reversible, while the 1st irreversible capacity mainly come from the SEI formation and residue of Zn. In summary, *in-situ* synchrotron HEXRD study illustrated that unlike SnO₂ anode and other transition metal oxide (Fe₂O₃, Co₃O₄, Mn₃O₄...) anode, ZnO/C hierarchical porous nanorods involved a two-step reversible lithiation mechanism, and part of ZnO and Zn remained at the end of the first discharge and charge process, respectively. These electrochemical characteristic will significantly affect its lithium storage performance in terms of reversible capacity, coulombic efficiency and cycle performance as discussed below.

The electrochemical performance of ZnO/C hierarchical porous nanorods as anode of lithium ion batteries was evaluated by using a standard Li/ZnO coin cell. The charge/discharge curves of ZnO/C hierarchical porous nanorods electrode in the 1st, 2nd and 30th and 60th cycle at 0.05 C are shown in **Figure 5a**, which present typical features of ZnO-based anode materials. The 1st discharge capacity of ZnO/C porous nanorods was measured to be 1357.1 mAh g⁻¹, which is higher than the theoretical capacity of ZnO (978 mAh g⁻¹). This phenomenon was commonly reported in the metal oxide-based anode materials [47, 51, 52], and was generally ascribed to the formation of SEI layer and the further lithium storage via interfacial charging at the metal/Li₂O interface [53]. Another reason may be due to the formation of lithium oxide since it continuously consumed lithium during discharge process, which would also contribute extra capacity. The 1st charge capacity was determined at 809.4 mAh g⁻¹, leading to an initial coulombic efficiency of 59.6%. Such a low initial coulombic efficiency was commonly reported in most of ZnO based anode materials and should

be mainly originated from the SEI formation and residue of Zn as indicated by *in-situ* synchrotron HEXRD results. Compared to the previous reported work about ZnO anode, we found that the 1st coulombic efficiency for most of the ZnO-based anode materials is in the range of 50%-70%. To the best of our knowledge, only few works has shown high coulombic efficiency over 70%. This is achieved by transition metal doping and fabrication of ZnO quantum dots material, which may be due to that quantum dot size particle [17] and transition metal doping [18] could enhance the reaction between ZnO and Li, thus increase the reversible capacity of ZnO anode. In the subsequent cycles, the voltage profile was similar to the 1st cycle but with an increased voltage polarization and capacity decreasing, which was owing to the structure changes and increase of the internal cell resistance that are commonly reported in other electrode materials [54-56]. The differential capacity curves of ZnO/C hierarchical porous nanorods at different cycles are shown in **Figure 5b**. In the 1st discharge process, two large reduction peaks appeared at 0.730 V and 0.539 V, which are owing to the formation of SEI layer, and the reduction of ZnO to Zn, respectively. The reduction peak started at about 0.25 V should be attributed to the alloying process between Li and Zn. In the 1st charge process, four small oxidation peaks were found at 0.258, 0.344, 0.534 and 0.678 V, which were ascribed to the multi-step de-alloying of LiZn [11]. The broad peak at 1.266 V was owing to the conversion of Zn back to ZnO. It is then found that a new reduction peak started from 1.25 V and centered at about 0.781 V was observed in the 2nd cycle and then decreased along with the cycling and finally stabilized after 10 cycles.

The cycling performance of ZnO/C hierarchical porous nanorods was recorded in **Figure 5c**. It can be seen that the reversible capacity decreased slightly in the initial 10 cycles and stabilized at about 570 mAh g⁻¹ after 30 cycles, and then slightly increased to 630 mAh g⁻¹ after 60 cycles, which showed much higher reversible capacity and better cycle stability than the commercial ZnO electrode at the same charge/discharge rate. While the commercial ZnO electrode rapidly decayed to a capacity lower than 100 mAh g⁻¹ in 10 cycles (see **Figure S2a** and **Figure S2b**), which may be related to its larger particle size (hundreds of nanometer, see **Figure**

S2c) and the irregular assembly morphology (see **Figure S2d**), which will be very easy to aggregate during repeated electrochemical cycling. The discharge capacities of the ZnO/C hierarchical porous nanorods are higher than the charge capacities in the initial 10 cycles, leading to the low coulombic efficiency in the initial few cycles, which was commonly reported in most of ZnO-based anode materials [8-11, 14-18, 21, 57-62] but rarely seen in other transition metal oxide (Co_3O_4 , Fe_2O_3 ...) anode materials based on conversion reaction [42, 47, 51]. Such phenomenon should be attributed to the gradual reduction of the residual ZnO at the end of the 1st discharge as confirmed by *in-situ* synchrotron HEXRD study, which will offer extra discharge capacities in the subsequent discharging process. Moreover, they cannot be completely converted back and part of Zn remained at the end of charge process, leading to the lower charge capacities than the discharge capacities in the initial few cycles. The residual Zn will then gradually reacted after tens of cycle, resulting in the slightly increase of capacities after 30 cycles. The rate performance was also measured to evaluate its fast charge/discharge property (**Figure 5d**). The cell was first cycled at 0.05 C, and then the charge/discharge rate was increased successively to 0.1 C, 0.2 C, 0.4 C, 0.8 C, 1 C, 2 C and 3 C, respectively. The corresponding average reversible capacities within 5 cycles were calculated to be 750.0, 604.8, 514.9, 454.9, 392.9, 375.0, 268.5 and 179.6 mAh g⁻¹, respectively. When the charge/discharge rate was decreased back to 0.1 C, an average capacity of about 558.7 mAh g⁻¹ was recovered, which is 92.3% of the initial average reversible capacity at 0.1 C. However, the reversible capacity at high rate of 3 C was only 179.6 mAh g⁻¹, which may be associated to the electronic conductivity of ZnO/C hierarchical porous nanorods and need to be further optimized.

In order to increase the reversible capacity and improve the rate performance of ZnO/C hierarchical porous nanorods, highly conductive PEDOT-PSS polymer layer (conductivity: 150 S cm⁻¹ as measured by manufacturer) was coated on the surface of ZnO/C hierarchical porous nanorods by ball milling to enhance its electronic conductivity. It's clearly observed that the nanorods morphology is well conserved and the surface became smoother after PEDOT-PSS coating from the SEM images

(see **Figure S3a** and **Figure S3b**). The TEM images of ZnO/C hierarchical nanorods without and with PEDOT-PSS coating are also characterized. As shown, the surface of ZnO/C hierarchical nanorods is coated with a homogenous layer after PEDOT-PSS coating (**Figure S4a** and **Figure S4c**). From the high resolution TEM images (**Figure S4b** and **Figure S4d**), it can be observed more clearly that there is a polymer layer (as indicated by the white line) coated on the surface of ZnO particles after PEDOT-PSS coating. On the other hand, the fluorinated electrolytes have been commonly used to improve the cycle and rate performance of battery materials [63]. **Figure 6a** shows the rate performance of PEDOT-PSS/ZnO/C nanocomposite in a fluorinated carbonate-based electrolyte (FC electrolyte) as received from an industrial partner. At a charge/discharge rate of 0.05 C, an average reversible capacity as high as 876.2 mAh⁻¹ could be delivered. The average reversible capacities were decreased along with increasing the charge/discharge rate, and were calculated to be 769.4 mAh g⁻¹ (0.1 C), 703.0 mAh g⁻¹ (0.2 C), 619.6 mAh g⁻¹ (0.4 C), 526.8 mAh g⁻¹ (0.8 C), 498.8 mAh g⁻¹ (1 C), 400.7 mAh g⁻¹ (2 C), respectively. Even at a high charge/discharge rate of 3 C, it can still maintain an average capacity of 362.8 mAh g⁻¹, which is almost the theoretical capacity of commercial used graphite anode (372.0 mAh g⁻¹), demonstrating excellent rate performance. When the charge/discharge rate was decreased back to 0.1 C, an average capacity of 787.8 mAh g⁻¹ could be recovered. **Figure 6b** shows the long cycling performance of PEDOT-PSS/ZnO/C nanocomposite at 0.5 C and 1 C. The cell was firstly cycled at 0.05 C for 3 cycles for cell formation, and then the charge/discharge rate was increased to 0.5 C and 1 C, respectively. It can be seen that PEDOT-PSS/ZnO/C nanocomposite could deliver a stable capacity of 748.1 mAh g⁻¹ after 500 cycles at 0.5 C, demonstrating excellent long cycle performance. At an even higher rate of 1 C, a stable capacity of about 623.94 mAh g⁻¹ was still measured after 1500 cycles, illustrating excellent cycle stability at high rate of charge/discharge (see **Table S1**). The SEM image (**Figure S5**) of the PEDOT-PSS coated ZnO/C hierarchical porous nanorods after 1500 cycles of charge/discharge showed that the nanorods could be still observed after long-term cycles of charge/discharge, indicating very good structure stability. The results

showed that the reversible capacity and the rate performance of ZnO/C hierarchical porous nanorods have been significantly improved by PEDOT-PSS coating and use of FC electrolyte (**Figure S6a**). In order to clearly illustrate the effect of PEDOT-PSS coating and FC electrolyte, the cycling performance of ZnO/C anode using GENII electrolyte without PEDOT-PSS coating and using FC electrolyte without and with PEDOT-PSS coating at a relatively high rate of 0.5 C are compared. As shown, the cycle performance are slightly improved by use of FC electrolyte and further greatly improved by PEDOT-PSS coating (**Figure S6b**). Therefore, the improved lithium storage performance of PEDOT-PSS/ZnO/C is major attributed to the high electronic conductivity of PEDOT-PSS coating layer and the hierarchical structure of ZnO/C porous nanorods, which can accelerate the electron transport and accommodate the volumetric changes during charge/discharge. It can be also seen that the reversible capacity of PDOT-PSS/ZnO/C anode are gradually increased upon cycling. The gradual capacity increasing during cycling process was also reported in other transition metal oxide anodes such as Co_3O_4 , Fe_2O_3 , MnO and etc. This phenomenon was generally attributed to the gradual decomposition of the irreversible Li_2O generated in the 1st discharge process [47] and/or the interfacial lithium storage [53]. Another possible reason is due to the wetting problem between the electrode and electrolytes, which will lead to a gradually increased utilization of active material upon continuous cycling.

Considering the excellent half cell performance of PEDOT-PSS/ZnO/C nanocomposite, a $\text{ZnO/LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ using PEDOT-PSS/ZnO/C anode (denoted as ZnO/NCM) lithium ion battery is preliminarily proposed. Owing to its low initial coulombic efficiency, PEDOT-PSS/ZnO/C anode was pre-electrochemical lithiation at 0.05 C for 3 cycles before assembled as an anode for ZnO/NCM full cell. The NCM cathode was bought from an industrial company and the NCM/Li half cell could deliver a reversible capacity of about 190 mAh g^{-1} at 0.1 C (**Figure 6c**). It's exciting to find out that the ZnO/NCM lithium ion battery could deliver a reversible capacity of about 180 mAh g^{-1} with an average working voltage range of 3.0-4.0 V at a low rate of 0.1 C and can maintain 126.1 mAh g^{-1} after 30 cycles at 1 C, indicating

strongly that the ZnO/NCM full cell is a very promising lithium ion battery. The gradual capacity fading of the assembled full cell may be due to the relatively low coulombic efficiency of PEDOT-PSS/ZnO/C anode material, which will consume extra lithium that come from the cathode during cycling. Therefore, part of lithium cannot be completely inserted back to NMC cathode, leading to the gradual capacity fading of the full cell. For the half cell, the lithium can be compensated by lithium anode. Therefore, the cycle stability of half cell is much better. In order to improve the cycle stability of the full cell, the improvement of the coulombic efficiency of ZnO anode material must be done ahead, which need more efforts in the future.

Conclusions

In this work, we have for the first time designed and synthesized a PEDOT-PSS coated ZnO/C hierarchical porous nanorods nanocomposite, in which ZnO/C porous nanorods were composed of numerous nanograins and synthesized through one-pot wet chemical reaction followed by thermal calcination. The electrochemical test illustrated that the reversible capacity and rate performance of ZnO/C porous nanorods have been greatly improved by PEDOT-PSS surface coating. It can still maintain a reversible capacity of about 362.8 mAh g⁻¹ at a high charge/discharge rate of 3 C and can manifest a stable capacity of 748.1 mAh g⁻¹ after 500 cycles at 0.5 C and even 623.94 mAh g⁻¹ after 1500 cycles at 1 C, demonstrating excellent rate performance and ultralong cycle stability. *In-situ* synchrotron HEXRD study revealed ZnO/C hierarchical porous nanorods involved a two step reversible lithiation mechanism, which is different to SnO₂ anode and other transition metal oxide (Co₃O₄, Fe₂O₃...) anode based on conversion reaction. It was also found that part of ZnO and Zn remained at the end of the initial discharge and charge process, respectively, which should be responsible for the low coulombic efficiency in the initial few cycles that were also reported in most of ZnO anode materials.

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Appendix A. Supporting materials

Supplementary data associated with this article can be found in the online version at DOI: xxxxx.

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Figure 1 a) XRD pattern of ZnO/C hierarchical porous nanorods, b) Crystal structure of ZnO and c) Raman spectra of ZnO/C hierarchical porous nanorods.

Figure 2 a) Low and b) high magnification SEM images, c) Low and d) high magnification TEM images, e) HRTEM image and f) SAED pattern of ZnO/C hierarchical porous nanorods.

Figure 3 *In-situ* synchrotron HEXRD measurements for ZnO/C hierarchical porous nanorods during the 1st charge/discharge cycle in GEN II electrolyte at 0.08 C: contour plot of HEXRD patterns collected at 2θ range of a) $1.0-6.0^\circ$, b) $2.25-2.75^\circ$ and c) $3.9-5.2^\circ$.

Figure 4 HEXRD patterns of ZnO/C hierarchical porous nanorods electrode collected at different potential: a) discharge process and b) charge process in GEN II electrolyte during *in-situ* measurement. c) proposed schematic for the phase evolution of ZnO/C hierarchical porous nanorods in the 1st cycle, A—amorphous and C-crystallized.

Figure 5 a) Charge/discharge curves, b) Differential capacity curves at different cycles and c) cycle performance at 0.05 C, and d) rate performance of ZnO/C hierarchical porous nanorods in GEN II electrolyte.

Figure 6 a) Rate performance, Cycling performance at b) 0.5 C and c) 1 C of PEDOT-PSS coated ZnO/C hierarchical porous nanorods in FC electrolyte, d) charge/discharge curves of $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2/\text{Li}$ half cell and $\text{ZnO}/\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ lithium ion battery at 0.1 C in FC electrolyte, inset shows the cycle performance of $\text{ZnO}/\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ lithium ion battery.

Vitae

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Graphical Abstract

PEDOT-PSS coated ZnO/C hierarchical porous nanorods were fabricated as anode of lithium ion batteries. Thanks to the unique hierarchical micro/nanostructures and PEDOT-PSS coating, it has demonstrated a high reversible capacity with an ultralong cycle life and excellent rate capability. *In-situ* synchrotron high energy X-ray diffraction was further utilized to study the lithiation mechanism of ZnO anode.