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Sol-gel synthesis of ZnO/TiO_2 core-shell nanocomposites and their structural and electrochemical characterization as anode for lithium ion battery

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This study focused on synthesis of ZnO/TiO₂ core-shell nanocomposites on copper substrate by sol-gel method and their structural and electrochemical characterization as anodes for lithium ion batteries. SEM and XRD results exhibited the high density of the ZnO/TiO₂ nanocomposite in core-shell morphology were synthesized on copper foil. Electrochemical studies showed more stable behavior, higher capacity, coulombic efficiencies and excellent reversibility and long-life cycling performance of ZnO/TiO₂ core-shell nanocomposite compared to the ZnO and TiO₂ films. EIS studies demonstrated the synergistic effect of ZnO/TiO₂ core-shell structures leading to improvement in the diffusion of lithium-ions into anode due to creation of the high surface area, short lithium-ions diffusion path and high electron transportation rate. Coulombic efficiency of ZnO/TiO₂ core-shell nanocomposites was achieved more than 98% which was higher than the obtained values of ZnO (94%) and TiO₂ (93%) films.

Keyword: Lithium ion battery; ZnO/TiO₂ core-shell nanocomposites; Coulombic efficiency; Capacity; Reversibility; Cycling performance

1. INTRODUCTION

For several decades, nickel-metal-hydride based batteries had been considered as portable battery for mobile communication equipment. Further researches have been shown that lithium-ion batteries can be considered as the most promising rechargeable batteries because of lithium suitable physical and chemical properties such as its lightness, low maintenance, low cost, low toxicity, greatest electrochemical potential, and the largest energy density for weight. For example, the selfdischarge of lithium-ion batteries is less than the nickel-cadmium and its energy density is more than the nickel-cadmium batteries which leads to miniaturization of the design of the electronic cell [1]. However, many studies are conducted to develop rechargeable lithium batteries because of increasing global demands and to overcome deficiencies such as safety problems and require to a protection circuit for maintaining safe operation, deterioration of capacity and aging negative effect. Accordingly, miniaturization and modification of chemical structure through nanotechnology and nanochemistry can be applied for improvement of lithium-ion battery properties such as capacity, safety, cycle life, and charge–discharge rates.

Therefore, modification of the electrochemical cell electrode have been investigated with the different nanomaterials such as carbon nanotubes, carbon nanofibers, graphene, nanocomposites and nanostructures of metal oxides, sulfides, nitrides, phosphides, and fluorides [2]. Among them, ZnO and TiO₂ as low cost, eco-friendly and high productivity transition metal oxides show high theoretical capacities of 978 mAh g⁻¹ and 330 mAh g⁻¹, respectively [3, 4]. However, there is insufficient electrical conductivity, low electrochemical reaction kinetics and low stability for ZnO and TiO₂ based anodes. Therefore, many studies were carried out on ZnO, TiO₂ based anodes and their composition to develop the performance of electrochemical lithium batteries such as zinc oxide/N-doped carbon [3], TiO₂/polyaniline composites [4], ZnO@TiO₂ heterostructure arrays/carbon [5], ZnO decorated TiO₂ nanosheet composites [6], TiO₂ coated ZnO nanorods [7]. These studies showed that the ZnO and TiO₂ nanostructured anodes demonstrate significant lithium storage performance, high cycling performance, excellent rate capability and high reversible capacity in lithium-ion electrochemical cells [5-7]. Thus, this study is focused on fabrication and electrochemical characterizations of ZnO/TiO₂ core-shell nanocomposite as an anode in lithium-ion batteries.

2. EXPERIMENTAL

The sol-gel method was applied to synthesize the ZnO/TiO₂ core-shell nanocomposite, ZnO and TiO₂ films [8]. For synthesis of ZnO/TiO₂ core-shell nanocomposite the mixture of ZnO (nanopowder, <100 nm particle size, 99%, Merck, Germany) and titanium isopropoxide (TTIP, 97%, Merck, Germany) was added in isopropyl alcohol with a mole ratio of 1: 1: 4, respectively. For synthesis of ZnO and TiO₂ films, the mixture of ZnO and titanium isopropoxide was added in isopropyl alcohol with a mole ratio of 1: 0: 4 and 0: 1: 4, respectively. Then, the prepared mixture was dispersed ultrasonically for 25 minutes. After then, deionized water was added to the dispersed mixture with a mole ratio of 1: 2 and the prepared mixture was dispersed ultrasonically again for 10 minutes. Afterward, the prepared suspension was transferred to autoclave at 60°C for 24 hours and then transferred on copper foil (1 cm^2) and calcined at 300 °C for 4 hours in air atmosphere.

Scanning electron microscopy (SEM, S360 Cambridge instrument, UK) was used for characterization of the structure and morphology of prepared anodes. X-ray diffractometer with Cu K α radiation ($\lambda = 1.5418$ Å) which operates at 40 kV and 30 mA was applied to crystallinity characterization of samples.

CR2032-type coin cells were prepared to study the electrochemical properties of synthesized anodes. The electrochemical cells were contained the synthesized ZnO/TiO_2 core-shell nanocomposite, ZnO and TiO₂ films on copper foil as the working electrodes, a lithium metal as both of the counter

and the reference electrodes and the commercial Microporous monolayer polypropylene as separator. An electrolyte solution was prepared with dissolve of commercial LiPF₆ (1.0 M) in a mixture of ethylene carbonate and dimethyl carbonate with a volume ratio of 1:1:1. The prepared coin cell was assembled in a glove box under the Argon atmosphere. The cycling performance analyses were carried out in a LAND battery measurement system (Land CT2001A, Wuhan, China). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were recorded on electrochemical potentiostat/galvanostat system (PGSTAT204 Autolab, Ecoe Chemie, Switzerland).

3. RESULTS and DISCUSSION

Figure 1 shows the SEM images of the synthesized ZnO nanorods and ZnO/TiO2 core-shell nanocomposite on copper foil. As observed in figure 1a, the high density of the ZnO nanorod morphology in hexagonal cross section as shell were synthesized. Figure 1b displays the SEM images of the synthesized ZnO/TiO₂ core-shell nanocomposite. The SEM images clearly display that ZnO aggregated under ultrasonically dispersing conditions and TiO₂ particles were incorporated into the ZnO nanorods. Results Zhao et al. [9] and amírez-Ortega et al. [8] for synthesis the ZnO/TiO₂ Core-Shell composites are evidence for the growth of ZnO/TiO₂ core-shell nanocomposite in rod-like shape.



Figure 1. SEM image of synthesized (a) ZnO nanorods, (b) ZnO/TiO₂ core-shell nanocomposite on copper foil.

In order to study the phase crystal formation in nanocomposites, XRD patterns of samples are presented in Figure 2. As shown in XRD pattern of ZnO, the diffraction peaks observed at $2\theta = 31.80^{\circ}$, 34.39° , 36.23° , 47.59° , 57.04° , 62.868° , 66.31° , 68.02° , and 68.98° which attributing the formation of (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (2 0 0), (1 1 2), and (2 0 1) planes of wurtzite structure

of ZnO according to JCPDS card No. 75-0576 [10]. XRD pattern of TiO₂ shows the diffraction peaks at $2\theta = 25.28^{\circ}$, 37.81° , 47.97° , 53.91° , 55.10° , 62.70° , 68.81° , 70.31° , and 77.02° which corresponding to (101), (004), (200), (105), (211), (213), (116), (220), and (107) planes of TiO₂ anatase phase according to JCPDS card No. 21-1272. XRD pattern of ZnO/TiO₂ core-shell nanocomposite shows simultaneously ZnO and TiO₂ diffraction peaks which denote the incorporation of TiO₂ to ZnO lattice.



Figure 2. XRD pattern of synthesized ZnO film, TiO₂ film and ZnO/TiO₂ core-shell nanocomposite.

Figure 3a displays the first three recorded CVs of ZnO/TiO_2 core-shell nanocomposite as anode between -0.5 and 3.5 V at a scan rate of 0.1 mV s⁻¹. According to the published literatures [11], the electrochemical mechanism for ZnO anode electrode towards lithium is demonstrated as reactions (1) and (2), respectively :

$$ZnO + 2Li^{+} + 2e^{-} \leftrightarrow Li_{2}O + Zn$$
(1)
$$Zn + Li^{+} + e^{-} \leftrightarrow LiZn$$
(2)

As shown in Figure 3a, there are small three peaks at 0.30 V, 0.14 V and -0.12 V in the initial cathodic sweep. The small peak at 0.30 V refers to the decomposition ZnO on liquid electrolyte and the formation a insoluble layer of primal solid electrolyte interphase [11]. The peak at 0.14 V is related to the conversion reaction (1) between Li and ZnO ion to formation Zn and Li₂O. The reaction (2) for production of LiZn alloy is conducted at -0.12 V [11, 12]. In the following anodic sweep of the first cycle, four peaks are observed at -0.06 V, 0.16 V, 0.56 V and 1.22 V. The first three peaks are associated with the de-alloying reactions of LiZn and re-oxidation of Zn. The peak at 1.22 can signify the formation of ZnO by the electrochemical reaction between Li₂O/Li₂TiO₃ and Zn [13]. In the recorded subsequent CVs it is observed relative satisfactory repeatability and reproducibility electrochemical responses of ZnO/TiO₂ core-shell nanocomposite which reveal high stability and reversibility of prepared nanocomposite. In order to further study the stability responses of ZnO and



 TiO_2 films are shown in Figure 3b and c. As seen, the recorded CVs of ZnO and TiO_2 films do not show stability and the surrounding areas in CVs were decreased after two and three successive scans.

Figure 3. The first three recorded CVs of (a) ZnO/TiO_2 core-shell nanocomposite, (b) ZnO and (c) TiO₂ films between -0.5 and 3.5 V at a 0.1 mV s⁻¹ scan rate.

1

2

Potential (V) vs Li⁺/Li

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-1

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Figure 4a displays the cycling performance of ZnO film, TiO₂ film and ZnO/TiO₂ core-shell nanocomposite at 450 mAg⁻¹ for 200 cycles at voltage range from 0.0 to 2.2 V. The decreasing in capacity is observed for ZnO and TiO₂ films after 50 and 40 cycles, respectively and capacity values of both films maintain at~180 mAh g⁻¹ after 200 cycles. As shown for ZnO/TiO₂ core-shell nanocomposite, the capacity is decreased in first ten cycles and shows stable treatment and reversible capacity of 402 mAhg⁻¹ for cycle numbers from 10 to 200 which indicating the great cycling performance of prepared ZnO/TiO₂ nanocomposite. Figure 4b shows the coulombic efficiency of samples at 450 mAg⁻¹ in voltage range from 0.0 to 2.2 V after 200 cycles. The coulombic efficiency of ZnO/TiO₂ core-shell nanocomposite was obtained more than 98% which was higher than the obtained coulombic efficiencies of ZnO (94%) and TiO₂ (93%) films after 200 cycles. Furthermore, it is presenting significant improvement of capacity retention. The comparison with obtained columbic efficiencies of ZnO–Se thin film [14], ZnO [15], ZnO@Graphene composites [16], radial ZnO microparticles deposited on graphene nanosheets [17], ZnO Microrod Arrays Grown on Copper [18], Ordered ZnO/Ni hollow microsphere arrays [19] and ZnSe [20], which demonstrating the much better



capacity retention treatment ZnO/TiO₂ core-shell nanocomposite than the other prepared anodes.

Figure 4. (a) Cycling performance and (b) the columbic efficiency of ZnO film, TiO_2 film and ZnO/TiO₂ core-shell nanocomposite at 450 mAg⁻¹ for 200 cycles in a voltage range from 0.0 to 2.2 V.

Figure 5a displays the rate capability response of ZnO/TiO_2 core-shell nanocomposite from 250 mAg^{-1} to 3000 mAg^{-1} which clearly shows considerable capacity retention at different current densities. The high capacity of ~ 320 mAhg^{-1} is observed for a current density of 3000 mAg^{-1} which illustrates a great rate performance of prepared anode. Repeatability and reversibility of prepared samples are also evaluated in Figure 5a which shows with the current density returning to 250 mAg^{-1} , the capacity values of ZnO film, TiO₂ film and ZnO/TiO₂ core-shell nanocomposite return to 100, 110 and 820 mAhg^{-1}, respectively. It demonstrates the high ability and reversibility of ZnO/TiO₂ core-shell nanocomposite in comparison to the poor rate reversibility of ZnO and

 TiO_2 films. In order to study the long-life, cycling performance of ZnO/TiO₂ core-shell nanocomposite was recorded at 450 mAg⁻¹ in the voltage range from 0.0 to 2.2 V. As seen in Figure 5b, the capacity slightly drops at the first twenty cycles and it is maintains at ~ 610 mAhg⁻¹ from 20 to 1000 cycles which referring to excellent cycling stability and long cycle life performance of ZnO/TiO₂ core-shell nanocomposite. Moreover, Table 1 summarizes the comparison between the most promising electrochemical results on TiO₂ nanostructures based anodes. As seen, the ZnO/TiO₂ core-shell nanocomposite shows better or comparable electrochemical performances than other TiO₂ nanostructure based anodes for lithium-ion batteries.



Figure 5. (a) Rate capability for ZnO film, TiO₂ film and ZnO/TiO₂ core-shell nanocomposite from 250 mAg^{-1} to 3000 mAg^{-1} in voltage range from 0.0 to 2.2 V. (b) The long-life cycling performance profile of ZnO/TiO₂ core-shell nanocomposite was recorded at 450 mAg^{-1} in voltage range from 0.0 to 2.2 V.

Table 2. Comparison	between the	electrochemical	performances	of various	TiO ₂	nanostructure	based
anodes.							

Composition	Synthesis	Capacity after 20th Cycle (mAhg ⁻¹)	Current Rate (mAg ⁻¹)	Number of Reversible Cycles	Ref
ZnO/TiO ₂ core-shell	Sol-gel	610	450	1000	This
nanocomposite					work
TiO ₂ nanoporous hollow	template-	230	33.5	50	[21]
spheres	assisted				
TiO ₂ nanotubes@graphene	hydrothermal	357	10	50	[22]
TiO ₂ /C hollow nanofibers	force spinning	229	100	1000	[23]
C-coated mesoporous	solvothermal	111	200	100	[24]
TiO ₂ @graphene sheets					
Ti-Mn-O nanotubes	anodization	474	175	30	[25]

Further study for characterizing the transfer of carriers and diffusion of ions was carried out using EIS analysis in open circuit potential (OCP) by applying an AC voltage at 5 mV and the frequency from 10⁻³Hz to 10⁵Hz. Figure 6a shows a semicircle in the high-medium frequency range $(10^3 \text{ Hz to } 10^5 \text{ Hz})$ and a tail at the low frequency range $(10^{-3} \text{ Hz to } 10^3 \text{ Hz})$ for all samples. The semicircle in the high frequency range associated with surface films can imply the generation of SEI layer and electrical impedance of contact between active materials on electrode surface and electrolyte (R_{SEI}). Moreover, the semicircle in medium frequency range related to the charge transfer process and it can be denoted to the interfacial charge-transfer resistance (R_{ct}) [26]. The tail at the low frequency range is attributed to solid state Warburg impedance (W) which assigns to the diffusion of solid state lithium-ions into the porous matrix of electrode material [26, 27]. Accordingly, the results of fitting of EIS data is presented in Figure 6b and Table 2. Where R_E is corresponded to electrolyte resistance and CPE as a constant-phase element is describing the depressed semicircle by the parallel connection of an ohmic resistor [27, 28]. As shown, the R_{SEI} and R_{ct} of ZnO/TiO₂ core-shell nanocomposite are lower than ZnO and TiO₂ films which indicating the mixture of ZnO and TiO₂ core-shell structures lead to decrease the R_{SEI} and R_{ct} and enhancement the diffusion of lithium-ions into ZnO/TiO₂ core-shell nanocomposite electrode [29]. In addition, the outstanding lithium storage performance of ZnO/TiO_2 core-shell nanocomposite is observed due to high porous shells of the ZnO and TiO₂ nanorods and spherical structures [30]. It is important the active area of ZnO nanorods are protected through the stable layer of TiO₂ nanoparticles [31]. Modification of electrodes with nanostructures provide high electron transportation rate, short lithium-ions diffusion path and high surface area which can revealingly promote the lithium specific capacity characterization, long-term cycling performance stability and great rate ability [30-35].



Figure 6. (a) EIS analysis of ZnO film, TiO₂ film and ZnO/TiO₂ core-shell nanocomposite in OCP by applying an AC voltage at 6 mV and the frequency from 0.001Hz to 10^{5} Hz. (b) Equivalent circuit model used for EIS data fitting.

electrode	$R_{ct}(\Omega)$	$\mathbf{R}_{\mathrm{SEI}}\left(\Omega ight)$	$\mathbf{R}_{\mathrm{E}}\left(\Omega ight)$
ZnO/TiO ₂ core-shell nanocomposite	600.5	19.2	2.9
ZnO film	798.2	25.1	3.8
TiO ₂ film	803.4	24.9	3.7

Table 2. Results of EIS analysis of ZnO film, TiO₂ film and ZnO/TiO₂ core-shell nanocomposite.

4. CONCLUSION

This study revealed the comparison of the electrochemical properties and cycling performance in lithium-ion batteries among ZnO/TiO₂ core-shell nanocomposites, ZnO and TiO₂ films as anode. The anodes were synthesized with the sol-gel method. SEM and XRD analyses were applied to characterize the morphological and structural properties of samples. CV, EIS and cycling performance analyses were used to study the electrochemical properties of prepared anodes. Electrochemical studies showed more stable behavior of ZnO/TiO₂ core-shell nanocomposite as anode compared to the other samples. The capacity of anodes showed the more stable treatment and reversible capacity of 402 mAhg⁻¹ for cycle numbers from 10 to 200 for ZnO/TiO₂ nanocomposite which indicated the great cycling performance of prepared ZnO/TiO₂ nanocomposite. The coulombic efficiency of ZnO/TiO₂ core-shell nanocomposite was obtained more than 98% which was higher than the obtained coulombic efficiencies of ZnO (94%) and TiO₂ (93%) films after 200 cycles which demonstrates the much better capacity retention treatment in ZnO/TiO₂ core-shell nanocomposite than the other prepared anodes. Results also showed the high ability, reversibility and long-life cycling performance of ZnO/TiO₂ coreshell nanocomposite compared to ZnO and TiO₂ films. EIS analysis indicated the mixture of ZnO and TiO₂ core-shell structures lead to enhancement at the diffusion of lithium-ions into ZnO/TiO₂ coreshell nanocomposite electrode and provide high surface area, short lithium-ions diffusion path and high electron transportation rate which can revealingly promote the lithium specific capacity characterization, long-term cycling performance stability and great rate ability.

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