Photoluminescence Properties and Electrochemical Performance of Fe:ZnO Nanoparticles in Li-ion Batteries

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Abstract

The pure and Fe doped ZnO nanoparticles with varying iron mole percentages of 3%, 4.5% and 6% were synthesized by using co-precipitation. Structural and morphological properties as well as electrochemical properties, serving as anode in Li-ion batteries, were studied. All samples have hexagonal wurtzite ZnO crystal structure and a slightly shift from x-ray diffraction patterns of Fe:ZnO samples have shown that Fe3+ ions substituted by Zn2+ ions. As the percentage of Fe mol increases from 3% to 4.5%, the size of the particles decreases, and as the percentage of Fe mol decreases from 4.5% to 6%, it also increases. The emission bands originated due to energy levels generated by ZnO intrinsic defects in all samples. In half cell configuration, 3% Fe:ZnO and 6% Fe:ZnO anode exhibit rapid capacity fading. ZnO anode with Fe mol percentage of 4.5 % results a substantially enhances specific capacity during 50 cycle.

Keywords: ZnO, doping, co-precipitation, photoluminescence, Li-ion battery

1. Introduction

With the growing demand for portable electronic devices and electric vehicles, achieving high-performance Li-ion batteries have been become crucial. Therefore, the challenges associated with energy density and power density have been investigated further with development of components of Li-ion batteries. Although graphite, which has a theoretical specific capacity of 372 mAh g⁻¹, is the most commonly used anode material in commercial Li-ion batteries, electronic and ionic transport limitations have led to the search for different anode materials [1]. To improve specific capacity and charge rate capability of electrodes many materials have been investigated such as transition metal sulfides [2], silisium [3], germanium oxides [4] and metal oxides [5] etc.. Among them conversion reaction-based transition metal oxides (Fe₂O₃, NiO, ZnO, TiO₂ etc.) have attracted particular attention due to their high
theoretical capacity (> 600 mAh g⁻¹), large amount of specific surface areas, abundant in nature and low toxicity [6]. The main drawbacks in their using are their poor cycling stability, large volume expansion and pulverization of active particles in the practical Li-ion battery applications [7,8].

As a promising high capacity anode material, ZnO is so attractive due to high theoretical capacity of 978 mAh g⁻¹, high chemical and mechanical stability, easy synthesis and low cost [9]. In the first cycle, Li⁺ ion insertion/extraction reactions of ZnO can be represented as follows;

\[
\begin{align*}
\text{ZnO} + 2 \text{Li}^+ + 2 e^- & \rightarrow \text{LiZn} + \text{Li}_2\text{O} \quad (1) \\
\text{LiZn} + \text{Li}_2\text{O} & \rightarrow \text{Li}_2\text{O} + \text{Zn} + \text{ZnO} \quad (2)
\end{align*}
\]

Pure ZnO electrodes exhibit uncontrolled agglomeration and dramatic volume expansion (~228 %) so rapid capacity fading occurs due to an inherent poor ionic conductivity of ZnO/Li₂O/Zn⁰ three-phase matrix forming can be emerge during the alloying/de-alloying process [10]. Low specific ZnO capacity of ~330 mAh g⁻¹ can be originated by reversible Li-Zn de-alloying reaction during discharge [11]. To overcome these problems, doping is effective way with metallic ions (Fe³⁺, Co³⁺, Cu²⁺, Ni²⁺ etc.) due to the increase of active nucleation sites can prevent nanoparticle agglomeration [12]. Therefore non-agglomerative particles can benefit to improve electrochemical reaction kinetics during cycling [13]. Iron has been studied often especially in magnetic applications due to ferromagnetic nature of Fe:ZnO and is also preferred to develop optical communication and optoelectronic devices [14]. In addition, Fe has a role to improve charge carrier transport by introducing impurity energy band states of ZnO [15].

However, few studies have investigated using of Fe:ZnO as anode material in Li-ion batteries. Mueller et. al. reported that although particle sizes decreased with increasing iron concentration in Zn₁₋ₓFeₓO (0.02<x<0.12) structures, no significant effect was found on the electrochemical performance that compared to Zn₀.₉Fe₀.₁O-C [16]. Bresser et. al. showed that Zn₀.₉Co₀.₁O electrodes exhibited higher capacity compared to Zn₀.₉Fe₀.₁O electrodes due to the intrinsically superior ability of cobalt to enable the reversible formation of Li₂O [17]. Fe-doped ZnO electrodes shown an increasing capacity contribution especially in the initial stages of lithiation with cationic vacancies at the tetrahedral sites, investigated by Giuli et.al. [11].

In this study, pure ZnO and Fe:ZnO nanoparticles were produced via co-precipitation method depending on iron mol percentage (3%, 4.5% and 6%) and characterized by XRD, SEM, EDX and PL. Iron mol percentage effect on the ZnO anode performance in the half-cell configuration was investigated in detail.
2. Experimental

All chemicals were analytical grade and used without any further purification. Zincacetate dihydrate (Zn(CH$_3$CO$_2$)$_2$.2H$_2$O) (99%), iron (III) sulfate hydrate (Fe$_2$(SO$_4$)$_3$.H$_2$O)(97%) ammonium hydroxide solution (NH$_4$OH, 28–30%) and ethylene glycol (C$_2$H$_6$O$_2$) (99%) were purchased from Sigma-Aldrich. Pure and Fe doped ZnO nanoparticles were produced by co-precipitation method. Starting materials were zincacetate dihydrate and iron (III) sulfate hydrate as Zn-source and Fe-source, respectively. 0.1 M zincacetate dihydrate dissolved in 100 ml. distilled water. Then, different amount of Fe source were added to the solutions and Fe mol ratio of Fe in the ZnO solution was kept as 3 %, 4.5 % and 6 %. 0.1 M citric acid and 10 ml. ethylene glycol were added. Complex agent ammonia was added drop by drop in this homogenous solution until pH=9. All chemicals mixed along 1 h on the magnetic stirrer at 70±5 °C. After one day waiting, precipitated particles washed with distilled water and acetone. Finally, all samples annealed at 500 °C along 2 h in the furnace to eliminate surface impurities.

The possible chemical reactions in the forming of Fe:ZnO nanoparticles as shown below;

\[
\text{Zn(CH}_3\text{CO}_2\text{)}\_2\cdot2\text{H}_2\text{O} \rightarrow \text{Zn(OH)}\_2 + 2\text{CH}_3\text{COOH} \quad (3)
\]
\[
2\text{CH}_3\text{COOH} + 2(\text{OH})^- \rightarrow \text{CH}_3\text{OH} + \text{CO}_2 + \text{H}_2 \quad (4)
\]
\[
\text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O} \rightarrow 2\text{Fe}^{3+} + 3 \text{SO}_4^{2-} \quad (5)
\]
\[
\text{Zn(OH)}\_2 + \text{Fe}^{3+} \rightarrow \text{ZnO}:\text{Fe} + \text{H}_2\text{O} \quad (6)
\]

x-ray diffraction (XRD) patterns were collected at Rigaku SmartLab X-ray diffractometer with CuK$_\alpha$ source ($\lambda = 1.5406$ Å), operating under 40 mA and 45 kV and using powder method. The surface morphology of the nanoparticles were depicted by JEOL JSM- 7100F-SEM (scanning electron microscope). Elemental microanalysis (wt%) of the samples was determined by OXFORD Instruments X-Max EDX (energy-dispersive X-ray spectrometer) which had been attached to SEM. Photoluminescence (PL) measurement of the samples were recorded by using Shimadzu RF-5301 PC under the excitation wavelength of 245 nm. Fourier transform infrared (FTIR) spectra of the samples were recorded using a VERTEX 70 Spectrophotometer with an attenuated total reflectance (ATR) accessory (Bruker, Germany).
Electrochemical experiments were carried out in CR 2032-type coin cell. The working electrodes were obtained by mixing active material, carbon black, and polyvinylidene fluoride (PVDF) at a weight ratio of 70%:20%:10% and pasting the mixture on pure copper foil. The working electrode slurries were dried on copper foil substrates and vacuum-dried for 24 h at 80 °C. The cells were formed using a Li metal negative electrode, an electrolyte of 1 M LiPF$_6$ in 1:1 ethylene carbonate and dimethyl carbonate mixture, a separator and a working electrode. Coin cells were assembled in a high-purity argon- filled glove box. The discharge–charge measurement of the cells was carried out at room temperature using a LAND-CT 2001A battery test system. The capacity values were calculated based on the total mass of active materials.

3. Results and Discussion

3.1. Structural Properties

Fig.1. shows the XRD patterns of pure and Fe doped ZnO nanoparticles depending on iron mol percentage. All measurable peaks of the samples corresponds to single-phase ZnO hexagonal wurtzite structure (JCPDS card no: 36–1451). No secondary phase, such as Fe(OH)$_3$ or Zn(OH)$_2$ phase formed by the interaction of Fe$^{3+}$ or Zn$^{2+}$ ions with O$^2-$ ions, is observed within the detection limit of XRD. Preferential orientation of the samples is (101) plane along a-axis, it may indicate crystal growth has preferred low-energy system so the dopant effect is determined on the growth kinetics [18]. The (101) peak position of 3% Fe:ZnO samples shift to lower angle and 4.5% Fe:ZnO and 6% Fe:ZnO samples shift to higher angles compared with pure ZnO. It indicates Fe$^{3+}$ ions (0.69 Å) substituted with Zn$^{2+}$ ions (0.74 Å) in the ZnO host lattice [19]. Typical ZnO peak of (100), (002) and (101) intensities decreases with Fe$^{3+}$ ions inclusion due to dopant can change host lattice strain and Fe$^{3+}$ ions can cause fast nucleation of the particles. As a result, increasing charge imbalance may be cause crystal defects and lattice disorders [20].
Structural parameters of the samples have been shown in Table 1. The average particle size of the samples (D) is measured by Debye-Scherrer equation without strain effect, as shown below by Equation (7):

$$D = \frac{0.94 \lambda}{\beta_{hkl} \cos \theta}$$  \hspace{1cm} (7)

Microstrain ($\epsilon$) of the samples is calculated by Equation (8):

$$\beta_{hkl} \cos \theta = 4\epsilon \sin \theta$$  \hspace{1cm} (8)

In addition, dislocation density ($\delta$) which is a measure of the amount of defects in the crystal is measured by Equation (9):

$$\delta = 1/D^2$$  \hspace{1cm} (9)

where $\lambda$ is the wavelength of x-ray radiation, $\beta$ is the full width at half maximum (FWHM) and $\theta$ is diffraction angle and $\epsilon$ is the strain. The average crystallite size of varies from 9 nm. to 12 nm. depending on the creation of new nucleation hub and rate of particle nucleation. The reduction of grain size may cause an increase microstrain and dislocation density. This can be interpreted as the inclusion of the iron additive in the ZnO overall crystal structure.
|          | $2θ$ (°) | FWHM | d (Å) | D (nm) | Micro strain ($\varepsilon$) (%) | Lattice constant | c/a (Å) | $\Delta$ (nm$^2$) |
|----------|----------|------|-------|--------|---------------------------------|-----------------|---------|-----------------|
| Pure ZnO| 36.57    | 0.038| 2.454 | 11     | 0.944                           | 3.198           | 5.174   | 1.61            |
| 3% Fe:ZnO| 36.48    | 0.062| 2.462 | 12     | 0.946                           | 3.218           | 4.896   | 1.52            |
| 4.5% Fe:ZnO| 36.51   | 0.031| 2.456 | 9      | 1.227                           | 3.200           | 4.886   | 1.53            |
| 6% Fe:ZnO| 36.66    | 0.026| 2.451 | 14     | 0.765                           | 3.184           | 4.888   | 1.52            |

**Table 1. Structural parameters of ZnO and Fe:ZnO samples**

Lattice parameters of $a$ and $c$ were calculated by Equation (9) for hexagonal structure:

$$\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + h k + k^2}{a^2} \right) + \frac{l^2}{c^2}$$  \hspace{1cm} (9)

The lattice parameters are $a = 3.25$ Å and $c = 5.20$ Å with the ratio $c/a = 1.6$ in an ideal wurtzite ZnO structure at room temperature. Although pure ZnO samples have ideal $c/a$ ratio of 1.6, lattice constants of Fe:ZnO samples have significantly smaller than ideal $c/a$ as a result of imperfections, defects and strain [21].

### 3.2. Surface Morphology

Surface morphology of the pure ZnO and Fe doped ZnO nanoparticles was shown in Fig. 2 (a-d) under high magnification ratio of x30000. Spherical-like and their agglomerative forms exhibits for all samples. Surface of the samples has composed particles in nano-dimension range. As can be observed, their dimensions changes with varying iron contribution in ZnO host due to the synthesis process that takes place in aqueous solutions reveals more hydroxyl groups [22]. These dimensions are consistent with the average crystalline sizes obtained using the Debye-Scherrer formula, as shown in Table 1. The surface of the 4.5 % ZnO samples appears to be more porous and homogeneous, allowing the facility to shorten the transport length for $Li^+$ ions upon insertion/deinsertion. Fe alloy nanocluster forms have been observed in 6% Fe:ZnO samples with granular ZnO forms have become more irregular due to less nuclei formation with lower nuclei rates [23].
3.3. Elemental Analysis

The presence of Zn, O and Fe as a elemental ratio of w% in the synthesized particles are confirmed by EDX measurements, as shown in Fig 3 (a-d). No other impurity element is detected. The reason why the difference in elemental ratio of w% differs from the amounts placed is due to ZnO crystal growth process.
3.4. Photoluminescence Spectrum

To determine emission bands and defect levels in the synthesized nanoparticles, photoluminescence (PL) spectra was used with using excitation wavelength 245 nm. in the 350-700 nm. range. All samples exhibit distinctive band at 489 nm. and weak emission bands at 587 nm. and 609 nm. Although no major intensity difference is detected at 587 nm. and 609 nm., emission band intensity of 4.5% Fe:ZnO is lower than 6% Fe:ZnO at 489 nm. The peak intensity of PL varies depending on the ratio of iron additives due to photogenerated electrons occupy shallow trap centers due to the substitution of Zn$^{2+}$ ions by Fe$^{3+}$ ions [24]. The bluish-green defect band have been oberved at 489 nm, indicating the transition between oxygen vacancies and oxygen interstitial defects, their formation energy is low compared to zinc interstitial defects [25]. The blue emission has been observed at 587 nm. and 609 nm. is originated from Fe$_{Zn}$-V$_{Zn}$ pair defects [26]. It is cleat that shallow acceptor defects have been observed in PL spectra.
Fig. 4. Room temperature PL spectra of ZnO and Fe:ZnO samples in the range between 350-700 nm.

3.5. Electrochemical Properties

Fig. 5. shows the variation of specific capacity with cycle number to determine the cycling stability for pure ZnO and Fe:ZnO anodes. It is clear that the iron molar ratio affect the ZnO growth mechanism so trap energy levels can appear such as oxygen vacancies and Fe\textsubscript{Zn}-V\textsubscript{Zn} defects [27]. Although all anodes exhibit high initial specific capacities for first 15 cycles, all anodes exhibit rapid capacity fading. 4.5% Fe:ZnO anode exhibits high stable cycle performance compared to pure ZnO anodes during 50 cycles. The capacity reduction with increasing crystallite size may be attributed to decreasing grain boundary surface area so an increase occur in the diffusion distance for Li\textsuperscript{+} ions [28, 29]. Accordingly these results, 4.5% Fe:ZnO anodes with small grain sizes and oxygen vacancies on the surface as shown by PL spectrum, can offer a large surface area for Li\textsuperscript{+} ions so the specific capacity of 4.5% Fe:ZnO anodes is higher.
4. Conclusion

Pure ZnO and Fe mol ratio of 3% Fe, 4.5% Fe and 6% Fe ZnO nanoparticles were produced by co-precipitation. Structural and morphological properties were investigated. Electrochemical characterization of the samples have been carried out to demonstrate the potential using as an anode in Li-ion batteries. X-ray patterns reveals all samples to be phase-pure, having the same wurtzite structure of pristine ZnO. Spherical-like agglomerative forms with different sizes were observed in synthesized samples depending on the Fe mol ratio. All samples exhibit bluish-green and blue emission bands in 350-700 nm range. 4.5% Fe:ZnO electrodes have high specific capacity compared to pure ZnO during 50 cycles.

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