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ORIGINAL ARTICLE

First-principles calculation on electronic properties of zinc oxide by zinc–air system

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Abstract First-principles calculations are performed to study the electronic properties of zinc oxide (ZnO) formed on an anode after discharging a Zn–air system. Prior to calculation, the ZnO is characterised by X-ray diffraction using Rietveld refinement. Diffracted patterns proved the formation of single phase ZnO, while Rietveld analysis shows that the ZnO has a hexagonal wurtzite structure with lattice parameters, a = 3.244 and c = 5.199 Å. Geometry optimisation of the hexagonal wurtzite structure of the ZnO is performed using various exchange–correlation energy functionals. The local density approximation functional method is used to explain the structure, electronic band structure and density of state properties of hexagonal ZnO. The calculated energy band gap was 0.75 eV while the density of states reveals that the O 2p (the top valence band) and Zn 4s (the bottom conduction band) states domination.

1. Introduction

Zinc oxide (ZnO) is an interesting material due to its low cost, chemical inert-ness, photo-stability, and excellent charge transport, and has received considerable attention as a potential solar cell material (Alias and Mohamad, 2014b, 2013). Synthesis of ZnO has been done by various techniques, such as, sputtering (Gabas et al., 2011), sol–gel (de la L Olvera et al., 2002; Alias et al., 2010), vapour–liquid–solid growth (Huang et al., 2001), physical vapour deposition (Kato et al., 2002) and zinc–air (Zn–air) system (Yap et al., 2009). X-ray diffraction (XRD) is still the main tool to characterise the formation of ZnO. Other characterisation methods, such as scanning/transmission electron microscopy and photoluminescence spectroscopy, have also been used to support observations; however, these supporting methods are costly and time

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consuming. Hence, no theoretical investigation of the ZnO obtained from Zn–air system has been reported. Simulation of ZnO properties can be utilised to predict the properties of the material, and an interesting method of simulation is first-principles calculation, which is based on density functional theory (DFT).

Scattered reports of first-principles calculations on pure ZnO and dopants are available (Wang et al., 2013; Xie et al., 2012; Yao et al., 2012; Guan et al., 2011; Li et al., 2009; Osuch et al., 2006; Ren et al., 2004). However, very little effort has been exerted to use experimental data of ZnO produced by the electrochemical system as crystal inputs for these calculations. The inputs from XRD can be used to predict material properties by first-principles calculations. XRD data of the crystal structure, such as its lattice parameters, volume and atomic positions, are the main inputs for simulation. If the values of the crystal structure are satisfied, the simulation proper will be a success.

The aim of the present work is to characterise the ZnO produced from the end product of a Zn–air system using the first-principles calculation. The data obtained from the first-principles calculation are compared with those of standard ZnO to validate the formation of ZnO from the Zn–air system. This study begins with XRD and Rietveld refinement of ZnO to obtain the relevant crystal structure properties. Prior to examining the electronic properties of the ZnO, structural (lattice) optimisation is initially performed using various exchange–correlation energy functions, namely, local density approximation (LDA), generalised-gradient approximation functional with Perdew–Burke–Ernzerhof (GGA-PBE), and GGA-PBE function for solids (GGA-PBESol). Structural optimisation is implemented to determine the best functional approximation to perform in examining the electronic properties of ZnO.

2. Experimental

2.1. Zinc–air system assembly

Cell components consisted of a Zn foil, air–cathode and electrolyte. The Zn foil ($1 \times 1\ cm^2$, 99.98% purity, Alfa Aesar) was used as an anode, while fibre-carbon-MnO_x (MEET Co. LTD, Korea) was used as an air–cathode. A mixture of 1.5 M potassium hydroxide pellets (KOH) and 0.04 M ZnO powder was used as an electrolyte. The cell was discharged using Neware BTS with a constant current of 10 mA at room temperature (27 °C).

2.2. Material characterisation

After discharging, the Zn anode was characterised by XRD (Bruker AXS D9) over 2θ ranging from 10° to 90°. The data were then analysed by Rietveld refinement using X'pert High Score Plus software. The morphology of the Zn anode was observed by a field emission scanning electron microscope (FESEM, Zeiss Supra 35VP) to support the findings during the anode characterisation.

2.3. First-principles calculation

First-principles calculation based on DFT with the plane-wave pseudo-potential method was performed as implemented in the Cambridge Serial Total Energy Package (CASTEP) program code (Segall et al., 2002). Exchange-correlation functional of LDA, GGA-PBE and GGA-PBESol were used to compare the ZnO lattice properties.

To obtain a stable structure, geometry optimisation was performed to refine the geometry of the 3D periodic system. All of the first-principles calculation areas were determined according to the softer ultrasoft pseudopotential method (Vanderbilt, 1997) in which only valence electrons are considered. A $(5 \times 5 \times 4)$ k-point grid generated using the Monkhorst–Pack method for Brillouin zone sampling with an energy cut-off of 340 eV was obtained. For energy minimisation calculation, convergence thresholds were set to 1×10^{-6} eV per unit atom for maximum energy change. The electrons of Zn ($3d$, $4s$) and O ($2s$, $2p$) were treated as valence states.

3. Results and discussion

3.1. Synthesis of ZnO

The Zn–air cell produced the open circuit potential of 1.28 V and flat discharge plateau at 1.10 V (Fig. 1). After 6.4 h, the cell stopped. Upon complete discharge, the Zn anode foil was cleaned by immediately rinsing in deionized water and then dried. The surface of Zn anode that exposed to the electrolyte was characterised by FESEM. Long needle-like ZnO structures covered the surface of the Zn anode (Fig. 2). These structures were scattered in different directions and formed rosette-like agglomerations. The formation of these structures on the surface of the anode separated the active Zn from the electrolyte and inhibited the discharge.

3.2. Structural and Rietveld analysis

The comparison of the Zn foil obtained before and after discharge was made by reference to the XRD patterns. The diffraction pattern was perfectly matched with the respective Zn (ICSD: 98-009-1553) and ZnO (ICSD: 98-002-7791) patterns. Pure Zn showed high crystallinity and intensity at

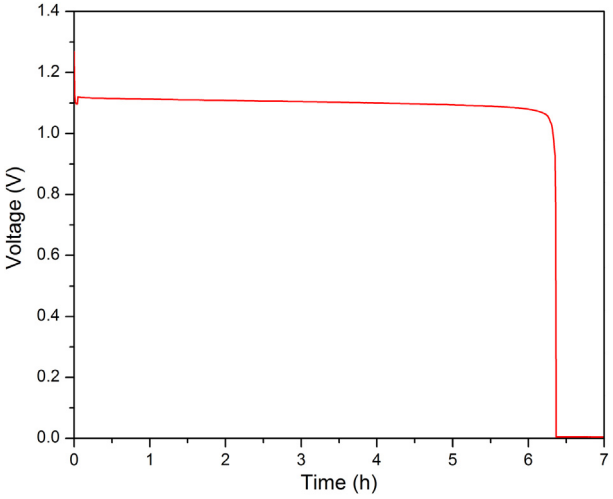

Figure 1 Discharge profile of Zn–air system at a constant current of 10 mA.