Chemical Microanalysis of SnO$_2$–MnO$_2$ Nanofibers in an Electron Probe Microanalyzer

Zariana R. Mobley$^1$, Shanell L. Jackson$^1$, Gibin George$^1$, and Zhiping Luo$^1$

$^1$ Department of Chemistry and Physics, Fayetteville State University, Fayetteville, USA.

Tin dioxide (SnO$_2$) is an N-type semiconductor for a wide range of applications [1]. Hierarchical SnO$_2$ nanocrystals, in the forms of nanoparticles, nanotubes or nanosheets, have been used for gas sensors [1, 2], supercapacitors [3], lithium-ion batteries [1], and solar cells [1]. With the addition of MnO$_2$, it was found that SnO$_2$–MnO$_2$ nanocomposite powders exhibited remarkable improvement in electrochemical performance in terms of discharge capacity and low capacity fading, compared with pristine MnO$_2$ [4]. SnO$_2$–MnO$_2$–SnO$_2$ sandwich-structured structure was also demonstrated to be a high-performance anode in a lithium-ion battery [5]. In this work, we synthesized SnO$_2$, MnO$_2$ and mixed SnO$_2$–MnO$_2$ nanofibers and conducted microanalysis using an electron probe microanalyzer (EPMA).

Polymer solutions were prepared by dissolving 2.0 g polyvinylpyrrolidone (PVP) (molecular weight ~1,300,000 g/mol) in a 20 mL (50/50) mixture of N,N-dimethylformamide (DMF) with ethanol. Tin chloride (SnCl$_2$), or manganese chloride (MnCl$_2$) or a mixture of both, was added to the polymer solution. The electrospinning was conducted at room temperature with applied voltage of 18 kV. The prepared nanofibers were subsequently calcined at 500 °C in air for 5 h to obtain oxide nanofibers. Samples were coated with carbon and analyzed in a JEOL field-emission JXA-8530F EPMA, which was equipped with a SDD X-ray energy-dispersive spectrometer (EDS) and five wavelength-dispersive spectrometers (WDSs), and xCLent IV Hyperspectral Cathodoluminescence System, worked at 10 kV.

Fig. 1(a) shows an SEM image of SnO$_2$ nanofibers after calcination. The nanofibers become porous, with a diameter of ~150 nm. After calcination, the fibers are in fact composed of small nanoparticles (~50 nm). The EDS analysis, as shown in Fig. 1(b), confirms that its composition is almost stoichiometry of SnO$_2$. The MnO$_2$ nanofibers, on the other hand, are composed of large nanoparticles (~150 nm) in the form of chains. Since the melting point of SnO$_2$ is 1,630 °C while the melting point of MnO$_2$ is only 535 °C, the MnO$_2$ nanofibers were melted during the calcination. The EDS spectrum of MnO$_2$ is shown in Fig. 1(d), with a stoichiometric composition of MnO$_2$.

The image of mixed SnO$_2$–MnO$_2$ nanofibers is shown in Fig. 2(a), with larger diameter (~300 nm) in a porous shape. As shown in Fig. 2(b) from the EDS analysis, the Mn content is very low although the starting molar ratio of Sn:Mn is 1:1, indicating the melting and volatilization of MnO$_2$ from the mixture during the calcination [6].

References:

The authors acknowledge funding from the NSF HRD 1436120 and HRD 1719511. The instrumentation at FSU was supported by DoD W911NF-09-1-0011, W911NF-14-1-0060, W911NF-15-1-0566 and NSF MRI Program DMR 1626376.

Figure 1. (a, b) SEM image of SnO$_2$ nanofibers and EDS spectrum; (c, d) SEM image of MnO$_2$ nanofibers and EDS spectrum.

Figure 2. (a) SEM image of SnO$_2$–MnO$_2$ nanofibers; (b) EDS spectrum.