ZrO_2-WO_3 Mixed Anodic Oxide Nanotubular Arrays as Electrochemical Capacitors

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Vertically oriented, ordered arrays of oxide nanotubes, such as TiO_2, WO_3, and Fe_2O_3 are considered for electrochemical capacitor application because of their morphology-assisted fast charge/discharge kinetics and large surface area.[1,2] Recently, Habazaki et al[3] reported enhanced capacitance of anodic ZrO_2 film by stabilizing the high permittivity tetragonal phase in a highly resistive amorphous oxide phase containing Al or Si. In this presentation, electrochemical capacitance of a binary ZrO_2-WO_3 oxide nanotubular arrays will be discussed.

ZrO_2-WO_3 mixed oxide nanotubes were synthesized by a simple electrochemical anodization of the Zr- 20 wt%W alloy substrate. Figures 1(a) – (c) show the morphology of the nanotubes. The as-anodized oxide nanotubes contained a mixture of metastable hexagonal WO_3 and monoclinic ZrO_2 phases. A mixed-oxide ZrW_2O_8 phase with a metastable tetragonal symmetry formed after thermal annealing the nanotubes. Formation of h-WO_3 and mixed oxide phase of ZrW_2O_8 was supported by both XRD and XPS data. Presence of the h-WO_3 in the nanotubes was considered critical for the enhancement of the capacitance because its ring like lattice structure containing hexagonal tunnels at the center of the rings that accommodated intercalation ions.

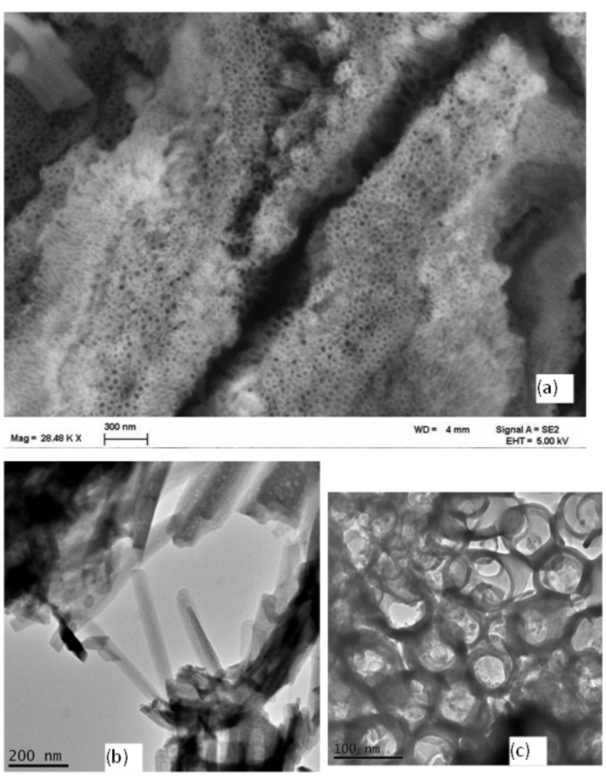

Figure 1: Electron microscopic images of oxide layers formed on the Zr-W alloy substrate after anodization at 40 V for 1 h in EG electrolyte containing 0.2 M NH_4F + 5 vol% H_2O. (a) FESEM image of the top surface of the anodic oxide layer revealing nanotubular morphology; (b) TEM image of the side view of the nanotubes; and (c) planar view of the nanotubes under TEM.

Cyclic voltammetry studies were carried out in 1 M H_2SO_4 and 1 M LiCl solution to evaluate the electrochemical capacitance of the nanotubes. Electrochemical impedance spectroscopy and Mott-Schottky measurements were carried out to determine the charge transfer resistance and defect concentration of the nanotubes, respectively. Figures 2(a) and (b) show typical cyclic voltammograms of the Zr-W oxide nanotubes in 1 M H_2SO_4 at different scan rates. The highest measured capacitance was 1900 μF/cm^2 at a scan rate of 100 mV/s and the lowest was 400 μF/cm^2 at 1 V/s in 1 molar sulfuric acid solution. This capacitance was comparable to that reported for the ordered mesoporous WO_3 material and higher than the capacitance reported for the TiO_2 nanotubes (181 μF/cm^2 at 100 mV/s).

The higher capacitance of Zr-W oxide nanotubes could be attributed to the distribution of high dielectric h-WO_3 and ZrW_2O_8 phases in the ZrO_2 matrix, presence of high concentration of oxygen vacancies (in the order of 10^{21} cm^{-3}), and high proton conductivity of the mixed ZrO_2-WO_3 oxide reported in the literature.

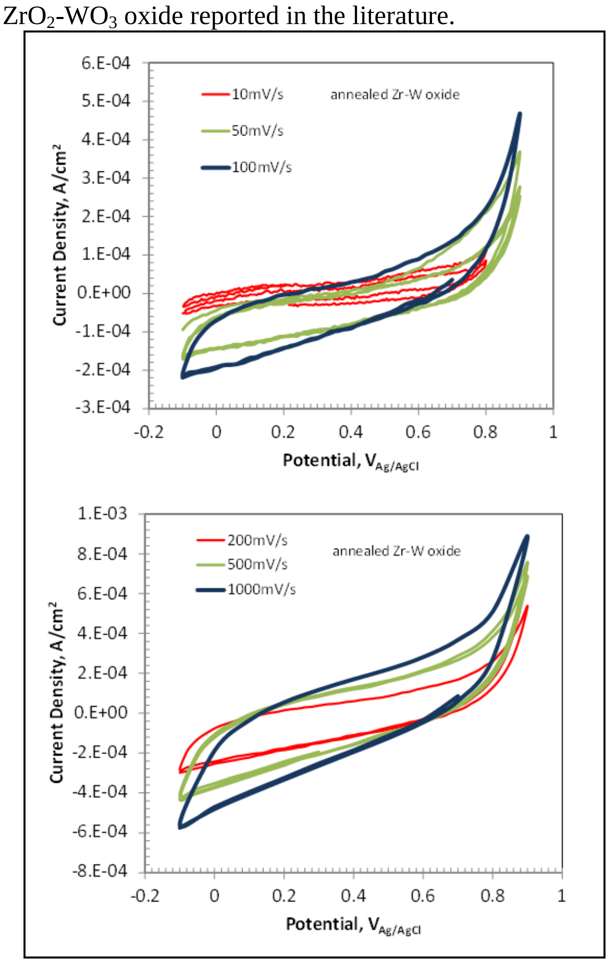

Figure 2: (a) Representative cyclic voltammetry (CV) results of annealed Zr-W oxide nanotubes (anodized for 1 h) tested in 1 M H_2SO_4 solution at three different scan rates 10, 50, and 100 mV/s. The results of 50th, and 100th cycles are shown. (b) Representative cyclic voltammetry (CV) results of annealed Zr-W oxide nanotubes (anodized for 1 h) tested in 1 M H_2SO_4 solution at three different scan rates 200, 500, and 1000 mV/s. The results of 50th, and 100th cycles are shown.

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[3] H. Habazaki, S. Koyama, Y. Aoki, N. Sakaguchi, S. Nagata, *ACS Appl. Mater. Interfaces* **2011**, 3, 2665–2670