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Capacitive Properties and Structure of RuO_2-HfO_2 Films Prepared by Thermal Decomposition Method

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Abstract

Binary RuO_2-HfO_2 films on Ti substrates were prepared by a thermal decomposition method. cyclic voltammetric and charge/discharge properties of the RuO_2-HfO_2 electrodes were characterized. It was determined that the incorporation of HfO_2 into RuO_2 greatly improved the capacitive properties of the material. The RuO_2-HfO_2 electrodes showed excellent cyclic stability, with no decay in charge capability during 1000 CV cycles in acidic solution. A nominal content of 50 mol% RuO_2 and 50 mol% HfO_2 gave the highest specific capacitance of 789.3 F/g (RuO_2). The excellent capacitive properties and stability were related to the hydrous amorphous mixed-oxides formed in the film. This work proves that high capacitive performance of RuO_2-based electrode materials can be obtained by thermal decomposition, even with the retained chloride in the film.

Keywords: RuO_2-HfO_2;film; supercapacitor; thermal decomposition method;

1. Introduction

Metal oxides are promising candidates for supercapacitor electrodes Simon et al. (2008) or Lokhande et al (2011) or Aricò et al (2005). In recent years, RuO_2 has been widely studied due to its good electrochemical reversibility,

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highest specific capacitance, and long cycle life in H_2SO_4. Electrochemical capacitors based on hydrous ruthenium oxide are known to achieve excellent specific capacitances, higher than 720 F/g Yuan et al. (2012). Some preparation methods, including chemical synthesis, sol-gel, and electrochemical deposition, have achieved high capacitance Patake et al (2008) or Chang et al (2009) or Patake et al (2010), but could not be applied to industrial production. In addition, despite the excellent performance of hydrous RuO_2 electrodes, their high material cost limits their widespread use in industry. Mixing RuO_2 with other oxides, including Ta_2O_5 Zheng et al (1995), Cr_2O_3, Chen et al (2011), and TiO_2 Bo et al (2006), has been considered a most effective way to reduce the cost. Thus, selection of other potential metal oxides and suitable preparation methods are essential to achieve the requirements for supercapacitors. The thermal decomposition method (TDM) is the easiest technique for obtaining mixed-oxide electrodes, but is not employed in preparing hydrous RuO_2 due to chlorine contamination Kurzweil et al (2009) or Chang et al (2006). Our exploratory work on RuO_2-SnO_2 has suggested that a very high specific capacitance can be achieved by a low-temperature sintering TDM Wang et al (2011). In this paper, RuO_2/HfO_2 oxides were deposited on Ti by TDM. Study of Ru/Hf molar ratio effects on RuO_2-HfO_2 electrode structure, capacitive properties, and stability will be conducted.

Nomenclature

$C_{S,RuO2}$ specific capacitance

2. Experimental

The details of TDM have been described elsewhere Wang et al (2007). 2 mm-thick industrial titanium (TA2) plates were degreased, polished, etched in 10 wt.% boiling oxalic acid for 1 h, ultrasonically cleaned, and then dried. The precursors $RuCl_3$ and $HfCl_4$ were separately dissolved in anhydrous ethanol and then homogeneously mixed. The Ru-loading in the films was 0.8 mg/cm^2 while that of HfO_2 was varied from 0 (pure RuO_2) to 100 mol% (pure HfO_2) in 10 mol% increments. The solutions were then brushed on the pretreated Ti and thermally decomposed at 300 °C in air for 1 h. Samples were labeled by HfO_2 content.

The electrochemical properties of the RuO_2-HfO_2 electrodes were characterized by cyclic voltammetric and charge/discharge tests in 0.5 M H_2SO_4 solution. The phase structures of the electrodes were examined using X-ray diffraction (XRD) (Philips X pert-MPD), X-ray photoelectron spectroscopy (XPS) (ESCALAB 250, Thermo Fisher Scientific, UK) and field emission high resolution transmission electron microscopy (TEM) (JEM-2010, JEOL Inc., Japan).

3. Results and Discussion

Cyclic voltammetry (CV) curves of the Ti/RuO_2-HfO_2 electrodes are presented in Figure 1. That of the pure RuO_2 sample (0 %) shows a tail-like peak below 0.1 V (versus SCE, the same hereafter), which is the reported Ru(II)/Ru(III) transition between 0.0 – 0.2 V and reveals some chloride impurities in the sample Kurzweil et al (2009) or Chang et al (2006). This chlorine contamination not only caused the CV curve asymmetry but also decreased the voltammetric charge. So, thermal preparation of RuO_2 from chlorides is generally not recommended.

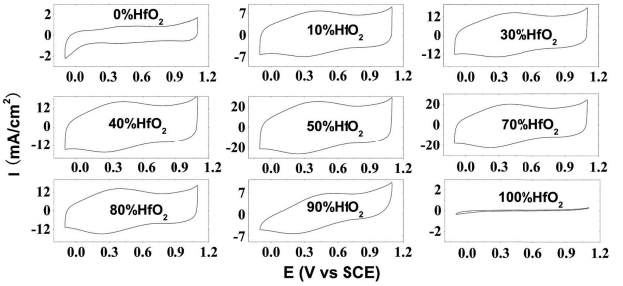

Fig. 1. Voltammetric curves of Ti/RuO_2-HfO_2 electrodes with different mol% HfO_2, at 25 mA/cm^2 in a 0.5 mol/L H_2SO_4 solution

Only nominal 10mol % HfO_2 content greatly enhanced the CV area, and the peak below 0.1 V vanished. This demonstrated that the Ru(II)/Ru(III) reaction was suppressed by adding a small amount of HfO_2 in the film, which clearly erased the chloride harmful effects on the electrodes. CV curves of samples with HfO_2 between 10 and 80 mol% were symmetrical and showed distinctive redox peaks, indicating that the active materials on the electrodes were highly reversible and thus suitable for use in supercapacitors. The voltammetric area first increased and then decreased with increasing HfO_2. The 50 mol% HfO_2 sample had the largest voltammetric area. The 90 mol% HfO_2 sample had a small and asymmetrical CV curve, revealing its inferior capacitive features. The pure HfO_2 film had almost no voltammetric response current due to HfO_2 being an inert oxide.

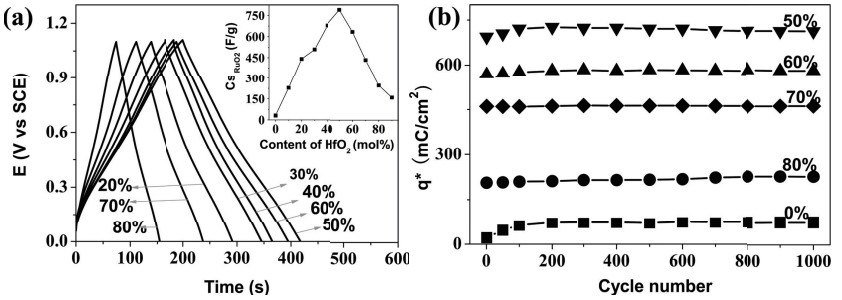

Fig. 2. Charge-discharge curves and specific capacitance, $C_{s,RuO2}$ (inserted in Fig. 2a) (a) and the $C_{s,RuO2}$ vs. CV cycle numbers (b) of the RuO_2-HfO_2 electrodes with different mol% HfO_2. Charge/discharge current density of 5mA/cm^2, CV scan rate of 50 mV/s, 0.5 mol/L H_2SO_4 solution.

Selected Ti/RuO_2-HfO_2 charge-discharge curves, measured in 0.5 mol/L H_2SO_4 at 5 mA/cm^2, are shown in Figure 2(a). Their triangular shapes indicate RuO_2-containing materials. The specific capacitance, $C_{S,RuO2}$, of the samples was calculated from the inset discharge curves. It is apparent that $C_{S,RuO2}$ was influenced greatly by HfO_2 content in the films. The pure RuO_2 $C_{S,RuO2}$ was as low as 30.6 F g-1, which is in agreement with that reported for pure RuO_2(around 50 F $g^{-1)}$ synthesized by TDM [11]. The $C_{S,HfO2}$ of 1.96 F g^{-1} of the pure HfO_2 sample indicated that this oxide was very inactive Zhang et al (2007). However, the highest specific capacitance of 789.3 F/g was measured for 50 mol% HfO_2 film, approximately 25 times higher than that of the prepared pure RuO_2. The volcano-like charge-composition peaks, also reported in some systems Rosario et al (2009) or Doubova et al (2002) or Wong et al (2004), imply synergistic effects in these binary oxides.

Figure 2b shows the samples stability in acid, evaluated by CV at a scanning rate of 50 mV/s, and indicates the prepared electrodes were stable in acid even after 1000 cycles. A slight increase in q*, anodic voltammetric charge, after the first 100 cycles may have been due to gradual wetting on/in these binary oxides and depended on their internal porosity.

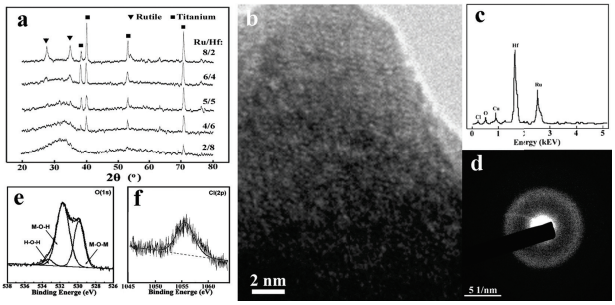

Fig. 3. XRD patterns (a), HRTEM image (b), EDX image (c), XPS spectra of O1s (d) and Cl(2p) (e), and SEAD pattern (f) for Ti/RuO_2-HfO_2 electrode with 50 mol% HfO_2

Figure 3a shows the XRD patterns of selected samples. For Ru-rich samples, peaks at 2θ from 28.0 to 35.5°, were assigned to rutile RuO_2. For Hf-rich samples, wide humps suggest the films were mainly amorphous. For further study of these amorphous structures, the morphology of the 50 mol% HfO_2 sample was observed by high-resolution transmission electron microscopy (HRTEM). The images (Fig. 3b) did not show any long-ranged arrangement, along with the SAED patterns (Fig. 3f), which clearly indicated the amorphous nature of the films. The molar ratio of Ru/Hf by EDX (Fig. 3c) was in accordance with that of the precursors. Residual chlorine was as expected, because above 400 °C, the chloride precursors used are completely decomposed [17].

The XPS spectrum of the 50 mol% HfO2 film is shown in Figs. 3e and 3f. The O(1s) spectrum was deconvoluted into three parts (Fig. 3d); bridged oxygen (M–O–M) with binding energy at 529.8 eV, hydroxide (M–O–H) at 531.9 eV, and molecular water (H–O–H) at 533.4 eV, which are in accordance with published data for hydrous RuO_2 Da Silva et al (2000), and indicate that this film was mainly hydrated RuO_2. The peak at 1055.2 eV (Fig. 3e) was assigned to Cl(2p), present because of the retained chloride in the film.

4. Conclusions

The present thermal decomposition method was proved to be useful to prepare RuO_2-based oxide coated electrode materials for supercapacitors. The 50%RuO_2+50%HfO_2 electrode prepared this way not only achieved a specific capacitance value of ca. 790 F/g but also overcame the negative effects of chloride. The thermal decomposition method allows preparation of these mixed oxides on the large-scale.

Acknowledgements

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