Solid State Ionics 268 (2014) 312–315

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Hydrous ruthenium oxide prepared by steam-assisted thermolysis: Capacitance and stability

Jie Wang, Youlong Xu *, Liang Li, Jun Lin

Electronic Materials Research Laboratory, Key laboratory of the Ministry of Education & International Center of Dielectric Research, Xi'an Jiaotong University, Xi'an 710049, China

ARTICLE INFO

Article history:
Received 26 July 2013
Received in revised form 2 January 2014
Accepted 5 March 2014
Available online 2 April 2014

Keywords:
Ruthenium oxide
Thermolysis
Steam
Supercapacitors

ABSTRACT

Hydrous ruthenium oxides ($RuO_2 \cdot xH_2O$) with ultra-stable cycling ability were directly prepared on tantalum substrate by thermolysis of $RuCl_3$ in heated steam environment. Characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), and wettability test, the $RuO_2 \cdot xH_2O$ showed lower crystallite and better hydrophilic than that are prepared by thermolysis in air. Their specific capacitance is twice as great as the latter. Moreover, this capacitance maintains nearly 100% after 100,000 cycles and its coulombic efficiency is 100% due to its good balance of electron/proton conductivity.

1. Introduction

Supercapacitors (also called electrochemical capacitors) have become an active research topic in recent years thanks to their high power density, highly reversible charging/discharging capability, and long cycling life [1–5]. Based on different charge storage mechanisms, they can be divided into two categories. One stores charge from ion adsorption and desorption, named as electric double layer capacitors. The other stores charge by Faradic reactions, thus named as pseudocapacitors [6].

Among materials with pseudocapacitive behaviors, ruthenium oxide (RuO_2) has attracted tremendous interest for its perfect electrochemical reversibility, high specific capacitance, and excellent cycling life in H_2SO_4 [7,8]. RuO_2 in both amorphous and crystalline forms has been widely recognized as the most promising electrode material to supercapacitor applications [9–15]. Amorphous RuO_2, especially sol–gel derived amorphous hydrous type ($RuO_2 \cdot xH_2O$), has very high specific capacitance up to 1000 F g^{-1} but poor cycling stability [16]. In contrast, crystalline RuO_2, often prepared by thermolysis method, has high electronic conductivity, good chemical stability and long cycling life but low specific capacitance. Since stability is crucial for practical use, annealing technique is often applied to transform amorphous RuO_2 to partial crystalline, so as to trade off some specific capacitance with stability [17–20]. Many sophisticated control may be required during annealing process to avoid over-crystallite in large scale manufacture. Hu et al. proposed hydrothermal annealing method to address this issue, i.e. annealing in a water-enriched environment after preparing amorphous RuO_2 [21].

However, there is little literature available on direct thermolysis derived RuO_2 in water-enriched environment. In this study, partial crystalline hydrous RuO_2 was prepared by a steam-assisted thermolysis method. Unlike hydrothermal preparation, $RuCl_3$ precursor is coated on the surface of substrate and heated by the steam, then directly transformed to hydrous RuO_2 electrode in the proposed method. Therefore, it is a simple and inexpensive technique to avoid annealing process and the typical electrode fabrication process. Moreover, the specific capacitance of the RuO_2 prepared by this method is up to 360 F g^{-1}, which is twice as that of prepared by simple thermolysis method, and maintain nearly 100% after 100,000 continuous charging/discharging cycles in H_2SO_4 electrolyte with 100% coulombic efficiency.

2. Experimental

RuO_2 electrodes were prepared by thermolysis of the slurry of $RuCl_3$ (Sigma-Aldrich) coated on tantalum (Ta) substrates. Ta substrates were coated with PTFE films to leave an exposed surface area of 1.0 cm × 1.0 cm before use. The Ta surface was mechanically polished by emery paper down to 1200 grade. Then it was degreased, washed and dried. The temperature of thermolysis was 220 °C. The thermolysis in steam was carried out by using the steam as heating media. The heating rate was 5 °C min^{-1}. The steam was used when the temperature in the oven was up to 150 °C.

All electrochemical preparations and tests were done on the Versatile Multichannel Potentiostat 2/Z (VMP2, Princeton applied research) with the ability of impedance measurements. The electrochemical performance was investigated by cyclic voltammetry (CV), galvanostatical charging/discharging and electrochemical impedance spectroscopy (EIS) techniques with 1 M H_2SO_4 aqueous solution as electrolyte and a

* Corresponding author. Tel./fax: +86 29 82665161.
E-mail address: ylxu@mail.xjtu.edu.cn (Y. Xu).

http://dx.doi.org/10.1016/j.ssi.2014.03.007
0167-2738/

saturated calomel electrode (SCE) as the reference electrode. The mass was determined by the electronic balance (AG 135, Mettler-Toledo, precision 0.01 mg). The static contact angles of electrolyte (1 M H_2SO_4) droplets were measured using contact angle meter (Solon Tech. (Shang Hai) Co. Ltd.) with a CCD camera. The morphology of samples was observed on a Field Emission Scanning Electron Microscope (JSM-6700F, JEOL Ltd.). X-ray diffraction (XRD, Rigaku D/MAX 2500) using Cu Kα radiation with a wavelength (λ) of 0.15405 nm was applied for structure characterization.

3. Results and discussion

Fig. 1 presents the SEM images of the $RuO_2 \cdot xH_2O$ electrodes prepared in steam and air, shorten as $RuO_2 \cdot xH_2O$–S and $RuO_2 \cdot xH_2O$–A, respectively. They both exhibit smooth surface without any peeling phenomenon (Fig. 1(a) and (c)), indicating a good adhesion. Under 20,000× magnification, they exhibit typically "mud-cracked" morphology (Fig. 1(b) and (d)) [22], which are favorable for the penetration of electrolytes. Insets of Fig. 1(b) and (d) show the surface wettability of two electrodes evaluated with electrolyte contact angle measurement. The electrolyte (i.e. 1 M H_2SO_4) lies on the surface of $RuO_2 \cdot xH_2O$–S (inset of Fig. 1(b)) and $RuO_2 \cdot xH_2O$–A (inset of Fig. 1(d)) with contact of 52° and 71°, respectively, which indicates that the former can offer better accessibility for the electrolyte.

Fig. 2 shows the XRD pattern of $RuO_2 \cdot xH_2O$–S and $RuO_2 \cdot xH_2O$–A. RuO_2 crystal in the form of rutile is observed in $RuO_2 \cdot xH_2O$–A. But its XRD patterns reveal broad diffraction peaks, indicating the formation of tiny $RuO_2 \cdot xH_2O$ nanocrystallites. Interestingly, the crystal growth of $RuO_2 \cdot xH_2O$ is effectively inhibited under steam condition, because

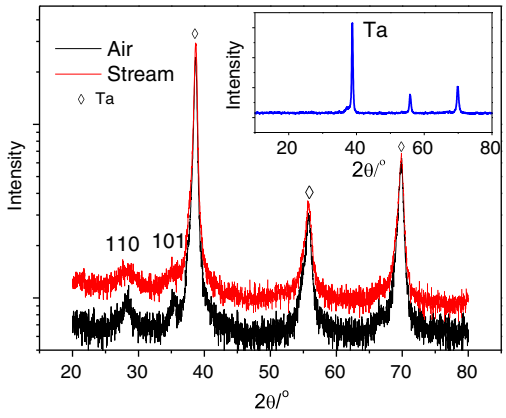

Fig. 2. XRD pattern of $RuO_2 \cdot xH_2O$ prepared in steam (red curve) and in air (black line), inset figure shows XRD pattern of Ta substrate.

(101) peak of $RuO_2 \cdot xH_2O$–S is not obvious and (110) peak is broader than that of $RuO_2 \cdot xH_2O$–A. Therefore, a better balance between electronic and protonic transport rates can be obtained in $RuO_2 \cdot xH_2O$–S.

Their electrochemical capacitance properties were examined by CV test at scanning rate of 10 mV s^{-1}, shown in Fig. 3(a). The response current has already been divided by the corresponding scanning rate and the mass, so that the mass specific capacitance (F g^{-1}) can be easily compared. There is a very broad redox peak around 0.5 V, which suggests a pseudocapacitance character of $RuO_2 \cdot xH_2O$ [7]. Capacitance of the $RuO_2 \cdot xH_2O$–S is twice as great as that of $RuO_2 \cdot xH_2O$–A, which is

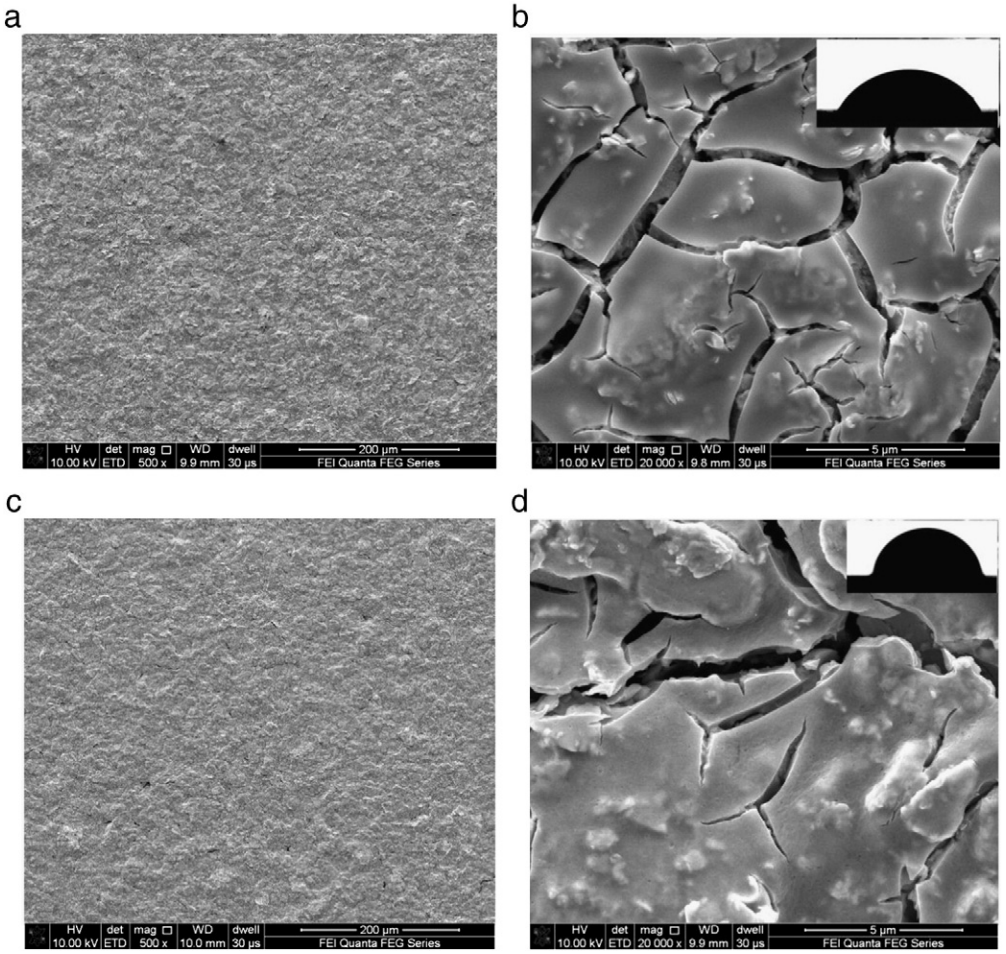

Fig. 1. SEM images of $RuO_2 \cdot xH_2O$ prepared in steam (a) ×500, (b) ×20,000 and in air (c) ×500, (d) ×20,000, inset figures show their electrolyte contact angle.