Annealing effect on the performance of RuO$_2$–Ta$_2$O$_5$/Ti electrodes for use in supercapacitors

Ho-Rei Chen, Huen-Hua Lai, Jiin-Jiang Jow*

Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Sciences, Kaohsiung, 80782 Taiwan

**Abstract**

The preparation of RuO$_2$–Ta$_2$O$_5$/Ti electrodes, by dip-coating, for use in supercapacitors was investigated. The stability and specific capacitance of the electrodes annealed at various temperatures was examined. The results show that highly stable electrodes with a specific capacitance of 170 F g$^{-1}$RuO$_2$ at approximately 250 °C, while electrodes with a lower capacitance (130 F g$^{-1}$RuO$_2$) were obtained at 300 °C. The annealing time needed to obtain a stable RuO$_2$–Ta$_2$O$_5$/Ti electrode at various temperatures correlates well with the activation energy ($E_a$) of the annealing reactions for the electrodes being estimated as 73.5 kJ mol$^{-1}$. SEM images of the electrodes show the coating films to have rough surface morphology with cracks 2–6 µm in width. XRD data indicate that the coating films obtained are composed of crystalline RuO$_2$ and amorphous tantalum oxide.

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1. Introduction

Electrochemical supercapacitors are becoming attractive energy storage devices for various applications needing high power [1–3]. Ruthenium oxides-based electrodes were investigated widely for use in the storage electrodes of supercapacitors due to their redox properties being readily reversible [1–6]. A considerable amount of effort has been devoted to improving their performance and commercial viability. Dispersing Ru oxides on carbon substrates with large surface areas [6–8], and alloying Ru with other metal oxides [9–12] has improved the effective efficiency of the Ru materials and minimized the cost of the electrodes. However, challenges remain in the manufacture of ruthenium oxide supercapacitors for commercial applications. One of problems is that the capacitance of these electrodes tends to decay gradually due to the corrosion of ruthenium oxides on the electrode during the charge/discharge cycle. The phenomena of capacitance decay have been observed in carbon supported ruthenium oxide [13,14], alloyed ruthenium oxide [10] and thin film ruthenium oxides electrodes [15,16].

Long-term stability of the electrodes is extremely important for practical applications because the cycle life of a capacitor is typically measured in hundreds of thousands. In addition, several dozens of cells have to be connected in series to obtain the desired high-voltage demanded for many applications, the stability of the electrodes and the capacity balance of the individual cells are very important considerations. The cell having a relatively lower capacitance in a capacitor may rupture as a result of over charge/discharge; due to the decomposition of the aqueous electrolyte.

Ruthenium oxide-based electrodes, known as dimensionally stable anodes (DSA), have been used for Cl$_2$ production and various applications concerning water electrolysis. The stability of the ruthenium oxides has been improved by alloying the oxides with valve metals, such as Ta, Ti, and Sn, etc., to increase the their corrosion resistance and to lower the cost [17–19]. These alloyed ruthenium oxides are promising materials, having long-term stability for incorporation in electrodes used in supercapacitors; e.g. the Ta-based electrodes, which have been shown to have a high corrosion resistance and service life [20]. However, the annealing temperature for these electrodes should be lower than that for DSA because the specific capacitance of the ruthenium oxides decreases significantly at annealing temperatures higher than ca. 300 °C due to increasing crystallization of the materials [14,21–23]. Hydrous ruthenium oxides with an amorphous structure were found to exhibit better pseudo-capacitive behavior [3,13].

In this work, RuO$_2$–Ta$_2$O$_5$/Ti composite electrodes were prepared by dip-coating for use in supercapacitors; the annealing effect on the capacitive properties of the electrodes was investigated in an attempt to obtain electrodes having a high specific capacitance and a long-term stability for use in supercapacitors.

2. Experimental

Isopropanol solutions, containing RuCl$_3$ (5.0 wt%) and TaCl$_3$ (3.0 wt%) provided by Ultracap Tech. Corp. (Taiwan), were used for dip-coating the RuO$_2$–Ta$_2$O$_5$ oxide films onto Ti substrates, which were pretreated as described in our previous paper [24]. Ti substrates were coated with PTFE films to leave an exposed surface area of...
Fig. 6. XRD spectra of the RuO$_2$–Ta$_2$O$_5$/Ti electrodes annealed at 220 °C for 12 h (a), 230 °C for 9 h (b), 240 °C for 7 h (c), 250 °C for 5 h (d), 300 °C for 1 h (e).

54.3° (JCPDS-40-1290), respectively. The difference in intensity of the peaks for RuO$_2$ is insignificant, showing that the surface structure and the extent of crystallization of the ruthenium oxides are approximately the same. These results are in accordance with the results shown in Fig. 2, namely that the $C_{sp}$ of the electrodes is approximately equal. A slight broadening of these peaks was observed in the pattern. This can be attributed to the interpenetration of the Ru lattice by Ta [25]. On the other hand, the characteristic peaks of crystalline Ta$_2$O$_5$ at 2θ values of 22.9°, 28.3°, and 36.7° (JCPDS-25-0922) are not obvious in Fig. 6, showing that the coating films obtained at annealing temperatures of 220–300 °C are composed of crystalline RuO$_2$ and amorphous tantalum oxide. The peaks due to Ti substrates at 2θ of 38.6° and 40.4° were explained in our previous paper [26].

4. Conclusions

RuO$_2$–Ta$_2$O$_5$/Ti composite electrodes, for use in supercapacitors, were prepared by dip-coating. The annealing effect on the capacitive properties of the electrodes was investigated thoroughly in the temperature range 220–300 °C, in order to obtain high stability electrodes with a higher capacitance. The results show RuO$_2$–Ta$_2$O$_5$/Ti electrodes with a long-term stability were obtained. The coating films having a high stability are composed of crystalline RuO$_2$ and amorphous tantalum oxide as indicated by the XRD data. The annealing time for obtaining the stable electrodes increases with a decrease in the annealing temperature. The reaction rate of annealing reaction for the RuO$_2$–Ta$_2$O$_5$ coatings correlates well with the Arrhenius’ law.

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References