Electrochemical Capacitor Behavior of RuO$_2$ vertically Aligned Rods Filled with RuO$_2$•xH$_2$O

Diah Susanti, Dah-Shyang Tsai*, Chia-Liang Cheng, Department of Chemical Engineering, Ying-Sheng Huang, Alexandru Korotcov, Department of Electronic Engineering, National Taiwan University of Science and Technology (NTUST), Taipei 106 Taiwan

Introduction and Experimental details

A designed microstructure is proposed to fabricate high capacitance capacitors based on ruthenium dioxide. One dimensional RuO$_2$ rods (RuO$_2$NR) of high corrosion resistance and electrical conductivity acted as the electron conduits to collect and distribute charge. Meanwhile the hydrous RuO$_2$ (RuO$_2$•xH$_2$O) of high capacitance was coated on RuO$_2$NR to store charge. The capacitor of hybrid structure may possess the merits of hydrous and anhydrous RuO$_2$ both. In this work, we prepare a micron-meter thick hybrid electrode of anhydrous and hydrous RuO$_2$, and analyze its electrochemical capacitive behavior using cyclic voltammetry and impedance spectroscopy.

Anhydrous RuO$_2$ vertical rods were grown on LiNbO$_3$(100) substrates via metalorganic CVD. The ruthenium source was a high-purity liquid precursor, bis(ethylcyclopentadienyl)Ru (Strem Chemicals). The substrate temperature was set at 340°C and the chamber pressure 2 Torr. Specimens of the RuO$_2$ rods on LiNbO$_3$(100) substrates are denoted as RuO$_2$VR. The hybrid electrode which was prepared by electrodepositing hydrous RuO$_2$ on RuO$_2$VR is denoted as RuO$_2$VR-H. Capacitive properties were measured using two voltage modulation methods. In cyclic voltammetry (CV), the voltage modulation was done at various scan rates. In electrochemical impedance spectroscopy (EIS), the voltage modulation was to apply a sinusoidal alternating voltage of frequency 10$^{-2}$ – 10$^6$ Hz.

Results and Discussion

Morphological features of RuO$_2$VR and RuO$_2$VR-H are illustrated in Fig. 1. Typical vertical rods are 110-180 nm in diameter and 2600 nm in height in the RuO$_2$ one-dimensional assembly, as shown in Fig. 1(a). These densely-packed rods have a pyramidal tip and connected at the roots of the rods assembly. Considerable pore space is present among the rods can be filled with hydrous RuO$_2$. Hydrous RuO$_2$ of RuO$_2$•0.46H$_2$O is estimated to fill 80% of the pore space in RuO$_2$VR. The top and cross-sectional views of RuO$_2$VR-H are shown in Figs. 1(c) and 1(d). Fig. 1(b) is a schematic diagram indicating the RuO$_2$VR-H structure and the porous nature of RuO$_2$•0.46H$_2$O.

Cyclic voltammograms of RuO$_2$VR at scan rate 5, 10, 25, 50, 100, 500 mVs$^{-1}$ are plotted as accessible capacitance versus potential in the range of 0.0 - 1.0 V, Fig. 2(a). The CV capacitance of RuO$_2$VR decreases slightly with the increasing scan rate, from 25.8 mFcm$^{-2}$ (32.3 Fg$^{-1}$) at 25 mVs$^{-1}$ to 22.3 mFcm$^{-2}$ (27.9 Fg$^{-1}$) at 1000 mVs$^{-1}$, indicating a weak dependence on the scan rate. The CV diagrams of RuO$_2$VR-H at various scan rates are illustrated in Fig. 2(b). In contrast to the low capacitance of RuO$_2$VR, the capacitance of RuO$_2$VR-H is much higher. The capacitance of
RuO₂VR-H is 464 mFcm⁻² (403 Fg⁻¹) at 5 mVs⁻¹. But the capacitance value of RuO₂VR-H is influenced by the scan rate considerably. Fig. 2(b) indicates that the enclosed area of RuO₂VR-H decreases with the increasing scan rate. The specific capacitance of RuO₂VR-H drops 70% when the scan rate is raised to 1000 mVs⁻¹, that is, from 464 mFcm⁻² at 5 mVs⁻¹ to 137 mFcm⁻² at 1000 mVs⁻¹. Apparently the proton storage capability of RuO₂•0.46H₂O is not fully utilized at high scan rates, because of the fractal nature of hydrous RuO₂ and the distributed resistance and capacitance in the remaining pores.

Nyquist plots of RuO₂VR and RuO₂VR-H at various potentials are plotted in Figs. 3(a) and 3(b). When the potential ≥ 0.2 V, the impedance plots display one or two depressed semicircles at high frequencies and a nearly vertical line along the imaginary axis Z″ at low frequencies. These nearly vertical lines suggest the characteristics of an ideally polarizable electrode. When the potential ≤ 0.2 V, a deviation from the 90° slope indicates a nonideally polarizable behavior, especially for RuO₂VR at 0.0 V. The marked deviation from 90° at 0.0 V is in line with the strong scan rate dependence of cathodic current below 0.1 V, shown in Fig. 2(a).

Insets of Figs. 3(a) and 3(b) display more impedance details around the semicircles. A region of 45° slope in the medium frequency range can be found in the Nyquist plot of RuO₂VR-H, but not RuO₂VR. The 45° slope at medium frequencies is a characteristic of transmission line behavior, in contrast to a Warburg 45° phase angle plot which arises at low frequencies when a diffusion-controlled process is rate-determining. The transmission line behavior is attributed to the distributed resistances and capacitances in RuO₂•0.46H₂O, which is the main structural difference between RuO₂VR-H and RuO₂VR.

Figs. 4(a) and 4(b) are the Bode plots showing the frequency dependence of |Z| and phase angle of RuO₂VR. The Bode plots of RuO₂VR-H are illustrated in Figs. 4(c) and 4(d). For the discussion purpose, it is convenient to divide the impedance behavior into the low, medium, and high frequency regions. The low frequency region is defined as the region where the |Z| plot shows a slope near -1 and the value of phase angle is between -90° and -45°. The low frequency range for RuO₂VR is ≤ 10 Hz. In contrast, the low frequency range of RuO₂VR-H is ≤ 0.4 Hz. The high frequency range is defined as the region where the magnitude of impedance |Z| is weakly dependent on the frequency and the phase angle is close to zero. The high frequency range for RuO₂VR is ≥ 10³ Hz, and that for RuO₂VR-H is ≥ 200 Hz. Hence the medium frequency range is between 10³ and 10 Hz for RuO₂VR, 200 and 0.4 Hz for RuO₂VR-H.

The |Z| value of RuO₂VR in the low frequency range (<1 Hz) is 6 or 8 times higher than that of RuO₂VR-H. Since impedance is a measure of the ability of a circuit to resist the electrical current, a lower |Z| value of RuO₂VR-H suggests the extra RuO₂•0.46H₂O makes the hybrid electrode less resistive. The frequency where the phase angle equals to -45° may be regarded as the capacitor response frequency. The capacitor response frequency of RuO₂VR ranges from 7 to 20 Hz, which means a response time of 0.14 - 0.05 s. On the other hand, the capacitor response frequency of RuO₂VR-H ranges from 0.3 to 0.9 Hz, giving a response time of 3.3 – 1.1 s. The sluggish response of RuO₂VR-H is mainly caused by its larger capacitance. We also calculated the capacitances according to \( C = \frac{2\pi f Z″}{f} \), in which \( f \) is frequency in Hz and Z″ the imaginary part of.
impedance in Ωcm². The RuO₂VR capacitances at 0.01 Hz are 14-26 mFcm⁻², those of RuO₂VR-H are 172-429 mFcm⁻² depending on DC potentials. These capacitance values are generally in line with those values measured by CV.

Fig. 1 (a) The morphology of RuO₂VR, (b) a schematic diagram of RuO₂VR-H structure, (c) a top view of RuO₂VR-H showing the surface is covered by hydrous RuO₂, (d) a cross-sectional view of RuO₂VR-H.

Fig. 2 CV diagrams of (a) RuO₂VR, (b) RuO₂VR-H at scan rate 5, 10, 25, 50, 100, 500 mV s⁻¹. Accessible capacitance is the ratio of response current divided by scan rate.

Fig. 3 Nyquist plots of (a) RuO₂VR, (b) RuO₂VR-H at various bias.

Fig. 4 Bode plots of (a) |Z| (b) phase angle of RuO₂VR versus frequency, (c) |Z| (d) phase angle of RuO₂VR-H.