

Electronic and Protonic Conduction of Hydrated Ruthenium Oxides Studied by EIS

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Electrochemical capacitors based on ruthenium oxides have attracted increased interest due to their high power density, high energy density and long cycle life. In particular, hydrated ruthenium oxide ($\text{RuO}_2 \cdot x\text{H}_2\text{O}$) can provide capacitance ranging from 600-800 F g^{-1} , making it one of the most promising materials for high energy electrochemical capacitors.¹ The higher energy density compared to anhydrous RuO_2 has been attributed to the mixed protonic-electronic conduction of $\text{RuO}_2 \cdot x\text{H}_2\text{O}$.

A different type of hydrated ruthenium oxide, layered ruthenic acid hydrate ($\text{H}_{0.2}\text{RuO}_{2.1} \cdot n\text{H}_2\text{O}$), is also a promising electrode material with mixed protonic-electronic conduction.² Unlike $\text{RuO}_2 \cdot x\text{H}_2\text{O}$, $\text{H}_{0.2}\text{RuO}_{2.1} \cdot n\text{H}_2\text{O}$ is a crystalline oxide with a layered structure, and the electronic conduction is provided via the crystalline ruthenium oxide nanosheets and the hydrated interlayer accounts for the protonic conduction. We have shown that layered $\text{H}_{0.2}\text{RuO}_{2.1} \cdot n\text{H}_2\text{O}$ can deliver specific capacitance up to 390 F g^{-1} and ruthenium oxide nanosheets derived from layered $\text{H}_{0.2}\text{RuO}_{2.1} \cdot n\text{H}_2\text{O}$ by chemical exfoliation can afford capacitance up to 700 F g^{-1} .

In order to further understand the properties and differences in the fundamental capacitive behavior of $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ with various water contents and layered $\text{H}_{0.2}\text{RuO}_{2.1} \cdot n\text{H}_2\text{O}$, it is important that the frequency response and protonic-electronic conduction of these materials is characterized. In this study, we have evaluated the change in the protonic and electronic conduction of $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ as a function of the water content as well as layered $\text{H}_{0.2}\text{RuO}_{2.1} \cdot n\text{H}_2\text{O}$ by electrochemical impedance spectroscopy.

Commercial $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ was heat treated at 200, 300, or 450°C for 24 h in air to prepare $\text{RuO}_2 \cdot 0.5\text{H}_2\text{O}$, $\text{RuO}_2 \cdot 0.3\text{H}_2\text{O}$ and anhydrous RuO_2 . Layered ruthenic acid hydrate was prepared as reported earlier.² A beaker-type electrochemical cell equipped with a Pt pseudo-reference electrode was used for electrochemical impedance spectroscopy. The working electrodes were prepared by the thin film electrode method. Impedance measurements were conducted in a constant voltage mode (0.2, 0.4, 0.6, 0.8, 1.0, 1.2 V vs. RHE) by sweeping frequencies from 10^5 to 0.01 Hz at an amplitude of 5 mV.

Figure 1 compares the complex-plane impedance plots of $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ ($x=0.5, 0.3, 0$) and layered $\text{H}_{0.2}\text{RuO}_{2.1} \cdot n\text{H}_2\text{O}$ at 1.0 V vs. RHE where the contribution of redox reactions is minimal. The diameter of the high-frequency arc increased with the decrease in water content in $\text{RuO}_2 \cdot x\text{H}_2\text{O}$, indicating an increase in interfacial resistance. The interfacial resistance was 0.8, 1.2, 1.7 Ω for $x=0.5, 0.3, 0$ and 0.6 Ω for layered $\text{H}_{0.2}\text{RuO}_{2.1} \cdot n\text{H}_2\text{O}$. The increase in the heat-treatment temperature should increase electronic conduction, thus the increase in the interfacial resistance can be attributed to the decrease in protonic conduction. The interfacial resistance of layered $\text{H}_{0.2}\text{RuO}_{2.1} \cdot n\text{H}_2\text{O}$ is smaller than $\text{RuO}_2 \cdot 0.5\text{H}_2\text{O}$. Therefore, it can be said that the protonic conduction of layered $\text{H}_{0.2}\text{RuO}_{2.1} \cdot n\text{H}_2\text{O}$ is similar to that of $\text{RuO}_2 \cdot 0.5\text{H}_2\text{O}$.

Figure 2 shows the Bode plots of the impedance data of $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ ($x=0.5, 0.3, 0$) and layered $\text{H}_{0.2}\text{RuO}_{2.1} \cdot n\text{H}_2\text{O}$ at 1.0 V vs. RHE. With the decrease in

water content in $\text{RuO}_2 \cdot x\text{H}_2\text{O}$, the frequency where the phase angle reaches 90° shifts to higher frequency, which can be realized as the frequency response to the ideally capacitive behavior. The threshold frequency was 0.03, 3, 10 Hz for $x=0.5, 0.3, 0$. The better frequency response to the ideally capacitive behavior most likely reflects the electronic conduction of the material. In other words, $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ with a smaller amount of water and higher crystallinity can be charged/discharged at a higher rate, but gives lower specific capacitance than a more hydrated one. The frequency where the phase angle approaches 90° in the Bode plots for layered $\text{H}_{0.2}\text{RuO}_{2.1} \cdot n\text{H}_2\text{O}$ is an order higher compared to $\text{RuO}_2 \cdot 0.5\text{H}_2\text{O}$ and is closer to the behavior of more crystalline systems. These results suggest that layered $\text{H}_{0.2}\text{RuO}_{2.1} \cdot n\text{H}_2\text{O}$ has protonic conduction comparable to the more hydrated, higher capacitance $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ and electronic conduction comparable to the less hydrated, well-crystalline $\text{RuO}_2 \cdot x\text{H}_2\text{O}$. Hence, layered $\text{H}_{0.2}\text{RuO}_{2.1} \cdot n\text{H}_2\text{O}$ can provide a combination of high capacitance (energy density) of hydrated oxides and high rate (power density) of crystalline oxides.

1. J.P. Zheng, P.J. Cyang, T.R. Jow, *J. Electrochem. Soc.*, **142**, 2699(1995).
2. W. Sugimoto, H. Iwata, Y. Yasunaga, Y. Murakami, Y. Takasu, *Angew. Chem. Int. Ed.*, **42**, 4092 (2003).

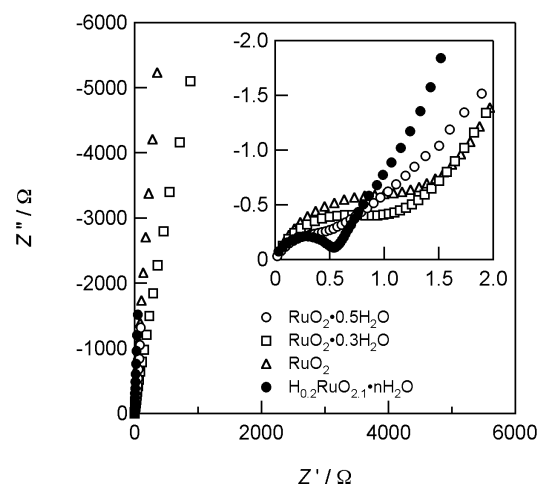


Figure 1. Complex plane impedance plots for $\text{RuO}_2 \cdot 0.5\text{H}_2\text{O}$ (open circles), $\text{RuO}_2 \cdot 0.3\text{H}_2\text{O}$ (squares), anhydrous RuO_2 (triangles), and layered $\text{H}_{0.2}\text{RuO}_{2.1} \cdot n\text{H}_2\text{O}$ (closed circles) at 1.0 V vs. RHE.

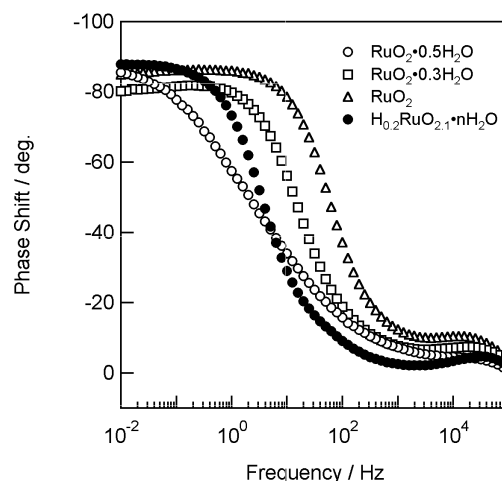


Figure 2. Bode plots for $\text{RuO}_2 \cdot 0.5\text{H}_2\text{O}$ (open circles), $\text{RuO}_2 \cdot 0.3\text{H}_2\text{O}$ (squares), anhydrous RuO_2 (triangles), and layered $\text{H}_{0.2}\text{RuO}_{2.1} \cdot n\text{H}_2\text{O}$ (closed circles) at 1.0 V vs. RHE.