

**Electrical Properties of Ion-Exchangeable Layered Ruthenium Oxides**

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Ruthenium oxides have attracted increased interest as electrochemical capacitors due to their high power density, high energy density and long cycle life. The hydrous form of ruthenium oxide ( $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ ) can provide capacitance up to  $720 \text{ F g}^{-1}$ .<sup>[1]</sup> The layered form of ruthenium oxide ( $\text{H}_{0.2}\text{RuO}_{2.1} \cdot n\text{H}_2\text{O}$ ) also gives a high capacitance. Layered  $\text{H}_{0.2}\text{RuO}_{2.1} \cdot n\text{H}_2\text{O}$  is a crystalline oxide, and the electronic conduction is provided via the crystalline ruthenium oxide nanosheets while the hydrous interlayer accounts for the protonic conduction. Layered  $\text{H}_{0.2}\text{RuO}_{2.1} \cdot n\text{H}_2\text{O}$  can deliver specific capacitance up to  $370 \text{ F g}^{-1}$  and ruthenic acid 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  $700 \text{ F g}^{-1}$ .<sup>[2,3]</sup>

In order to further understand the properties of layered ruthenium oxides, it is important that the electrical properties are characterized. In this study, we have evaluated the electrical properties of layered ruthenium oxides by comparing it with anhydrous crystalline ruthenium oxide ( $\text{RuO}_2$ ) using the four probe method, magnetic susceptibility measurements and in-situ electrochemical impedance spectroscopy (EIS).

Layered potassium ruthenate ( $\text{K}_{0.2}\text{RuO}_{2.1}$ ) was prepared following the previous work.<sup>[2]</sup> Briefly, a mixture of  $\text{K}_2\text{CO}_3$  and  $\text{RuO}_2$  was reacted at  $850^\circ\text{C}$  for 12 h under a flow of Ar and washed with copious amounts of water. Layered caesium ruthenate ( $\text{Cs}_{0.2}\text{RuO}_{2.1}$ ) was obtained from a mixture of  $\text{Cs}_2\text{CO}_3$  and  $\text{RuO}_2$ . Sintered pellets were used for the electrical resistivity measurements. Magnetic susceptibility was measured with powder samples. In-situ EIS was measured using a beaker-type electrochemical cell equipped with a Pt pseudo-reference electrode. Impedance measurements were conducted in a constant voltage mode (1.0 V vs. RHE) by sweeping frequencies from  $10^5$  to 0.01 Hz at an amplitude of 5 mV in 0.5 M  $\text{H}_2\text{SO}_4$  ( $25^\circ\text{C}$ ).

Figure 1 shows the normalized resistivity as a function of the temperature. The electronic property of layered ruthenium oxides was similar to that of anhydrous  $\text{RuO}_2$ . The room-temperature resistivity of  $\text{K}_{0.2}\text{RuO}_{2.1}$ ,  $\text{Cs}_{0.2}\text{RuO}_{2.1}$  and anhydrous  $\text{RuO}_2$  was 2.1, 1.7 and  $0.5 \text{ m}\Omega \text{ cm}$ , respectively. Figure 2 shows the magnetic susceptibility of various forms of layered ruthenium oxides. The Cs, K and H forms all showed Curie-Weiss like behavior, typical of metallic behavior. The resistivity and susceptibility data suggests that layered ruthenium oxides have electronic and magnetic properties similar to that of rutile-type  $\text{RuO}_2$ .

Figure 3 compares the in-situ EIS data of  $\text{RuO}_2$  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 indicates the interfacial resistance. The interfacial resistance was  $1.7 \Omega$  for  $\text{RuO}_2$  and  $0.6 \Omega$  for layered  $\text{H}_{0.2}\text{RuO}_{2.1} \cdot n\text{H}_2\text{O}$ . The difference in the interfacial resistance can be attributed to the higher protonic conduction of layered  $\text{H}_{0.2}\text{RuO}_{2.1} \cdot n\text{H}_2\text{O}$ .

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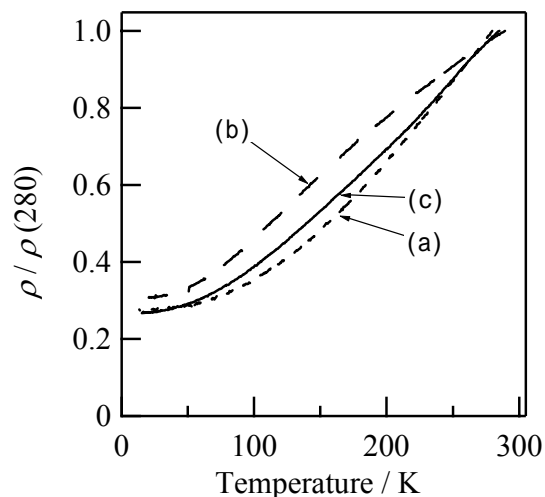


Figure 1. Normalized resistivity of (a)  $\text{RuO}_2$ , (b)  $\text{K}_{0.2}\text{RuO}_{2.1}$  and (c)  $\text{Cs}_{0.2}\text{RuO}_{2.1}$ .

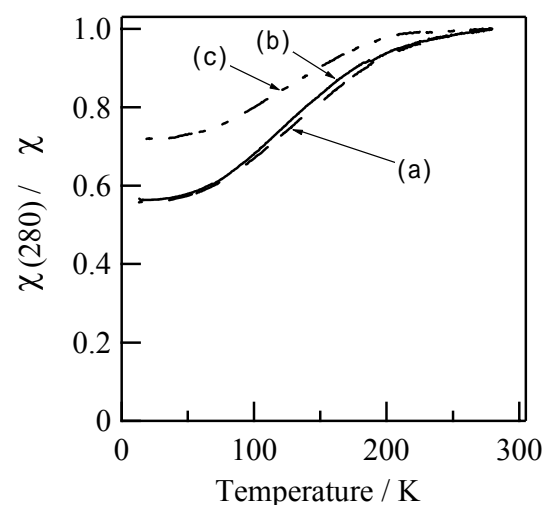


Figure 2. Normalized susceptibility of (a)  $\text{K}_{0.2}\text{RuO}_{2.1}$ , (b)  $\text{Cs}_{0.2}\text{RuO}_{2.1}$  and (c)  $\text{H}_{0.2}\text{RuO}_{2.1}$ .

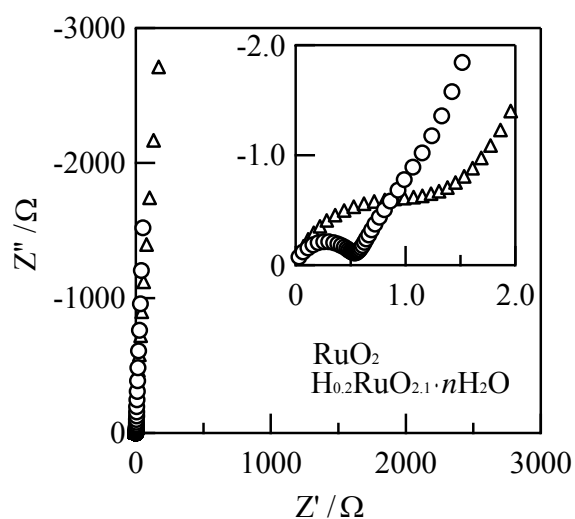


Figure 3. Complex plane impedance plots after subtraction of the solution resistance for  $\text{RuO}_2$  (triangles) and layered  $\text{H}_{0.2}\text{RuO}_{2.1} \cdot n\text{H}_2\text{O}$  (circles) at 1.0 V vs. RHE in 0.5 M  $\text{H}_2\text{SO}_4$  at  $25^\circ\text{C}$ .