Solid state NMR investigation of hydrous ruthenium oxide

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Abstract

Amorphous hydrous ruthenium oxide (RuO2·xH2O) with different composition x has been studied using solid-state nuclear magnetic resonance (NMR) spectroscopy. The 2D NMR spectra at different temperatures illustrate that the water molecules undergo fast molecular motion even if the temperature is as low as 213 K. The static 1H NMR spectra indicate the composition dependent proton–proton dipolar interaction. It is demonstrated that the mobility of the water molecules and their interaction with ruthenium oxides play an important role in the proton charge density. In conclusion, the competition between these two antithetical effects provides a mechanism for the proton charge storage of the RuO2·xH2O materials. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Hydrous ruthenium oxides (RuO2·xH2O) have attracted great interest recently because of important technological applications in electrocatalysis [1,2] and high-charge storage-capacity devices (e.g., electrochemical capacitors) [3–7]. For example, the presence of hydrous ruthenium oxide in the nanoscale Pt–Ru electrocatalysts used in the direct methanol fuel cell provide important contributions to the electrocatalytic oxidation of methanol due to its mixed electron–proton conductivity [1]. Moreover, RuO2·xH2O is an excellent electrode material for electrochemical capacitors [3,4,6,7] because it exhibits high specific capacitance (i.e., maximum charge density), high conductivity, good electrochemical reversibility, as well as high power and high energy density. However, this material has not been well characterized due to its amorphous nature and compositional variability. Here, we utilize solid-state nuclear magnetic resonance (NMR) spectroscopy, a unique technique well suitable for dynamics characterization in materials even in an amorphous phase [8], to study the hydrous ruthenium oxide material, thus providing insights into the implications of its structural water.

Anhydrous RuO2, whose crystalline structure is rutile, is one of the best pseudocapacitive materials and its energy storage mechanism is believed to be the so-called fast faradaic reactions with ions. Such reactions are typically limited to the surface area due to its rutile structure. In contrast, RuO2·xH2O is amorphous and the protons can easily intercalate and diffuse into the bulk of the
material. As a result, the surface interaction area is effectively increased resulting in a higher specific capacitance. The maximum specific capacitance of amorphous RuO$_2 \cdot x$H$_2$O obtained yet [6] was over 768 F/g, which is more than two times greater than that from the RuO$_2$ material. However, this is still a largely qualitative theory to explain why the amorphous ruthenium oxide is superior to the crystalline material. In addition, the specific capacitance of RuO$_2 \cdot x$H$_2$O is also affected by the hydrogen concentration [4]. Although a high water content provides more protons available for the intercalation, it results in a low specific capacitance. A very lower concentration also gives rise to a low specific capacitance. The maximum specific capacitance is normally obtained in the range $x = 0.5-0.7$. Furthermore, the impurities such as lithium and sodium in the hydrous ruthenium oxide could dramatically affect the specific capacitance. For instance, 2% sodium in the amorphous ruthenium oxide could cause a 20% reduction in the specific capacitance [3,4], while the incorporation of Cr into the hydrous ruthenium oxide slightly increases the specific capacitance [9]. Although many studies of electrochemical properties of the RuO$_2 \cdot x$H$_2$O material have been carried out, the role of the structural water in the amorphous hydrous ruthenium oxide has not yet been well understood. A $^2$D NMR observation was reported on the isotope-exchanged RuO$_2 \cdot x$D$_2$O and D$_2$RuO$_2 \cdot x$D$_2$O samples, indicating substantial molecular mobility in the materials [10]. Mckeown et al. [11] characterized the structures of the hydrous ruthenium oxides (RuO$_2 \cdot 2.32$H$_2$O, RuO$_2 \cdot 0.29$H$_2$O and anhydrous RuO$_2$) by a combined use of thermogravimetric analysis (TGA), X-ray diffraction, X-ray absorption near-edge structure (XANES), and extended X-ray fine structure (EXAFS) analysis. It was found that the local structures of RuO$_2 \cdot 2.32$H$_2$O and RuO$_2 \cdot 0.29$H$_2$O hypothesised from the EXAFS data are remarkably different due to the presence of structural water. However, because the orientation of water is not discernible from the EXAFS data, the relation between the structural water and the proton charge storage is not yet clear.

In the present Letter, we use the solid-state NMR technique to characterize RuO$_2 \cdot x$H$_2$O materials with different water contents. The $^2$D NMR spectra at different temperatures are obtained to demonstrate the mobility of the water molecules, while the static $^1$H NMR measurements allow for characterization of the residual proton--proton dipolar couplings. We will further discuss the correlation between the mobility of the water molecules and the proton charge storage, based on the electrochemical measurements.

2. Materials and experiments

A sample of RuO$_2 \cdot 2.662$H$_2$O was purchased from Alfa Aesar®/Johnson Matthey Company and was used without further purification. A series of ruthenium oxide RuO$_2 \cdot x$H$_2$O materials were prepared through the annealing processes. The original RuO$_2 \cdot 2.662$H$_2$O sample was weighted and then placed in an oven where different temperatures (from 323 to 573 K) were set to allow the sample to be annealed for about 24 h. Only the water of the sample is lost during the annealing process, thus the water content $x$ can be calculated through the weight change of the sample before and after the annealing process. The $x$ values obtained at different annealing temperatures are shown in Table 1.

The RuO$_2 \cdot 2.82$D$_2$O powder material was prepared using a sol–gel process. The required

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<tr>
<th>$T$ (K)</th>
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<tr>
<td>298</td>
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<td>323</td>
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<td>348</td>
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amount of anhydrous RuCl₃ was dissolved in 99.8% deuterium oxide (D₂O) to give a concentration of about 0.3 M, and a LiOD solution with a concentration of about 2.8 M was prepared by reacting a 99.9% pure lithium metal with the D₂O. The LiOD solution was added slowly into the RuCl₃ solution until the pH value of the mixture reached 7.0. During the mixing, the RuCl₃ solution was stirred by a magnetic stirring bar. At the pH value of 7.0, the stirring was stopped, and black powders precipitated in a clear LiCl solution. The powders were separated from the LiCl solution by a filter and washed three times in D₂O.

The specific capacitance of the RuO₂₉·xH₂O material was measured by cyclic voltammetry (CV) experiments, in which a three-electrode configuration was employed. A saturated calomel electrode (SCE) was used as a reference electrode, a Pt plate as a counter electrode, and the RuO₂₉·xH₂O electrode as the working electrode. The RuO₂₉·xH₂O electrode was made from RuO₂₉·xH₂O powder mixed with about 5% Teflon binder and then pressed on the Pt mesh. During the CV experiments, the voltage between the working and the reference electrodes was linearly swept at a constant scan rate of \( s \), at the same time, the current \( i \) flowing from the working electrode to the counter one was measured. The capacitance of the working electrode was calculated by the equation \( C_P = i/s \). The specific capacitance is defined as the capacitance per unit weight of the electrode material.

The ²D NMR experiments were carried out on a CMX-400 NMR spectrometer (\( B_0 = 9.4 \) T) operating at a ²D Larmor frequency of 61.5 MHz, equipped with a home-built ²D wideline NMR probe. A standard quadruple echo sequence (i.e. 90°, τ, 90°, τ-acquisition) was used to record the ²D NMR spectra. The echo time \( \tau \) used in the experiments was 30 µs and the 90° pulse length was 3 µs. For each experiment, 128 scans were accumulated with a recycle time of 1 s. All temperatures were controlled within ±1 K. The static ¹H NMR measurements were performed on a Bruker DMX-300 NMR spectrometer (\( B_0 = 7 \) T) with a ¹H Larmor frequency of 300 MHz. The temperatures were controlled within ±0.1 K by a Bruker BVT2000 unit. For each experiment, 8 scans were used for signal averaging with a recycle delay of 2 s.

3. Results and discussion

In order to illustrate the mobility of the water molecules in the RuO₂₉·H₂O material, the ²D NMR spectra of amorphous RuO₂₉·2.82D₂O were obtained at different temperatures, as shown in Fig. 1. At room temperature (i.e. 300 K), a narrow peak with a linewidth of 3 kHz at the half-height is obtained in the center of the spectrum. Such a narrow peak reflects fast motional averaging, indicating fast mobility for the deuterons in the bulk of the material [12,13]. When the temperature is 213 K, the peak becomes broader (~3.5 kHz at the half-height), implying that the mobility of the deuterons slows down slightly. When the temperature reaches 183 K, two resonance signals are superimposed in the spectrum. The peak in the center is further broadened, implying that the mobility of the deuterons decreases, while a broad peak (~200 kHz broad) starts to appear, indicating that some of the deuterons become rigid. At 173 K, the peak in the center becomes broader and smaller, and the broad peak

![Fig. 1. Static ²D NMR spectra of amorphous RuO₂₉·xD₂O (x = 2.82) recorded on a CMX 400 NMR spectrometer at different temperatures.](image-url)
gains in intensity, which means that most of the deuterons are rigid.

A three-cell electrochemical capacitor was made with amorphous RuO$_2$ · $x$H$_2$O powders ($x = 0.769$) as the electrode and 39 wt% sulfuric acid solution as the electrolyte. The capacitor was charged and discharged under constant current at different ambient temperatures. Fig. 2 shows the capacitance as a function of the temperature for the capacitor. As in Fig. 2, the maximum capacitance appears at about 255 K. When the temperature decreases, the measured capacitance steadily becomes lower, which is consistent with the decrease in the mobility of the deuterons at lower temperatures as indicated in Fig. 1. It was found experimentally that the feature of the CV curves of the commercially synthesized RuO$_2$ · $x$H$_2$O and the sol–gel synthesized RuO$_2$ · $x$D$_2$O is very similar, although the latter possesses about 15% lower specific capacitance (unpublished results). It is anticipated that the capacitance could become very small when the temperature reaches 173 K, where most of the deuterons in the bulk material become rigid and do not participate in energy charge storage. Surprisingly, the measured capacitance is low at higher temperature (e.g., >340 K), where the hydrogen in the bulk are supposed to be highly mobile. It is believed that the water content should not be affected when the operating temperature is lower than the annealing temperature (e.g. 408 K for $x = 0.769$) at which the sample was prepared. Thus, the reduced capacitance does not result from the loss of the water. In fact, the mobility of the hydrogen is inversely proportional to the interaction (i.e., the hydrogen bonding) between the water molecules and the RuO$_2$ lattices. Highly mobile water molecules, which allow more protons to participate in the energy charge storage, exhibit a weak hydrogen bonding with the RuO$_2$, while rigid water molecules present a strong hydrogen bonding with the lattices. Therefore, it can be reasonably concluded from Figs. 1 and 2 that the capacitance is associated with the competition between these two antithetical effects resulting from the mobility of the water molecules and their interaction with the RuO$_2$ lattices. The mobility of the water molecules tends to enable the protons to intercalate into the bulk of the material, while their interaction with ruthenium oxides provides a mechanism for retaining the protons with the lattice ultimately resulting in high proton charge density.

Fig. 3 shows the specific capacitance as a function of water content $x$. Crystalline structures of RuO$_2$ · $x$H$_2$O were characterized using an $X$-ray diffractometer. No diffraction peak was obtained for materials annealed at temperatures lower than 428 K (i.e., $x = 0.638$) and the diffraction peaks corresponding to anhydrous RuO$_2$ were observed when the temperature was up to 438 K ($x = 0.586$) (spectra not shown). These peaks became narrower and gained in intensity with further

![Fig. 2. Capacitance of a three-cell electrochemical capacitor made with the RuO$_2$ · $x$H$_2$O ($x = 0.769$) powder as a function of temperature.](image)

![Fig. 3. Specific capacitance of the amorphous RuO$_2$ · $x$H$_2$O samples as a function of water content $x$. The potential in the CV experiments was scanned in the range 1–0 V at a scan rate of 5 mV/s.](image)
increases in the annealing temperatures. These results indicate that the material is in an amorphous phase at the lower annealing temperatures (<428 K). As shown in Fig. 3, the specific capacitance of the RuO$_2$·$x$H$_2$O material increases gradually as the water content decreases from $x = 2.662$ with the maximum value of 730 F/g appearing at $x = 0.847$. After the appearance of anhydrous RuO$_2$ peaks ($x = 0.586$), the specific capacitance decreases rapidly. This observation is consistent with the previous measurement [4]. Obviously, the water content of the RuO$_2$·$x$H$_2$O material is structurally important and plays an active role in energy charge storage.

Fig. 4 shows the static $^1$H NMR spectra of amorphous RuO$_2$·$x$H$_2$O samples at different water contents. Different from a rigid sample where the typical $^1$H linewidth at the half-height is several 10-kHz [14], all spectra here exhibit a relatively narrow resonance (<8 kHz linewidth at half-height), again indicating that the structural water in the RuO$_2$·$x$H$_2$O undergoes fast molecular motion. However, the residual proton–proton dipolar coupling is still strong enough so that the resulting linewidths here are broader than that of the randomly oriented water absorbed in polyimide film [15], implying that the water molecules in the RuO$_2$·$x$H$_2$O interact weakly with the ruthenium oxide. Furthermore, it can be noticed from Fig. 4 that the $^1$H NMR resonance is slightly shifted by the amount of water content, indicating that the local structures of the RuO$_2$·$x$H$_2$O may depend on the water content [11]. Importantly, the $^1$H linewidth is strongly dependent upon the water content, as shown in Fig. 5. At the water content $x = 2.662$, the $^1$H linewidth observed at room temperature (i.e., 300 K) is 3.4 kHz. The $^1$H linewidth becomes broader with less water and reaches its maximum of about 7.8 kHz in the vicinity of $x = 0.7$. When the water content becomes very small (e.g., $x = 0.280$), where some crystalline particles are formed, the $^1$H linewidth is narrow again. A similar linewidth versus water content behaviour can also be observed at 260 K (also shown in Fig. 5). However, the $^1$H linewidth at 260 K is broader than that at 300 K, which indicates the lower mobility of the water molecules and the stronger hydrogen bonding with the ruthenium oxides at the lower temperature. Such a stronger interaction indeed results in the higher capacitance, as shown in Fig. 2.

![Fig. 4. Static $^1$H NMR spectra of amorphous RuO$_2$·$x$H$_2$O samples recorded on a Bruker DMX 300 NMR spectrometer at room temperature (300 K).](image)

![Fig. 5. Linewidths of the $^1$H NMR spectra of the hydrous RuO$_2$·$x$H$_2$O samples at different temperatures as a function of the water content $x$. All the linewidths were measured at the half-height of the corresponding maximum peak intensity. The circles and the squares indicate the $^1$H linewidths at 300 and 260 K, respectively.](image)
An important point to be noted from Figs. 3 and 5 is that the maximum specific capacitance appeared in the vicinity of $x = 0.7$, where the relatively broader $^1$H linewidth is observed. Although there are more protons at $x = 2.662$ available for the intercalation, the water molecules are overwhelmed in the bulk of the material and thus become nearly randomly oriented resulting in narrow $^1$H NMR linewidth [15]. Such mobile water molecules exhibit a very limited interaction with the ruthenium oxide and consequently the specific capacitance becomes low. At a lower water content (e.g., $x = 0.280$), on the other hand, the water molecules are limited to the surface of the crystalline particles and thus the surface interaction areas are effectively reduced, resulting in the reduction in the specific capacitance. In contrast, in the vicinity of $x = 0.7$, the $^1$H NMR linewidth is broader, indicating relatively less proton mobility and a stronger residual proton–proton dipolar interaction. In other words, the water molecules exhibit a relatively stronger interaction with the ruthenium oxides, probably forming intermolecular hydrogen bonds with the ruthenium oxides and thus resulting in the coexistence of the $\text{Ru}^{2+}$, $\text{Ru}^{3+}$, and $\text{Ru}^{4+}$ valency states, which could dramatically change the local structure of $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ [11]. Such a highly disordered structure allows the protons to diffuse easily from one site to the another in the bulk of the material while preserving the relatively strong hydrogen bond between the water molecules and the ruthenium oxides. Thus, the resulting capacitance is greater in the vicinity of $x = 0.7$. Therefore, it is demonstrated once again that such competition between the two antithetical effects resulted from the mobility of the water molecules and their interaction with the ruthenium oxides provides a mechanism for the energy charge storage of the $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ materials. As a result, the specific capacitance can be optimized through the control of the mobility versus the interaction. In fact, by lowering the temperature to 260 K the mobility of the water molecules slows down and their interaction with the ruthenium oxides thus becomes stronger (cf. Fig. 5) leading to the greater capacitance, as shown in Fig. 2. The impurities may also strengthen the interaction between the water molecules and the lattice so as to increase the specific capacitance [9].

4. Conclusion

We have demonstrated here that solid-state $^1$H/$^2$D NMR spectroscopy is a very powerful technique for the characterization of amorphous $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ electrode material with different water contents. To our knowledge, this is the first comprehensive NMR investigation of the amorphous $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ materials, although NMR spectroscopy has been widely used in ionic conductivity materials [16–18]. The variable-temperature $^2$D NMR spectra indicated that the water molecules undergo fast molecular motion even if the temperature is as low as 213 K, while the $^1$H NMR spectra showed that the residual proton–proton dipolar interaction is composition dependent. The latter implies that the interaction (i.e., the hydrogen bonding) between the water molecules and the ruthenium oxides varies with the water content. Based on the electrochemical measurements, it is concluded from the NMR measurements that the specific capacitance (i.e., the maximum charge density) is associated with the competition between the two effects resulting from the mobility of the structural water molecules and their interaction with the ruthenium oxides. The mobility tends to allow the protons to intercalate and diffuse easily into the bulk of the material, while the interaction provides a necessary force to retain the protons with the ruthenium oxides so as to increase proton charge density. The conclusion suggests that the specific capacitance could be optimized through the control of the two antithetical effects from the mobility and the interaction, either by the temperature or by the incorporation of impurities. The impurity effect is currently under investigation in our laboratory. Therefore, this fundamental study describes a quantitative basis for understanding the mechanism of the proton charge storage of amorphous hydrous ruthenium oxides, and would provide a guideline for future development of electrode materials and also for the formulation of analogous materials.
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