Hydrous Ruthenium Oxide Thermally Stabilized by Carbonate Ions

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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 ruthenium oxide ($RuO_2 \cdot nH_2O$) can provide capacitance ranging from 600-800 F g^{-1} after annealing at 150°C.[1] The specific capacitance remarkably decreases after annealing at 200°C. We have developed another method to prepare a hydrous ruthenium oxide from an aqueous solution of $RuCl_3$ by using NH_4HCO_3.[2] The particle size of the hydrous ruthenium oxide decreased with increasing amount of NH_4HCO_3. The electrode with the hydrous ruthenium oxide heated at 250°C for several minutes gave a high specific capacitance of 587 F g^{-1}.[3] It suggests that the hydrous ruthenium oxide prepared by using NH_4HCO_3 is thermally stabilized compared with that prepared by Zheng et. al.

Hydrated ruthenium oxide was prepared following the previous work.[2] Briefly, 15 mL of a 0.067 M $RuCl_3$ solution was reacted with 10 mL of a 0.5 or 2.0 M NH_4HCO_3 solution at 25°C and washed with water. Evolved gases of H_2O and CO_2 during heating process were identified using a TG-MS. The heating rate was 5°C min^{-1}. The specific capacitance was measured by cyclic voltammetry. The as-prepared sample was annealed at 200°C for 24 h and dropped on a GC substrate to prepare the working electrode. 40 μg of the sample was loaded on GC. An aqueous solution of 0.5 M H_2SO_4 was used as the electrolyte.

Figure 1 compares TG-MS data of hydrous ruthenium oxides prepared from the different ratio mixtures of $[NH_4HCO_3]/[RuCl_3]$, *r*. In the case of $r = 20$, a simultaneous evolution of H_2O and CO_2 was observed at about 220°C. It would be due to a decomposition of bicarbonate. In the case of $r = 5$, the evolution temperature of bicarbonate increased to about 250°C and another evolution of only CO_2 was observed at about 450°C. The CO_2 evolution would be due to a decomposition of carbonate. The particle size is 97 nm in diameter in the case of $r = 5$, considerably larger than that of 30 nm in diameter in the case of $r = 20$. Thermally stable carbonate seems to be formed only in larger particles. DTA data shows that the hydrous ruthenium oxide was crystallized with the evolution of CO_2 due to the decomposition of carbonate ions in the particles in the case of $r = 5$.

Figure 2 shows cyclic voltammograms of the two different hydrous ruthenium oxides. In the case of $r = 5$, the high specific capacitance of 630 F g^{-1} was obtained, while in the case of $r = 20$, a specific capacitance was 240 F g^{-1}. The specific surface area of the former (15 m^2 g^{-1}) was smaller than that of the latter (26 m^2 g^{-1}) because of the large particle size. The hydrous ruthenium oxide was thermally stabilized by carbonate ions contained in the particles and gave a high specific capacitance even after annealing at 200°C for 24 h.

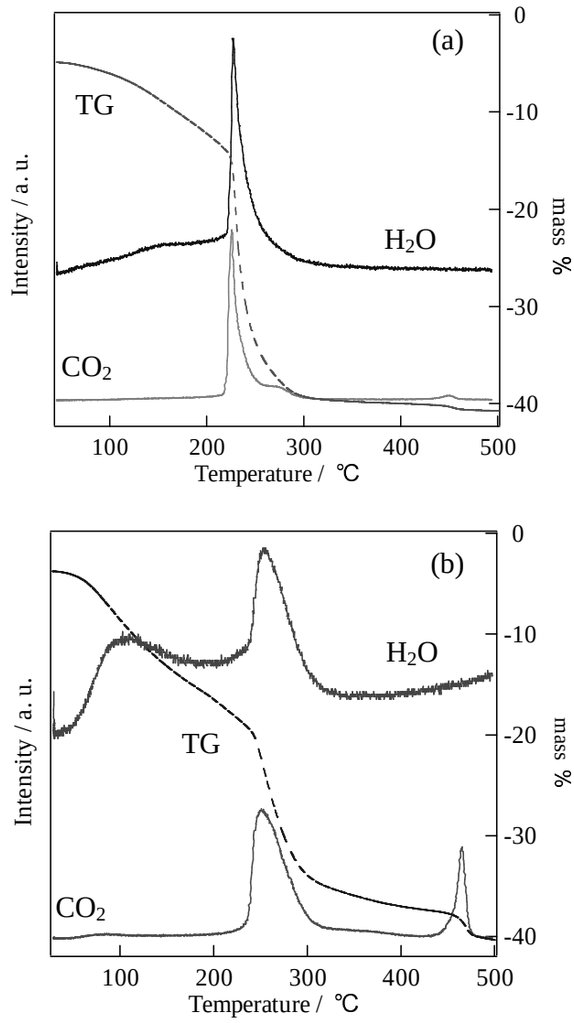

Figure 1 TG-MS data of hydrous ruthenium oxides prepared from the mixtures of (a) $r = 20$ and (b) $r = 5$ ($r = [NH_4HCO_3]/[RuCl_3]$).

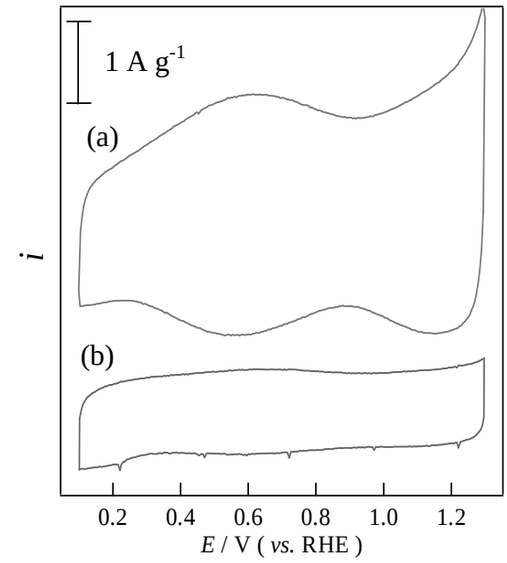

Figure 2 Cyclic voltammograms of hydrous ruthenium oxides prepared from the mixtures of (a) $r = 5$ and (b) $r = 20$ ($r = [NH_4HCO_3]/[RuCl_3]$).

1. J. P. Zheng, P. J. Cyang and T. R. Jow, *J. Electrochem. Soc.*,**142**, 2699 (1995).
2. Y. Murakami, S. Ichikawa and Y. Takasu, *Denki Kagaku*, **65**, 992 (1997).
3. Y. Takasu, Y. Murakami, *Electrochim. Acta*, **45**, 4135 (2000).