THE PROTON INSERTION IN HYDROUS RUTHENIUM OXIDES

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Hydrous ruthenium oxides ($RuO_2.xH_2O$) were found to be able to store more proton than anhydrous ruthenium oxides.[1,2] The proton density in $RuO_2.xH_2O$ was strongly dependent on the structure of the ruthenium oxide and the annealing temperature during the sample preparation. It was found that the $RuO_2.xH_2O$ with the maximum proton density was always obtained at the temperature near the phase transition from amorphous to crystalline.[2,3]

Microstructure of $RuO_2.xH_2O$ was studied by transmission electron microscope (TEM) and selected area electron diffraction (SAED) techniques. Figures 1 shows the TEM image of a chunk of particles from the $RuO_2.0.60H_2O$ sample annealed at 150 ^oC. The maximum value of specific capacitance was obtained from this sample. It can be seen that the $RuO_2.0.60H_2O$ was formed by particles with a size of about 50 nm. Figure 2 shows the SAED pattern from the $RuO_2.0.60H_2O$ sample. The center position of the SAED ring corresponded to the (111) and (020) planes of rutile RuO_2 structure, indicated that the Ru atoms approximately remain at their positions in the rutile unit cell within the particle. It was found that the width of the ring pattern from $RuO_2.0.60H_2O$ was narrower than that from sample prepared at low temperatures. It can be concluded that the $RuO_2.0.60H_2O$ was an amorphous phase; however, became progressively more ordered in local structure than that prepared at low temperatures. Figure 3 shows the SAED pattern from a proton-inserted sample of $RuO(OH).0.60H_2O$. The broadening in SAED pattern indicated that the local order was destroyed by proton insertion.

The ^1H nuclear magnetic resonance spectroscopy at various temperatures was used to study the proton dynamic in $RuO_2.xH_2O$ samples annealed at different temperatures. Figure 4 shows the proton activation energy as a function of sample annealing temperature from theoretical fittings of experimental results. It was found that that the activation energy was highly correlated with the specific capacitance. The minimum value of activation energy 2.47 kJ/mol was obtained from the sample with the maximum specific capacitance.

A model of describing the proton insertion in the bulk of $RuO_2.xH_2O$ has been established based on the proton dynamic and microstructural studies of $RuO_2.xH_2O$. In the model, the structural water and the local structure of $RuO_2.xH_2O$ seem to be extremely crucial for the proton transport. The proton insertion would cause a locally structural change that could only occur in amorphous phase of $RuO_2.xH_2O$. The proton insertion would easily occur in $RuO_2.xH_2O$ that had a local order and less structural water content, because the proton diffusion, as a insertion mechanism, would increase with decreasing the Ru-Ru distance. Therefore, $RuO_2.xH_2O$ sample annealed at 150 ^oC, which contented the lowest structure water in among amorphous phase of $RuO_2.xH_2O$, had the highest specific capacitance.

1. J. P. Zheng and T. R. Jow, *J. Electrochem. Soc.* **142**, L6 (1995).
2. J. P. Zheng, P. J. Cygan and T. R. Jow, *J. Electrochem. Soc.* **142**, 2695 (1995).
3. Y. U. Jeong and A. Manthiram, *Electrochem. and Solid-State Lett.* **3**, 205 (2000).

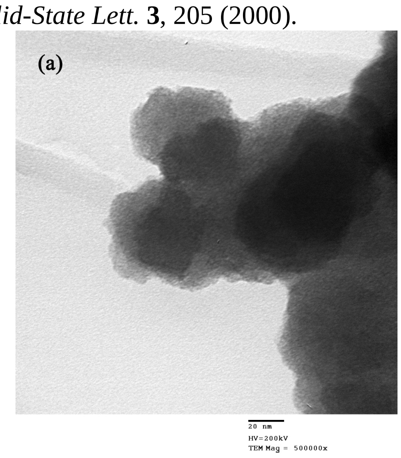

Figure 1 TEM image from the $RuO_2.xH_2O$ sample prepared at 150 ^oC with a magnification of 500k∆.

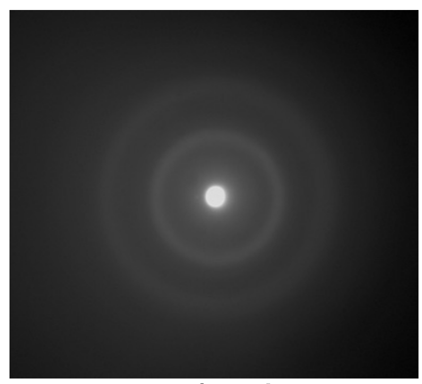

Figure 2 SAED pattern from the $RuO_2.xH_2O$ sample prepared at 150 ^oC.

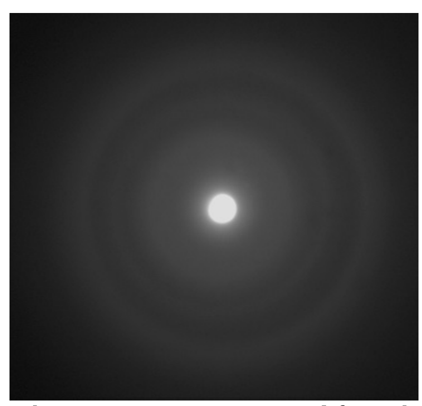

Figure 3 The SAED pattern measured from the proton-inserted $RuO_2.xH_2O$ sample

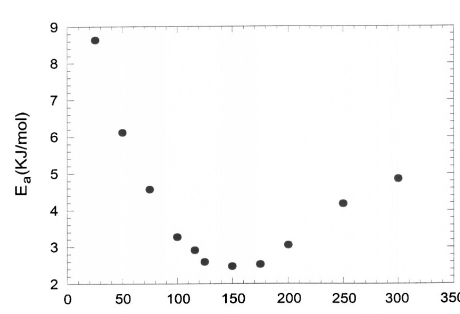

Figure 4 The activation energy of proton in $RuO_2.xH_2O$ samples as a function of the sample annealing temperature.