

Structure-Modification of Ruthenium Oxide

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Owing to the pseudo-capacitive characteristics of oxides, electrochemical capacitors with oxide electrodes, typically ruthenium oxide electrodes¹⁾, have a potential to provide higher energy density than those with activated carbon electrodes. Since ruthenium is an expensive material, it is important to bring out the hidden talent in the oxide by its structure-modification. Several methods attempted by our research group to modify the structure of ruthenium oxide will be presented. Such structure modification can also be applied for the preparation of less-expensive oxides.

1. Synthesis of ruthenium oxide particles by various soft chemistry methods

Various soft chemistry methods, such as sodium ethoxide method²⁾, ammonium carbonate method^{3,4)} and polymerizable complex method⁵⁾ were applied to the synthesis of ultrafine ruthenium oxide particles. In **Fig.1 (a)**, a SEM image of the crystalline RuO₂ nanoparticles prepared by the polymerizable complex method is shown.

2. Synthesis of Ru-based binary oxide particles by soft chemistry methods

Similar methods were adopted to synthesize Ru-Ti-O²⁾, Ru-V-O⁵⁾, Ru-Sn-O⁶⁾ and Ru-Ir-O⁷⁾ binary crystalline oxide particles. The Ru_{0.36}V_{0.64}O₂ oxide particles, shown in **Fig.1 (b)**, provided capacitance of 1220 F per gram of RuO₂ in 0.5 M H₂SO₄ solution.

3. Transformation of RuO₂ into layered structure^{8,9)}

In order to utilize the inner part of ruthenium oxide particles, a layered potassium ruthenate was exposed to proton-exchange through acid treatment to form H_{0.22}RuO_{2.11}·nH₂O (**Fig.2**).

4. Ruthenic acid nanosheets prepared by exfoliation of the layered H_{0.22}RuO_{2.11}·nH₂O

The exfoliation of the layered H_{0.22}RuO_{2.11}·nH₂O to form ruthenic acid nanosheets was carried out through an intercalation-exfoliation process¹⁰⁾. **Figure 3** shows a SEM image of the exfoliated nanosheets. The steady state cyclic voltammograms of the H_{0.22}RuO_{2.11}·nH₂O and the exfoliated nanosheets are shown in **Fig.4**. The specific capacitance of the former and the latter specimens were 390 and 660 F g⁻¹, respectively.

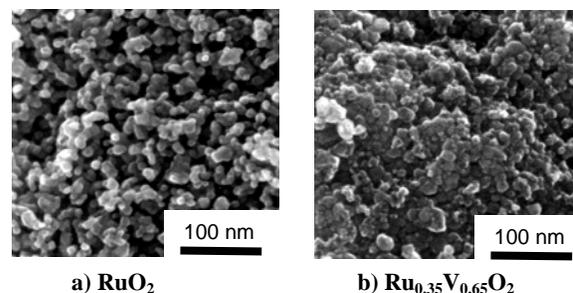
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a) RuO₂ b) Ru_{0.36}V_{0.64}O₂

Fig.1 SEM images of RuO₂ and Ru_{0.36}V_{0.64}O₂ nanoparticles synthesized by the polymerizable complex method.

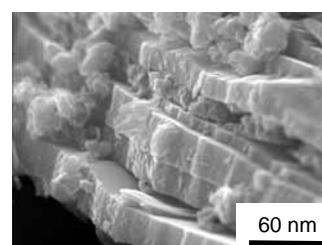


Fig.2 A SEM image of the layered ruthenic acid H_{0.22}RuO_{2.11}·nH₂O.

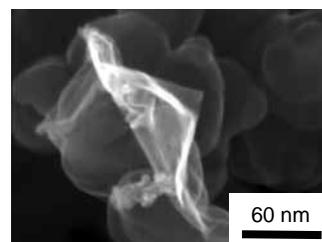


Fig.3 A SEM image of the exfoliated ruthenic acid nanosheets.

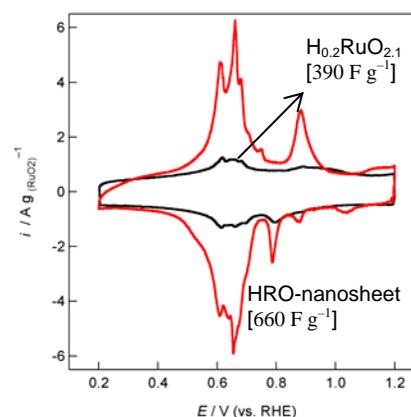


Fig.4 Steady state cyclic voltammograms of the layered ruthenic acid hydrate H_{0.22}RuO_{2.11}·nH₂O (inner CV) and the exfoliated ruthenic acid nanosheets (outer CV) in 0.5 M H₂SO₄.