

**Increasing the surface area of ball-milled RuO<sub>2</sub> electrodes by addition of graphite**

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Electrochemical capacitors (or supercapacitors) are devices using the double layer effect to store electrical energy. Noble metal oxides like RuO<sub>2</sub> and IrO<sub>2</sub>, however, store energy mostly via faradaic reactions than by the double layer effect. Charging and discharging these metal oxide electrode imply a continuity of redox reactions, resulting in a characteristic rectangle-shaped cyclic voltammogram (Figure 1a). To reach high capacitance levels, the material used should offer a very large surface area. Aiming towards smaller particles must therefore be a major concern of electrode material preparation procedures. Preparation of RuO<sub>2</sub> electrode material by ball-milling offer such desired nanoparticles (average size of 15 nm). Unfortunately, the nanocrystals tend to agglomerate to micro-sized clusters, resulting in a severely reduced surface area. In order to increase the surface area available for energy storage, we have investigated different electrode preparations containing RuO<sub>2</sub> and graphite as a dispersing agent.

We prepared our electrode material by ball-milling anhydrous RuO<sub>2</sub> for several hours, followed by a shorter milling step (< 1 hour) of the nanocrystalline RuO<sub>2</sub> with graphite. The powder obtained that way was suspended in a 1:4 Nafion:water solution, and then painted on titanium substrate (geometric area of 2 cm<sup>2</sup>).

SEM-EDX microscopy of these powder showed a good dispersion of RuO<sub>2</sub> clusters over graphite particles. This observation correlates well with the increase in charge for an electrode made with the material, as measured by cyclic voltammetry (Figure 1b). The rectangular shape characteristic of RuO<sub>2</sub> is conserved. X-ray diffraction spectrum of the RuO<sub>2</sub>-graphite powder showed no alteration in RuO<sub>2</sub> structure or in crystallites average size after such short treatment. Longer milling times of RuO<sub>2</sub>-graphite resulted in reduction of the oxide in ruthenium metal. This apparition of Ru(0), which was observed by XRD analysis, was accompanied by a severe loss of charge. An interesting feature of Figure 1 is that for similar material weights, a appreciable increase in current density is observed. When taking into account that the graphite-RuO<sub>2</sub> electrode (dashed line CV on Figure 1) contains only 50% of its weight in RuO<sub>2</sub>, an even higher increase in specific charge arises (Figure 2). To verify that the higher current density is not due to the contribution of graphite charging but to a larger RuO<sub>2</sub> surface area, we subtracted the charge of graphite from the total electrode charge. Results from various graphite loading were then normalized for RuO<sub>2</sub> weight (results presented in Figure 2).

Results of undergoing investigations on different parameters such as the type and duration of ball-milling treatment will also be presented.

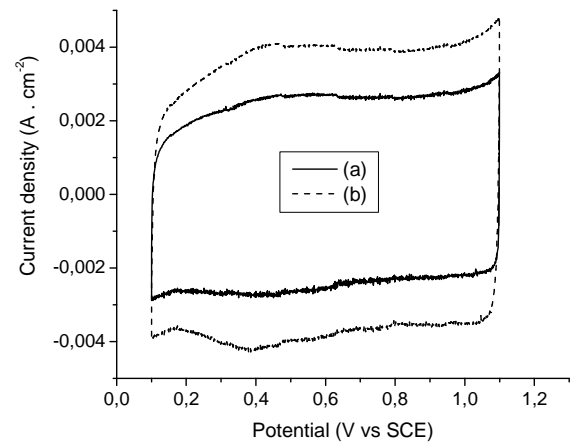


Figure 1. Cyclic voltammograms ( $v = 0.010 \text{ V s}^{-1}$ ) in 1M H<sub>2</sub>SO<sub>4</sub> of (a)-nanocrystalline RuO<sub>2</sub> and (b)-nanocrystalline RuO<sub>2</sub> ball-milled for 0.5 h with 50 % (w/w) graphite.

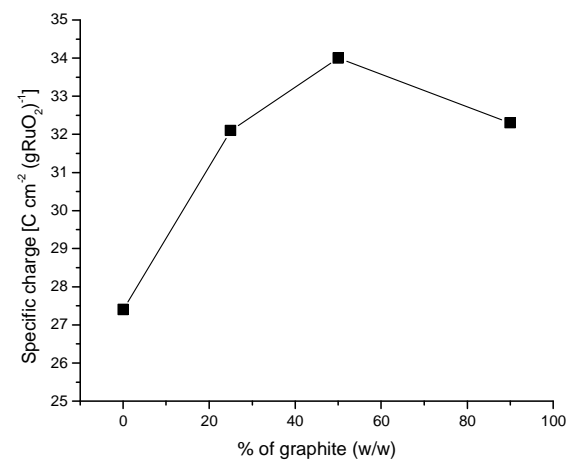


Figure 2. Increase of the specific charge of nanocrystalline RuO<sub>2</sub> ball-milled for 0.5 h with different graphite loading.