The pseudo-capacitance of hydrous RuO_2 accompanied by mass changes

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Pseudocapacitve reaction of ruthenium oxide was investigated by cyclic voltammetry (CV) measurements combined with electrochemical quartz-crystal nanobalance. RuO_2 was synthesized by one-pot microwave assisted hydrothermal method. CV measurements were conducted in H_2SO_4 and Na_2SO_4 solutions. The ruthenium oxide electrode as a working electrode was prepared by drop casting the water suspension of RuO_2 on Au covered quartz electrode. Beside influence of different electrolyte, the effect of thermal treatment of RuO_2 was also investigated since pseudocapacitive behavior of RuO_2 strongly depends on its hydrous form. The obtained results were compared to those of commercial RuO_2. The results indicate that during the redox reaction of RuO_2, various types of charge occur simultaneously. The mass loss or mass gain depends on the specific potential applied and the electrolyte employed.

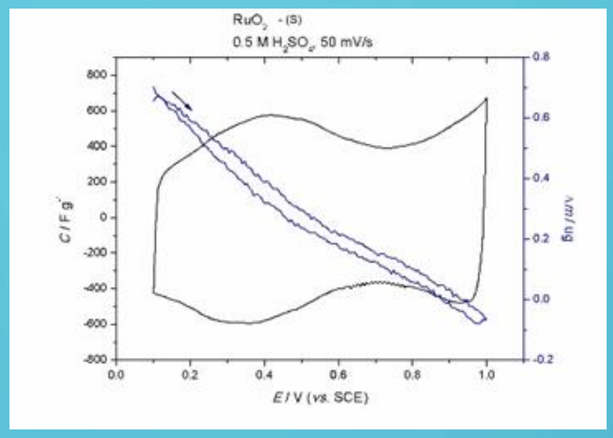

Fig. 1. Simultaneous cyclic voltammogram and cyclic voltmassogram of as-prepared RuO_2 in H_2SO_4.

Synthesis

Hydrated RuO_2 sample was synthesized by microwave (MW) one-step thermal synthesis (Monowave 300, Anton Paar, USA). The precursor was 6.82 mmol dm^{-3} $RuCl_3$ aqueous solution (ruthenium(III) chloride hydrate, 99.98 % trace metal base, Sigma Aldrich). This solution was MW-treated at 200 °C for 5 minutes

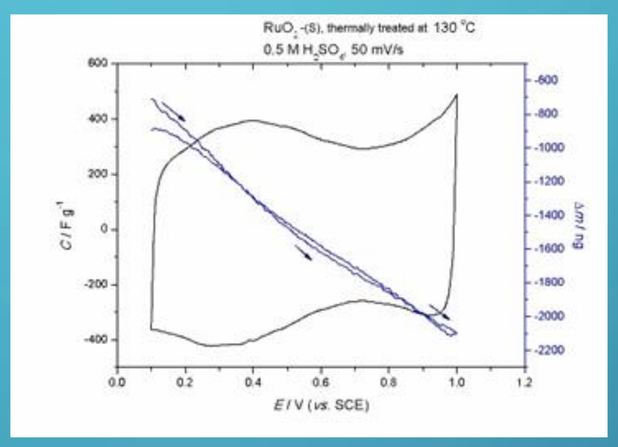

Fig. 2. Simultaneous cyclic voltammogram and cyclic voltmassogram of thermally treated RuO_2 in H_2SO_4

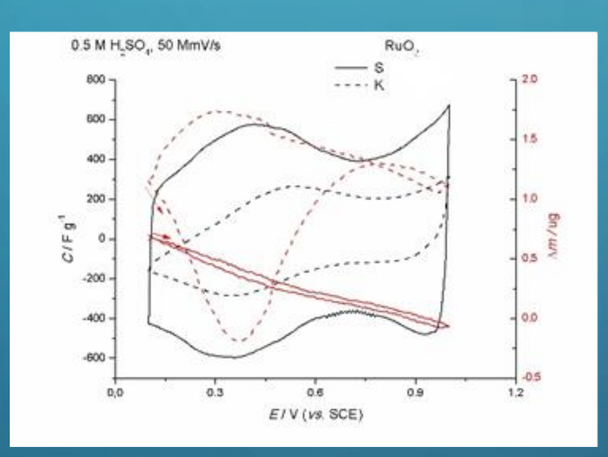

Fig. 3. The comparison of simultaneous cyclic voltammogram and cyclic voltmassogram of commercial and synthetized RuO_2 in H_2SO_4.

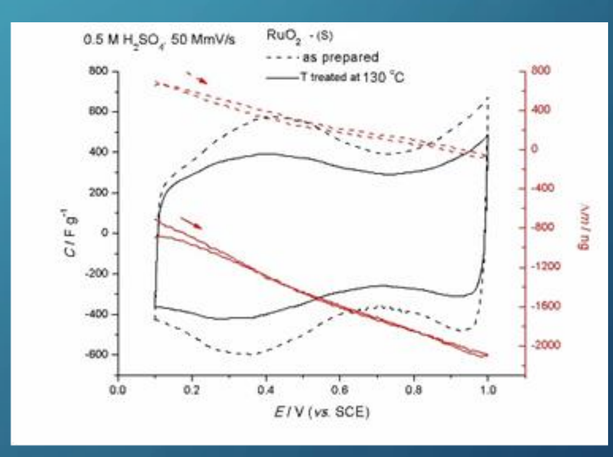

Fig. 4. The comparison of simultaneous cyclic voltammogram and cyclic voltmassogram for both synthetized as prepared and thermally treated RuO_2 in H_2SO_4.

Pseudo-capacitance is a phenomenon that arises in electrochemical capacitors, often referred to as supercapacitors or electrochemical double-layer capacitors. Unlike traditional capacitors that store energy through the separation of charges at the electrode-electrolyte interface, supercapacitors store energy through the reversible faradaic redox reactions occurring at the electrode surface. These reactions are typically associated with the reversible adsorption and desorption of ions from the electrolyte.
It has been a while since the finding that ruthenium (IV) oxide (RuO_2), prepared by thermal decomposition of hydrous $RuCl_3$ at moderate temperatures, below 550 °C, shows an interesting difference in behavior from RuO_2 prepared as a single crystal from vapor-phase. Further discoveries showed that such RuO_2 exhibits capacitive responses over a wide range of potentials, as well as it has exceptionally reversible electrochemical behavior.

In summary, *pseudocapacitance* in hydrous RuO_2 arises from the reversible redox reactions of ruthenium ions in the electrode material. These reactions involve the insertion and extraction of ions from the electrolyte, leading to mass changes in the electrode, both mass loss and mass gain influence the overall process. This behavior contributes to the enhanced energy storage capabilities of supercapacitors utilizing hydrous RuO_2 as an electrode material. Since these processes are rather complex, they shouldn't be described through simple adsorption of protons on the active surface sites.

Acknowledgements

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