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Nanocrystalline Ruthenium Supercapacitor Material

Electrochemical supercapacitors (1) can be power sources for a large range of equipment. They store large quantities of charge and can be repeatedly charged/discharged either quickly or slowly over tens of thousands of cycles. The high energy density is due to an electric double layer, while the rapid charge/discharge ability comes from being made of materials having either rectangular capacitive cyclic voltammograms (CVs) or pseudocapacitive behaviour, such as high surface-area activated carbons or conducting polymers. Both can be used in aqueous or nonaqueous media.

Ruthenium oxide has a very high charge storage capacity when used in aqueous solutions. In attempts to optimise its capacitive properties, prior work has looked at the hydration of Ru oxide, its crystallinity and particle size. As Ru is costly, other elements have often been mixed with it.

Now scientists from the Université du Québec à Montréal, INRS-Energie et Matériaux and Institut de recherche d'Hydro-Québec, Canada, have produced nanocrystalline $Ti_xFe_yRu_zO_n$ powders by ball-milling, and have examined their structures and electrochemical characteristics (P. Soudan, J. Gaudet, D. Guay, D. Bélanger and R. Schulz, *Chem. Mater.*, 2002, 14, (3), 1210–1215). When the O:Ti ratio was > 1 , the Ru atoms were in an hexagonal phase. Electrodes made from the powders had an increase in capacitance from ~ 5 to $\sim 50 \text{ F g}^{-1}$ on cycling in H_2SO_4 or NaOH – due to the growth and modification of a surface layer, $\text{RuO}_2 \cdot x\text{H}_2\text{O}$. When O:Ti < 1 , Ru was in a cubic phase and after cycling or (preferably) leaving the electrode in 1 M NaOH , the maximum capacitance was near 50 to 60 F g^{-1} , also due to the growth and modification of a surface oxide layer.

The Ru material produced by ball-milling had a specific surface area of only a few $\text{m}^2 \text{g}^{-1}$ and agglomerated into larger grains, so reducing the electrochemical surface area. However, a leaching process

(milling the nanocrystalline material with Al, then removing the Al) increased the specific area 10-fold. CVs of this nanocrystalline Ti_2FeRuO_2 in NaOH had 110 F g^{-1} capacitance, even when returned to H_2SO_4 .

It is concluded that the crucial factors for improving the capacitance of Ru-containing materials are: the electrochemical behaviour of the matrices used to dissolve the Ru and preventing the Ru agglomeration.

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3D Platinum Nanoparticle Networks

Assembling nanosized metal particles from their basic components, such as colloids or molecules, into ordered arrays is believed to offer ways of creating new nanostructured materials with properties different to the bulk material. For instance, adding a few hundred atoms or less to electronic or optical devices, allows a single particle to show quantum size effects. A number of nanocrystal superlattices and colloidal networks have already been produced, but the 'bottom-up' preparation of nanoparticles to give three-dimensional (3D) structures remains a challenge.

Now a team in Germany have produced nanostructured metal/organic networks by cross-linking Al-organic-stabilised Pt nanoparticles with bifunctional organic spacer molecules (H. Bönemann, N. Waldöfner, H.-G. Haubold and T. Vad, *Chem. Mater.*, 2002, 14, (3), 1115–1120). Pt particles were formed by reacting Pt(II) acetylacetonate with $\text{Al}(\text{CH}_3)_3$ at 60°C in Ar, forming an air-sensitive Pt colloid with a Pt:Al ratio of $\sim 1:2$. The Pt is thought to be surrounded by a highly reactive protective shell which allows protonolytic chemical reactions to occur. The colloidal particles can be cross-linked by bifunctional alcohols. Incorporating spacer molecules increases the interparticle distance. This method may thus form the basis for preparing highly ordered networks.