Nanocomposites based on conducting polymers, preparation, characterization and applications

Vezető polimer nanokompozitok előállítása, jellemzése és alkalmazása

Kutatási pályázat (K 71771, 2008.04.01 – 2012.04.30) zárójelentése

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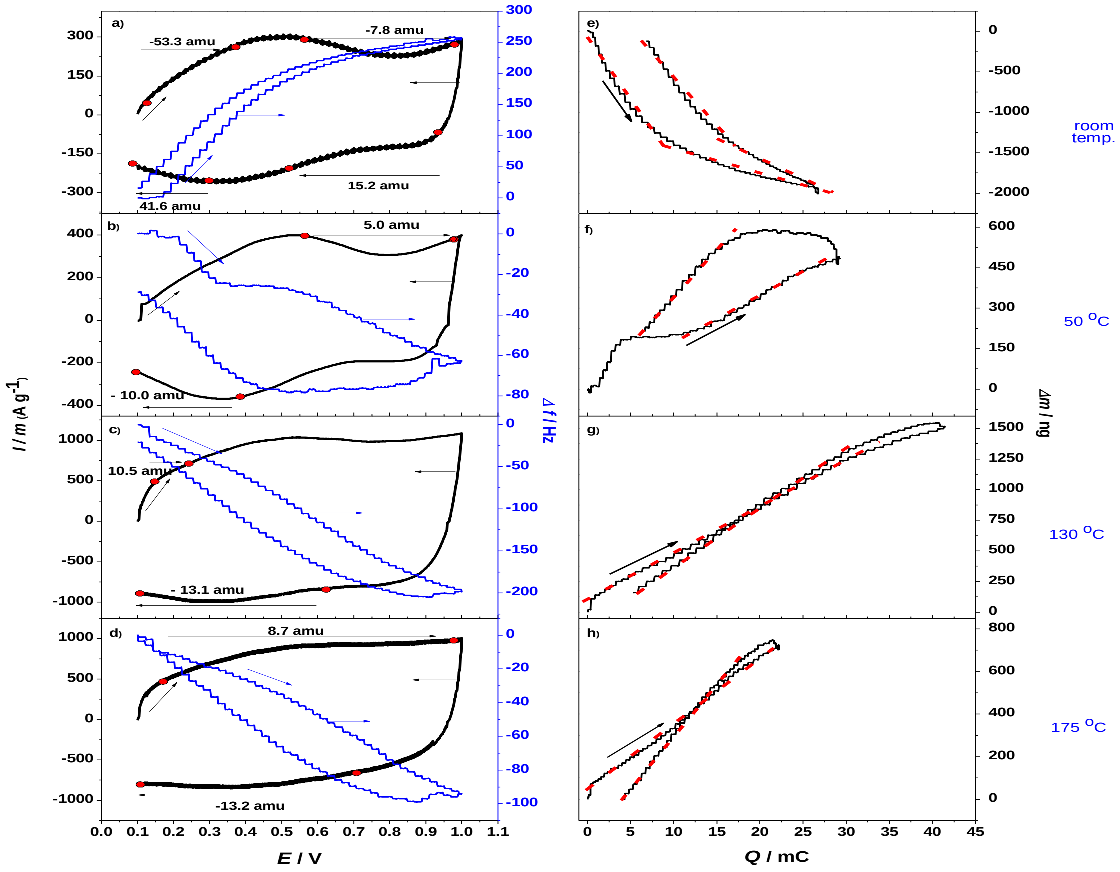
According to the main goals of the present project we have prepared several composites including nanocomposites based on conducting polymers and inorganic compounds. The characterization of the new materials and the individual components has been carried out by electrochemical quartz crystal nanobalance, rotating disk-ring electrode, impedance spectroscopy, atomic force microscopy and scanning electron microscopy. Their catalytic activity and supercapacitor behavior have been tested in polymer membrane fuel cells (PEMFcs) designed and fabricated in the PI's laboratory.
The results obtained in the period of 2008-2012 have been published in different leading journals of the field (Electrochimica Acta, Journal of Solid State Electrochemistry, Journal of Power Sources, Electrochemistry Communications etc.). The project leader and his students have taken part at 11 conferences with 24 presentations. The PI has published several books and book chapters during this period, among others on the Conducting Polymers, Springer (2008 and 2nd edn. 2012, the latter one was extended by an extensive discussion on composites). The composites have been utilized in two vehicles (HYGO and HYGO 2.0), which won the prizes (The most Innovative Vehicle, 1st Prize of Prototype in both years as well as the Honda Prize in 2009) at the competition of alternatively driven vehicles called 5th and 6th Széchenyi race in Győr in 2009 and 2010, respectively. The two Ph.D. students, A. Róka and Á. Kriston, whose names have been mentioned in the original proposal, have defended their Ph.D. thesis in 2010 and 2012, respectively. 3 BSc students (Á. Csorbai, Á. Nemes, A. Székely) and 1 MSc (B. Berkes) defended their diploma work. They also won several prizes at the students' conferences (OTDK). Zs. Pröhle (BSc), Nemes (MSc), Berkes (PhD) and Kriston (postdoc) still have been working on this project. The co-operation with Croatian colleagues (M. Kraljic-Rokovic, S. Sopsic, Z.Mandic, E. Bura-Nakic, and I. Ciglenecki-Jusic) under the framework of TéT projects has resulted in 5 papers. It should be mentioned that Kraljic-Rokovic and Bura-Nakic also have defended their Ph.D. theses in a large extent based on the common research.

Some highlights of the research

New recognitions concerning RuO_2 supercapacitors

Despite its apparently monotonous cyclic voltammetry behaviour, the pseudocapacitive reaction of hydrous ruthenium oxide is a complex reaction consisting of two different Faradaic reactions superimposed on the double-layer capacitance. First Faradaic reaction, described as double proton-electron exchange reaction, is favoured in acid media and at lower anodic potentials. It proceeds with the mass release resulting in the EQCN resonant frequency increase during the anodic sweep. Another Faradaic reaction is described as a dissociative adsorption of water and proceeds with the incorporation of oxygen atom into the structure of ruthenium oxide leading to the mass gain and EQCN resonant frequency decrease. The latter reaction takes place predominantly in neutral media and at higher anodic potentials. The overall frequency changes depend on the relative contribution of these reactions in the total pseudocapacitance. The contribution is affected by the electrolyte used, temperature pre-treatment and potential window.

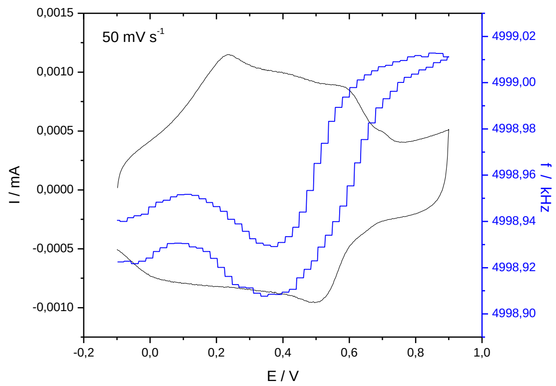
The importance of electronic resistance on the pseudocapacitive reaction is also demonstrated. It was confirmed that optimization of water content and inter-particle electronic resistance is achieved at temperatures around 150 °C. As a consequence of the optimization, the specific capacitances as high as 1500 F/g are obtained with Au/RuO_2 electrode.



Cyclic voltammograms and quartz crystal resonant frequency change, (e)-(h) mass change vs. charge plots for Au/RuO_2 electrodes annealed at different temperatures indicated on graphs. Electrolyte: 1 M H_2SO_4, scan rate: 200 mVs^{-1}

RuO_2 – polyaniline (PANI) composites

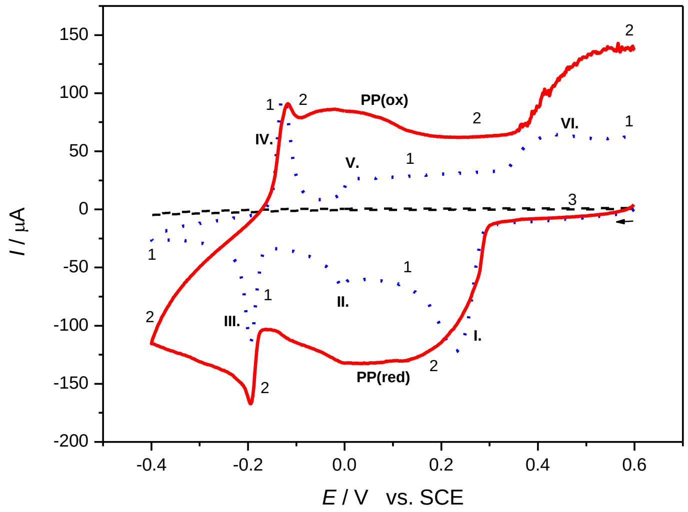
A new method has been suggested to prepare RuO_2 – polyaniline (PANI) composite electrodes for supercapacitor purposes. The protocol is based on the reaction between Ru (IV) sites of the RuO_2 attached to the electrode surface and aniline added to an acid solution . The Ru sites that had been reduced due to the reaction have been regenerated by application short positive potential pulses which can be executed as many times as necessary in order to achieve the desirable RuO_2 – PANI ratio in the composites. In this way the working potential range and the capacitance of the supercapacitors can be extended. Furthermore, the stability problem, which a serious hindrance in respect to the application of conducting polymers in supercapacitors, can be overcomed since this system shows a remarkable long-term stability. It is remarkable that in these composites the electrochemical activity of polyaniline is preserved even at higher pH values.



Cyclic voltammogram and the simultaneously obtained EQCN frequency curve of a Au / RuO_2 + PANI electrode. Electrolyte: 0.5 M H_2SO_4. Scan rate: 50 mV s^{-1}.

(Polypyrrole)$_x$(RuCl$_3$)$_y$ nanocomposites

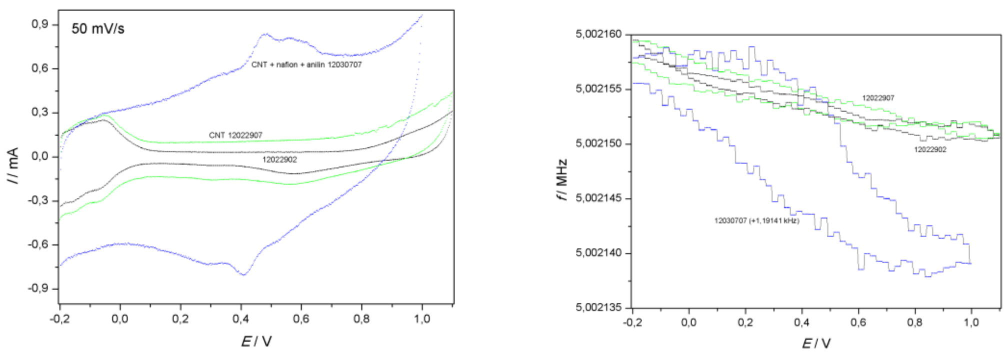
Nanocomposites were prepared by in situ redox intercalative polymerization method, in which α-$RuCl_3$ microcrystals were soaked in pyrrole. Polypyrrole (PP) was formed as a result of the intercalation of pyrrole into the layered structure of $RuCl_3$ crystal and the reaction between pyrrole and the host material. The appearance of polypyrrole was proven by infrared spectroscopy. The redox behavior of the composite shows the electrochemical transformations of both the polypyrrole and $RuCl_3$. The redox waves of PP are similar to those observed for very thin PP films. It attests that the response is originated from monolayer-like PP film situated between $RuCl_3$ layers. The transport of the charge-compensating ions reflects the variation of the oxidation states of both PP and $RuCl_3$. The nanocomposites behave as self-doped layers in the potential region when both constituents are charged.



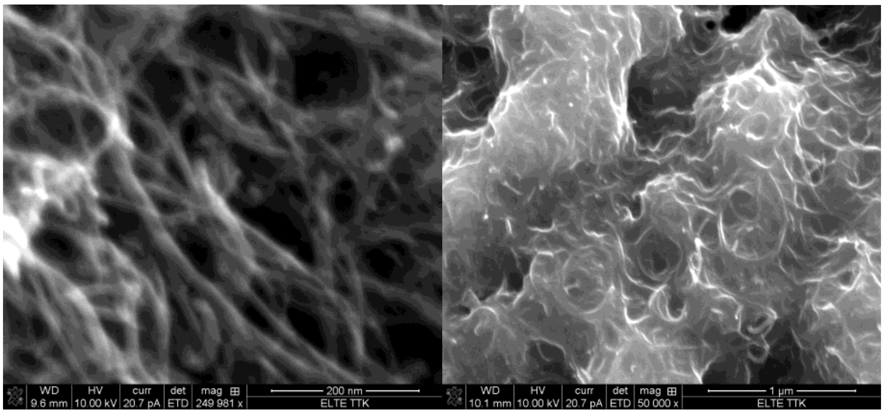
Cyclic voltammograms of $RuCl_3$ (1), PP- $RuCl_3$ nanocomposite (2) and the background current (3). Electrolyte: 0.5 M NaCl. Scan rate: 20 mVs^{-1}.

Polyaniline - double-walled carbon nanotubes (DWCNT) composites

Preliminary studies have been carried out with these systems that gave very promising results



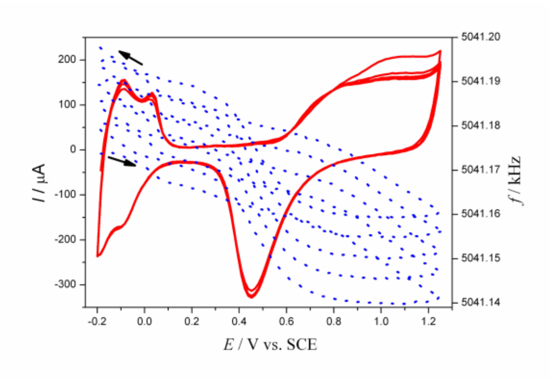
Demonstration of the increase of the capacitance. Comparison of the cyclic voltammograms and the respective EQCN responses of platinum, Pt+DWCNT and Pt+DWCNT+polyaniline. Electrolyte: 0.5 M H_2SO_4.



SEM pictures of DWCNT+Polyaniline and DWCNT+Polyaniline+Nafion

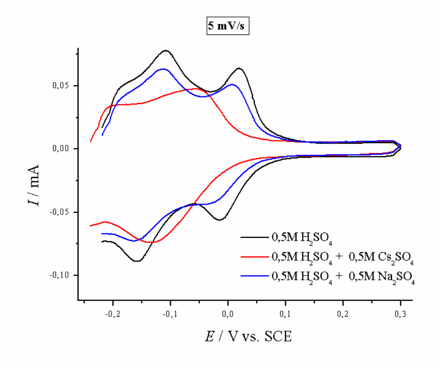
Investigation of platinum electrodes

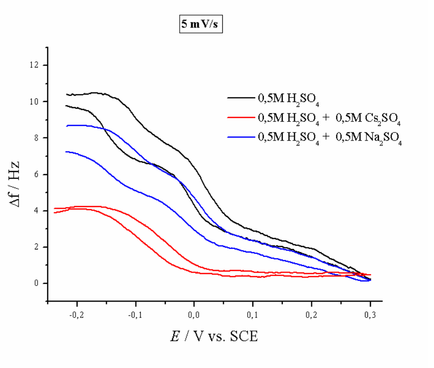
Platinum and platinized platinum electrodes have been studied in order to explain some unusual phenomena observed concerning the Pt catalysts in fuel cells at elevated temperatures. The most interesting discovery was the “cathodic” dissolution of platinum.



While the cyclic voltammograms do not change in the course of consecutive cycling, the EQCN frequency change clearly attests the mass decrease, which occurs during the reduction of platinum oxides.

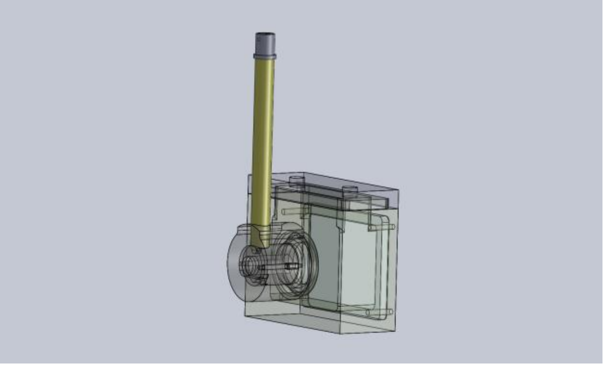
Another new phenomenon observed was the specific adsorption of Cs^+ ions on Pt.





The cyclic voltammograms and the EQCN frequency changes show the specific adsorption of Cs^{+} ions.

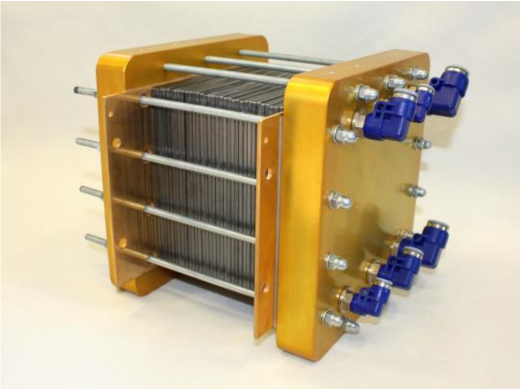
Improvement of techniques of investigation



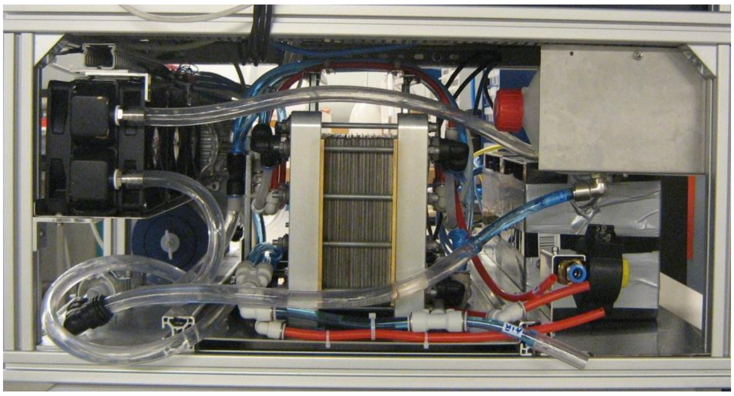
Cell for combined EQCN and spectroelectrochemical measurements was designed and applied.

Construction and testing of the new materials in fuel cells

Membrane electrode assembly "Ink" containing the catalyst



A PEMFC stack assembled in our laboratory The FC test station



The whole FC modul system in the HYGO. Other units: air compressor, water circulating pump, hydrogen valves, pressure transformer, controlling units and sensors

The HYGO 2.0 at the Széchenyi race in 2010.

The dissemination of the knowledge accumulated for the specialists and the general public

Beside the lectures at conferences and the papers published in scientific journals many lectures have been delivered and papers published in order to inform the general public concerning the importance of this research including our achievements. The PI has participated at several programs in different media. A long interview appeared in the Researcher of the Month section of the OTKA Magazin, as well. The different recognitions (ISE Fellow 2009, Széchenyi Prize 2011, Szilárd Leo Professorship 2011) of the PI provided also good opportunities for the dissemination of the results.