EXTENDED ABSTRACT

Supercapacitive characteristics of electrochemically active porous materials§

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Abstract: The results of an investigation of the capacitive characteristics of sol––gel-processed titanium- and carbon-supported electrochemically active noble metal oxides, as representatives of porous electrode materials, are presented in the lecture. The capacitive properties of these materials were correlated to their composition, the preparation conditions of the oxides and coatings, the properties of the carbon support and to the composition of the electrolyte. The results of the electrochemical test methods, cyclic voltammetry and electrochemical impedance spectroscopy, were employed to resolve the possible physical structures of the mentioned porous materials, which are governed by the controlled conditions of the preparation of the oxide by the sol–gel process.

Keywords: porous electrodes; sol–gel procedure; oxide sols; supercapacitors; dimensionally stable electrodes.

High surface area porous materials, applied as electrodes in many electrochemical processes and in energy-storage devices, are comprehended as so-called quasi-3D electrochemical systems.[1] Opposed to planar smooth electrode surfaces, the electrochemical and capacitive properties of porous electrodes are characteristic functions of their morphology and physical structure.[2] Due to the ever--growing interest for the investigation of dispersed Pt-based electrocatalysts[3–5] and electrochemical supercapacitors[1,6] of highly extended surfaces, it is extremely important to develop powerful tools which model in detail the applicative behavior of disperse electrodes, taking into account their physical state.[7–9]

Carbon black[10] supercapacitors and carbon black-supported noble metal oxides pseudo-supercapacitors, as well as porous coatings, consisting of noble metal

oxides on activated titanium anodes are typical examples of porous electrochemical systems. It is known that the capacitive properties of these materials are strongly influenced by the real surface area, porosity and particle size and distribution, due not only to diffusion limitations of the pseudocapacitive redox transitions but also to the difficult double layer charging/discharging transients at the inner surfaces of the porous material.[1,11–13] Electrocatalytic activity and electrolytic stability of titanium anodes activated by sol–gel processed RuO_2–TiO_2 in chlorine and oxygen evolution were found to be sensitive to particle size and distribution owing to so-called geometric factor, related to real surface area changes.[14–16] The above-mentioned structure-related electrochemical characteristics of porous electrode materials emerge if they are subjected to a time-dependent input signal – the electrode potential, in most cases. Hence, a variety of information related to porous electrode system can be obtained using the methods of cyclic voltammetry (CV), with changeable potential ramp input signal, and electrochemical impedance spectroscopy (EIS), with a sinusoidal potential signal of adjustable frequency.

In this lecture, a survey of the results of an investigation of the capacitive properties of carbon blacks (CB) and two types of RuO_2-based porous materials is presented. Two commercial CBs, with a near 10-fold difference in BET surface area, and the from them obtained C/RuO_2 composite materials (first type of RuO_2-based porous materials), with different particle sizes of the sol–gel processed RuO_2, were investigated as supercapacitive materials in the form of a thin layer over an appropriate current collector. The influence of the amount of Ti-supported RuO_2 coating (second type of RuO_2-based porous materials) on its capacitive properties in H_2SO_4 and NaCl solution was examined for RuO_2 coatings prepared by an alkoxide ink procedure.

For all the investigated porous materials, the capacitive response can be interpreted by a layer (coating) in-depth distribution of the capacitance. From CV measurements, the response of the external layer (coating) surface, directly exposed to the bulk electrolyte, and the internal one, exposed to the electrolyte only through the pores, can be resolved. More detailed in-depth capacitance profiling is available from EIS measurements, since these materials were found to be electrically equivalent to the transmission line circuit.[1] This electrical circuit comprises n parallel branches with $R_{p,n}$ and C_n, being the pore resistance and associated capacitance, respectively, in series in each branch. In comparison to CV data, EIS profiling offers refined distributions of R_p and C with respect to the layer (coating) depth, qualitatively reflected through the value of n. An analysis of the capacitance in-depth profile thus aids in resolving whether a certain porous electrode would be suitable for a certain electrochemical process and/or charging/discharging regime.

The results for the CBs showed that the larger surface area the internal surface is less available for charging/discharging processes. In the case of CBs with

a surface area of the order of 1000 $m^2 g^{-1}$, the internal surface participates almost 90 % to the overall capacitive response, while for low surface area CBs (several hundreds of $m^2 g^{-1}$), this participation is below 50 %. Analysis of the EIS data by fitting to the transmission line model showed that high surface area CBs, as a rule, require higher n values than low surface area ones. In addition, the EIS data indicated that the pore resistance increases by up to two orders of magnitude in going from the external towards the internal surface (from the first to the nth branch of transmission line).

Depending on the particle size of the oxide, CB-supported RuO_2 composite supercapacitors can behave twofold. In the case of small oxide particles combined with a high surface area CB, the total layer capacitance could be even smaller than that of the pure CB. The detailed in-depth capacitance profile by EIS indicates the hindered response of the internal CB surface, since small oxide particles block the pores required for the electrolyte to penetrate to the internal surface of the CB, which appears not to be impregnated by the oxide due to steric difficulties. The oxide pseudocapacitance superimposed on the CB double layer capacitance is not high enough to replace the capacitance of the blocked internal surface. However, if the oxide particle size is greater, the pores become partially unblocked, which manifests itself as an increase in the capacitance of the composite with respect to the CB-supported small oxide particles, due to the contribution of the internal surface of the CB. Similar observations also hold for composites involving a low surface area CB but, in this case, the composite capacitance is considerably higher in comparison to the CB, irrespective of the particle size of the oxide.

A similar behavior was also registered for RuO_2 coatings on Ti prepared by the alkoxide ink procedure.[17] A thick coating required a higher n value than a thin one, hence a more refined capacitance in-depth distribution was obtained for the thick coating. Additionally, the distribution was dependent on the composition of the electrolyte; a higher n value was required for a NaCl solution of rather high concentration than for a 1.0 M H_2SO_4 solution. This effect can be explained by the different ion mobility in electrolytes of different composition and concentration, bearing in mind the diffusion limitation of oxide redox transitions, as well as the slow response of the ions to a fast perturbation of the input charging/discharging signal.

Generally, an increase in surface area and a decrease in the particle size of electroactive porous materials (for composites, these features are not straightforwardly interconnected!) should lead to an improvement of the electrochemical characteristics, but the regime in which the material is to operate should be considered carefully.

И З В О Д

СУПЕРКОНДЕНЗАТОРСКЕ КАРАКТЕРИСТИКЕ ЕЛЕКТРОХЕМИЈСКИ АКТИВНИХ ПОРОЗНИХ МАТЕРИЈАЛА

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У оквиру предавања су приказани резултати испитивања капацитивних карактеристика електрохемијски активних превлака оксида племенитих метала формираних на титанском носачу и композитних угљенично–оксидних материјала као најчешћих типова планарних порозних електрода. Капацитивна својства ових електрода испитивана су у функцији њиховог састава, услова под којима су добијени оксиди и превлаке, карактеристика угљеничног носача и састава електролита, методама цикличне волтаметрије и спектроскопије електрохемијске импеданције. Резултати електрохемијских метода корелисани су са могућом структуром ових материјала коју дефинише контолисани процес добијања оксида сол–гел поступком.

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