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INTERFACIAL REDOX PHENOMENA IN HYBRID AQUEOUS SUPERCAPACITORS

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Abstract

Electrochemical capacitors are excellent devices for power demands but they suffer from low energy density. Specific energy of electrochemical capacitors might be improved by operational voltage increase and certainly carbon electrode has remarkable impact on it. Recent studies confirm that positive and negative electrode should reveal different textural properties, oxygen content and pore size distribution.

Our investigations performed for negative electrode have demonstrated that the voltage range of this electrode might be shifted towards hydrogen evolution potential and even easily exceeding this value. It is noteworthy that the interactions between the electrode and electrosorbed hydrogen are the strongest in case of 6 mol/L KOH solution. Hydrogen stored *in statu nascendi* in the ultramicropores of the activated carbon keeps the potential of the electrode in deep cathodic region and allows reaching a higher voltage of the total system. Additionally, faradaic type of electrochemical storage permits to benefit from additional capacitance of the electrode (ca. 30% prior to initial value). More detailed investigations were focused on the influence of carbon microstructure on self-discharge of the electrode (loss of electrosorbed hydrogen) – preliminary results confirmed that electrode should be polarized closely to the hydrogen evolution potential, and there is no direct influence of carbon porosity on the overpotential value. Probably in the cathodic reductive conditions, oxygen content in the electrode did not affect remarkably the electrode performance.

Typical oxidative working conditions of positive electrode resulted in a fast aggravation of the electrode material and significant capacitance fade in alkaline, neutral and acidic electrolyte, whatever type, especially for electrode with relatively high oxygen and micropore content. Briefly, the lowest overpotential of oxygen evolution (ca. 120 mV) was recorded in acidic electrolyte (1 mol/L H₂SO₄) for carbon with major contribution of micropores, specific surface area of 2500 m²/g and ca. 4% of oxygen. In order to avoid electrolyte decomposition and to improve electrode potential window, several electrolytes with redox activity (e.g. based on iodides, vanadium or cerium) have been investigated. Results obtained suggest that redox activity of aforementioned species shifts the oxygen evolution potential towards higher value and prevents capacitance fade during cycling. The most recent studies suggest that electrolyte for positive electrode should retain the pH value during operation; in this case, the electrochemical response is sensitive for oxygen functionalities which might influence the pH value directly on the electrode/electrolyte interface.

Full physicochemical characterization of carbon materials, i.e., specific surface area and porosity measurements by nitrogen adsorption, type of functionalities by thermogravimetry coupled with mass spectrometry or by potentiometric titration with pK_a distribution as well as by Raman spectroscopy allowed elucidating the electrochemical performance.

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