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Carbide Derived Carbon as a support for Pt and Pt-Ru nanocluster activated catalysts

Enn Lust, Eneli Härk, Kersti Vaarmets, Jaak Nerut,
Silver Sepp, Jaanus Eskusson, Indrek Tallo, Heisi Kurig,
Thomas Thomberg, Vahur Steinberg

Institute of Chemistry, University of Tartu
Ravila 14 A, Tartu, 50304, Estonia

Carbide derived carbons (CDC) are interesting micro-meso-porous materials with tunable total porosity and variable ratios of micopores and mesopores volumes and areas. These materials have been used in high power density supercapacitors based on non-aqueous electrolytes and room-temperature ionic liquids [1,2]. The wide region of ideal polarizability (up to 3.6 V) has been demonstrated. CDC have superior electrchemical stability in Na_2SO_4 and other neutral aqueous electrolyte solutions (up to 2.0 V) due to the very low concentration of oxygen containing functional groups and defect amorphous surface areas [3].

This paper analyses the behaviour of different ordered micro-meso-porous Mo_2C, TiC and WC derived carbon supported catalysts as possible cathodes for polymer electrolyte membrane fuel cell (PEMFC) [4,5]. CDC with different specific surface area up to 2000 m^2g^{-1} have been prepared at synthesis temperatures from 600 to 1100^{o}C using chlorination method [1-3]. Pt and Pt-Ru alloy catalysts have been deposited onto CDC with high dispersion (particle size from 1.5 to 2.1 nm for Pt-Ru and from 5.0 to 8.0 nm for Pt, loading from 10 wt.% to 20wt.%). Analysis of X-ray diffraction, X-ray fluorescence, high-resolution transmission electron microscopy, X-ray photoelectron and energy-dispersive X-ray spectroscopy data confirms that Pt-Ru alloy has been formed and the atomic fraction of Ru in the alloy varies from 0.43 to 0.46. The Pt-Pt and Pt-Ru interatomic distances have been calculated (being shorter for Pt nanoclasters than that for Pt-Ru alloy). HRTEM, EELS, EDX and XRF data confirmed that the Pt-CDC or Pt-Ru-CDC catalysts are clean and there is no contaminants (raw Co_2C, TiC or WC, Cl-containing components or Cl_2 inside CDC under study.

Cyclic voltammetry and rotating disc electrode data show that high cathodic oxygen reduction current densities (up to -180 A m^{-2} at 3000 rev min^{-1}, calculated per flat cross-section surface area) have been achieved in 0.5 M H_2SO_4 solution and in 1.0 or 0.1 M $HClO_4$ even higher current densities have been demonstrated. The behaviour of the Pt and Pt-Ru catalysts has been determined by mixed kinetic processes within the electrode potential range from 0.1 V to 0.3 V vs. MSE (mercury | mercury sulfate reference electrode) and the diffusion within the range from 0.1 V to -0.35 V vs. MSE. It was found that the porosity of a support has noticeable influence on the oxygen electroreduction half-way potential as well as on the hydrogen evolution overpotential. The half-way potential somewhat depends on the ratio of micropores and mesopores in CDC. The number of electrons transferred per electroreduction of one O_2 molecule (~4) at Pt-CDC, calculated from Levich plots, is in a good agreement with literature data. Analysis of impedance spectra indicates that for Pt-CDC and Pt-Ru-CDC (similarly to Ru/RuO_2 system in H_2SO_4 aqueous solution) pseudocapacitive behaviour has been observed at very low *ac* frequencies, that could be explained by very quick cathodic and very slow electrical double layer formation processes caused by adsorption of reaction intermediates or reaction products at/inside porous Pt-CDC and Pt-Ru-CDC catalysts. The surface blocking effect depends strongly on the pore size distribution and specific surface area of CDC. Very high series and parallel capacitance values (~200 F g^{-1}) have been established at -0.51 V vs. MSE, attractive for hybrid aqueous supercapacitor applications. The parallel and series capacitance values depend on the total porosity, pore size distribution as well as on the ratio of micropore and mesopore areas (volumes) of CDC.

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