

Micromesoporous VC and WC derived carbons supported catalysts as cathodes for polymer electrolyte membrane fuel cells in sulfuric and perchloric acid solutions

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VC and WC have been used as raw material for synthesis of micromesoporous carbons (CDC) with exact pore size distribution. It has been recognized that, depending on the heat-treatment temperatures different CDCs exhibit tunable properties, such as surface area, porosity, electrical conductivity and cathodic oxygen electroreduction activity [1-3]. Intensive research has focused on the development of electrocatalyst for the oxygen electroreduction reaction (ORR) because in a PEM fuel cell, the major limit on performance is the slow kinetics of the cathodic oxygen electroreduction [4-8]. The main aim of this work was to investigate the behavior of the micromesoporous carbon supports, prepared from VC or WC using chlorination process (noted as C(VC) and C(WC)) at various temperatures as electrocatalysts for the ORR [1-3] and to analyze ORR kinetics in sulfuric and perchloric acid solutions.

CDCs with very high specific surface area have been prepared using chlorination method. Gas adsorption at liquid nitrogen temperature was used for the porosity analysis of materials and results were as follows: C(WC) 1100°C or C(VC) 900°C with specific surface area 1580 m²g⁻¹ and 1348 m²g⁻¹, respectively.

The electrochemical measurements were carried out in a three-electrode electrochemical cell. Electrochemical characteristics for unmodified and modified micromesoporous carbons have been studied by cyclic voltammetry (CV), rotating disc electrode (RDE) as well as electrochemical impedance (EIS) methods have been established. For ac impedance measurements a potentiostat Autolab PGSTAT 100 with FRA was used. Potentials were measured against Hg|Hg₂SO₄, K₂SO₄ (saturated) reference electrode (MSE). Cyclic voltammograms and RDE data were measured at rotation rates from 0 to 3000 rpm ($v=10 \text{ mV}\cdot\text{s}^{-1}$) and in the region of potentials from +0.3 to -0.6 V vs. MSE.

Electrochemical data for unmodified micromesoporous C(VC) and C(WC) electrodes show that the rate of ORR noticeable depends on the porous structure of carbon electrode, i.e. mainly on the micro/meso porosity and specific surface area of electrode under study. Cyclic voltammetry and rotating disc electrode data show that high cathodic oxygen reduction current densities have been achieved in 0.5 M sulfuric acid aqueous solution.

Pt and Pt-Ru alloy catalysts were deposited onto CDC with high dispersion, and particle size being approximately 2.1 nm for Pt-Ru and 7.4 nm for Pt at loading of 10 wt.% or 20wt.%, respectively. Analysis of X-ray diffraction, X-ray fluorescence, high-resolution transmission electron microscopy, X-ray photoelectron, scanning electron microscopy with energy-dispersive X-ray spectroscopy data confirms that Pt-Ru alloy has been formed and the atomic fraction of Ru in the alloy is ~0.43.

The behavior 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. Hg/Hg₂SO₄ reference electrode (MSE) and the diffusion current plateaus within the range from 0.1 V to -0.35 V vs. MSE. Analysis of impedance spectra indicates that for

Pt-CDC and Pt-Ru-CDC, similarly to Ru/RuO₂ system in sulfuric acid aqueous solution, pseudocapacitive behavior has been observed at very low ac frequencies, explained by very quick cathodic and very slow electrical double layer formation processes caused by adsorption of reaction intermediates at/inside micromesoporous Pt-CDC and Pt-Ru-CDC catalysts. Very high series and parallel capacitance values ~200 F g⁻¹ have been established at -0.51 V vs. MSE.

Main findings can be summarised as:

- ✓ The Pt-Ru alloying causes a noticeable decrease of the lattice parameter.
- ✓ The scanning electron microscopy with energy-dispersive X-ray spectroscopy studies show that the materials with highly porous structure have been formed and Pt as well as Pt-Ru nanoclusters have been deposited into/onto C(VC) and C(WC) carbon supports quite uniformly.
- ✓ The j_k values noticeably depend on the material studied and very high j_k values have been obtained for Pt-Ru-CDC and Pt-CDC nanocluster materials, in comparison with corresponding data for unmodified CDC electrode.
- ✓ The characteristic time constant for catalyst under study increases along the series: Pt-CDC < CDC < Pt-Ru-CDC.
- ✓ Very high series and parallel capacitance values have been established for carbide derived carbon supports modified with Pt and Pt-Ru catalysts.

Mentioned findings make these investigated materials attractive for applications in hybrid aqueous supercapacitors and as cathodes for polymer electrolyte membrane fuel cells.

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