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MODIFICATION OF CARBON SUPPORTS FOR PROMOTION THE OXYGEN REDUCTION REACTION OVER SPINEL ELECTROCATALYSTS

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Introduction

Rapid development of energy consumption combined with a growing ecological consciousness has promoted a wide-ranging search for eco-friendly energy sources. Design and synthesis of highly efficient electrocatalysts to facilitate sluggish 4 electron oxygen reduction reaction (ORR) is, therefore, a key issue in the context of full commercialization of fuel cells[1]. Transition metal oxides of spinel structure represent a promising group of potential catalysts that may substitute the widely used Pt based materials[2]. Due to low electrical conductivity and tendency to undesired aggregation of spinel nanoparticles it is important to support them on appropriate carbon carriers. Modification of the carbon lattice with heteroelements (HE) or/and incorporation of oxygen-containing functionalities onto the carbon surface are regarded as an efficient method to enhance the interaction of nanoparticles with the support, improving the electrical conductivity thereby. Simultaneous inclusion of two HE (for example N and S) drastically change the carbon frame structure in order to form more active sites as well as to modify electronic properties of those sites[3]. Our research focus on determination of the influence of the carbon supports modification on the catalytic activity and on the ORR mechanism catalyzed by nanometric mixed spinel with a different chemical composition (Co, Mn, Fe).

Materials and Methods

The obtained catalysts are based on manganese-cobalt and iron-cobalt spinels, supported on mesoporous carbon matrix simultaneously doped with HE, such as nitrogen and sulphur or modified multiwall carbon nanotubes (MWCNTs). For preparation of mesoporous HE-doped carbons, the hard-template method, in the presence of the heteroelements precursors, was used. Mn-Co and Fe-Co oxides were synthesized by the microwave assisted hydrothermal route and deposited on the synthetized carbon carriers according to the previously described method[2]. The MWCNT were modified by nitric acid and oxygen plasma. The catalytic properties of well-characterized materials were studied by rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) methods.

Results and Discussion

The spinel structure was confirmed by XRD and Raman spectroscopy measurements. The average crystallite size estimated by Debye–Scherrer formula was ~8 nm. Due to the complex nature of the Raman spectra of carbon, a deconvolution into individual components was performed. The obtained results, based on the I_{D3}/I_G ratio, show that modification of the mesoporous carbon support by nitrogen (2.6 wt%) and sulphur (1.4 wt%) improved their crystallinity. The catalytic performance of spinel catalysts was found to depend strongly on

properties of carbon supports. As can be seen in Figure 1 the onset potential (E_{onset} defined as the potential at which a current density of 0.1 mA cm^{-2} is generated) of the CMK-1(NS) supported catalysts exhibits positive shift compared to the non-modified mesoporous carbon matrix. The number of electrons (*n*) as determined by RRDE was equal to 3.72 for Mn-Co/CMK-1(NS) and 3.64 for Fe-Co/CMK-1(NS), indicating that the ORR proceeds mostly by desired 4-electrons pathway.

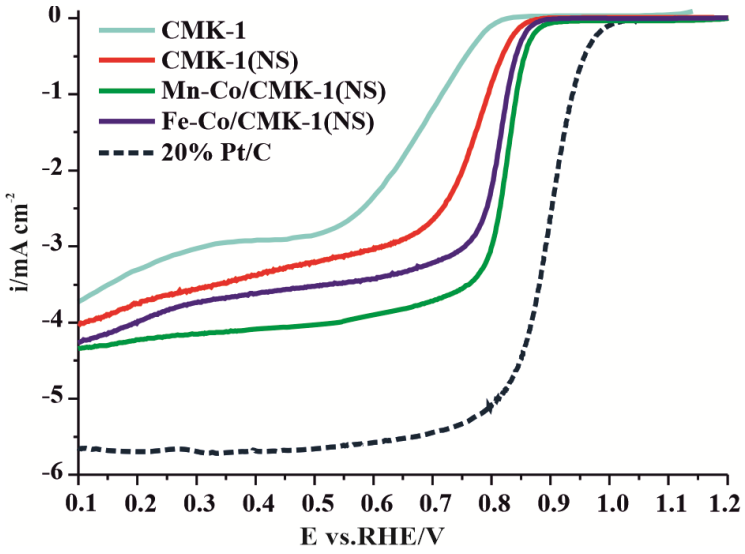

Figure 1. LSV curves of spinel catalysts deposited on N, S-doped mesoporous carbon support in O_2-saturated 0.1 M KOH solution recorded at 1600 rpm.

Conclusions

The catalytic performance of spinel catalysts was found to depend strongly on both the spinel composition and the nanocrystal morphology as well as on the chemical nature of the carbon supports. Modification of the mesoporous carbon lattice by the incorporation of nitrogen and sulphur led to enhancement of the crystallinity of the carrier, which improves the ORR activity and selectivity towards the desired $4e^-$ dioxygen reduction.

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