Temperature Study on Zr-Oxides for the ORR in DMFCs

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A major prerequisite for large-scale commercialization of polymer electrolyte fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) is a significant reduction and, ultimately, replacement of platinum as cathode catalyst material for the oxygen reduction reaction (ORR). However, no alternative catalysts like Pt alloys with transition metals, Pt-free catalysts, or even non-noble-metal catalysts have yet emerged from the research stage. Major constraints in the use of non-noble metals are the required activity towards the ORR, stability in the acidic environment of a PEMFC and – for oxides – electronic conductivity. For the application in DMFCs, cathode catalysts additionally require tolerance towards methanol, as typically a considerable amount of methanol permeates through the proton-exchange membrane. Most non-noble metals and most of their oxides are immediately ruled out due to these constraints, and even Pt shows serious dissolution effects in a PEMFC cathode [1]. However, during the last years, group 4 and 5 metal oxide-based materials have emerged as possible ORR catalysts (e.g., [2]).

In this work, a system of zirconium-oxide nanoparticles supported on Ketjen-Black carbon (ZrO_2/KB) is studied. The synthesis route makes use of organo-metallic precursors, obtaining particles of sizes below 10 nm. These are morphologically analyzed using XRD, SEM, TEM, and chemical analyses. Electrochemical measurements are performed from 20 to 60°C in a rotating disk electrode (RDE) set-up and from 50 to 120°C in a small-scale single-cell PEMFC, respectively. From these measurements, conclusions about the intrinsic catalytic activity towards the ORR can be drawn, showing that carbon-supported ZrO_2 exhibits activity for the oxygen electroreduction. This had already been shown for sputtered valve metal oxides at 30°C [3]. The temperature dependence of the ORR activity demonstrates an Arrhenius behavior for both the studied ZrO_2/KB and the Pt-Black reference system. Additionally, in the RDE configuration, methanol tolerance is studied in the range from 20 to 60°C via introducing methanol (5 mmol/l) into the high-purity perchloric acid during ORR experiments.

Figure 1a) and b) show the ORR activity obtained from RDE experiments, normalized either by the mass loading of the respective electrode (Fig. 1a) or by the catalyst surface area (Fig. 1b). In the latter case, the Pt-Black surface area was determined by the charge for hydrogen underpotential deposition from cyclic voltammograms in Ar; for ZrO_2/KB, the particle size distribution of ZrO_2 was obtained from TEM micrographs, from which their specific surface area was calculated assuming spherical particles, as described in Ref. [1] and neglecting the surface of KB, which is justified by its minimal catalytic activity (Fig. 1b); finally, for non-catalyzed KB-carbon, the specific surface area was obtained from BET measurements (≈ 830 m^2/g_{carbon} [4]). From Figure 1, a clear indication for the ORR activity of 12% ZrO_2/KB is given. Correction for mass transport is neglected comparing the specific current of ZrO_2/KB of Fig. 1b) to the one of Pt-Black at a current of -10 $\mu A/cm^2_{cat.surface}$ (ZrO_2/KB < 25, Pt-Black < 5 % correction). Here, the potential difference is less than 500 mV. A variation of operating temperature can reveal the activation energies at constant overpotential and therefore the behavior of the intrinsic catalytic ORR activity of the ZrO_2/KB compared to Pt-black over a broad temperature range (20 to 120°C).

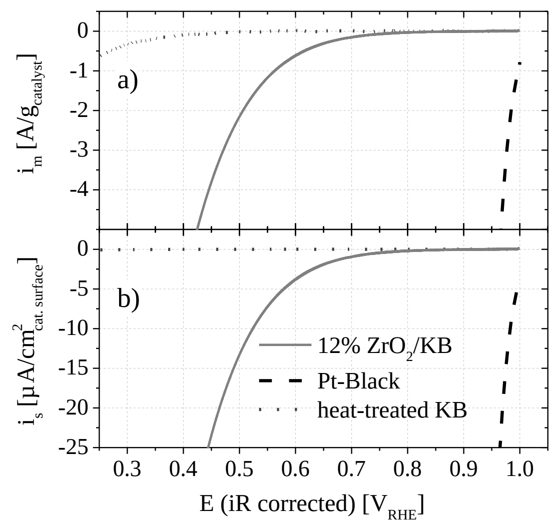

Figure 1: Curves for the ORR obtained by RDE in 0.1 M $HClO_4$ at 20°C, 1600 rpm and 5 mV/s without diffusion correction. ORR currents are obtained by subtracting capacitive currents (in Ar) from the measured currents in O_2. The electrode loading was 71 $\mu g_{KB}/cm^2$ for both KB and 12% ZrO_2/KB, and 50 $\mu g_{Pt}/cm^2$ for Pt-Black (Nafion loading:20 $\mu g_{Nafion}/cm^2$). ORR currents normalized to a) catalyst mass; and, b) surface area of the respective catalyst.

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