

Application of Tin Oxide-based Support Materials for Durable Cathode Catalysts in PEFCs

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Catalyst support materials used for oxygen reduction reaction (ORR) in polymer electrolyte fuel cells (PEFCs) needs to be able to withstand harsh conditions like strong oxidizing environment and potentials as high as 1.5 V (1). Therefore, materials with higher electrochemical stability than state-of-the-art carbon blacks are investigated for application as support for Pt catalysts (2). In this contribution we will report on the electrochemical properties of tin oxide as support and Pt-supported on tin oxide ORR catalysts with different loadings of Pt.

To investigate the potential of tin oxide as support material we prepared model thin film electrodes by reactive magnetron sputtering on glassy carbon discs. Material properties of thin oxide films are characterized by X-ray photo electron spectroscopy (XPS), X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM). Cyclic voltammetry (CV) in acidic electrolyte was used to investigate electrochemical properties of the oxide support. Different loadings of Pt are deposited by magnetron sputtering on the tin oxide supports. The activity of the tin oxide supported Pt model catalysts is analyzed by rotating ring disc electrode (RRDE) measurements. Additionally, tin oxide powders are synthesized by a modified sol-gel method to determine the electrochemical stability.

Reactive magnetron sputtering using slightly different Ar-O₂ partial pressures followed by a heat treatment in Argon results in tin dioxides samples with different characteristics. XRD analysis indicates that both SnO₂ samples possess a cassiterite crystal structure, but one shows a [110] preferential orientation which indicates differences in surface stoichiometry. Indeed, XPS analysis reveals different Sn-O surface compositions depending on the orientation of the crystal structure. For SnO₂ with [110] preferential orientation a stoichiometric SnO₂ surface composition is found (named oxidized SnO₂ hereafter). For the SnO₂ with typical cassiterite crystal structure an understoichiometric (close to SnO) surface composition is present (named understoichiometric SnO₂ hereafter) (3).

Cyclic voltammograms of both supports in the potential range from 0-1 V vs. RHE (0.1 M HClO₄) show mainly double layer charging. Only the understoichiometric SnO₂ shows a redox couple at about 0.4 V for the surface oxidation of Sn²⁺ to Sn⁴⁺. Potential cycling in the given potential range (100 cycles) shows nearly no change in charge for both supports, suggesting good stability under given conditions. Different loadings between 1 µg/cm² to 10 µg/cm² Pt were deposited on both kinds of SnO₂ supports to obtain isolated Pt particles at low loadings up to Pt thin films at higher loadings. Isolated Pt particles have diameters in the range of 2-3 nm.

To ensure comparable results all Pt/SnO₂ catalysts were activated by potential cycling between 0.05-1.20 V vs. RHE (50 mV/s, 0.1 M HClO₄). In general, all CVs of the activated model catalysts show the typical Pt features. RRDE measurements to analyze the

ORR activity are performed for all Pt/SnO₂ catalysts by recording polarization curves between 1.0-0.0V at 5 mV/s for different rotation rates between 400-2500 rpm in O₂-saturated electrolyte, resulting in the typical curves expected for the ORR on Pt and supported Pt-catalysts. At potentials below 0.1 V the oxygen reduction current decreases concomitant with an increase of the H₂O₂ formation currents determined on the ring electrode. The H₂O₂ formation below 0.1 V for Pt catalysts supported on understoichiometric SnO₂ is about 10% whereas for Pt on the oxidized SnO₂ 15-22% are found.

For the kinetic analysis Tafel plots are derived from the ORR polarization curves for all Pt/SnO₂ catalysts. To compare the activity of the different model catalysts kinetic currents i_{kin} were taken at 0.9 V. In general, i_{kin} values increase with increasing Pt loading but i_{kin} values for the Pt supported on understoichiometric SnO₂ are doubled compared to those for Pt deposited on oxidized SnO₂ pointing to a strong effect of the different electronic environments on both oxidic supports.

Besides model electrodes, doped-tin oxide nanopowders are prepared by a modified sol-gel method, showing a surface area of $60 \pm 10 \text{ m}^2\text{g}^{-1}$. For the electrochemical characterization, thin porous films are prepared by spin-coating of a cathode ink made by the oxide nano-powders and an organic binder on glassy carbon discs. Cyclic voltammetry measurements are carried out to evaluate the oxide electrochemical stability in acid media and towards applied potential up to 1.6 V. On the porous oxide thin films, Pt nanoparticles are deposited by magnetron sputtering and cyclic voltammetry and RRDE measurements are performed on the Pt/oxides system to evaluate their electrochemical stability and activity towards ORR.

In summary, the Pt/oxide systems show improved stability compared to state-of-the-art Pt supported on carbon blacks as well as comparable or improved activity towards ORR, demonstrating the feasibility and the benefits in developing such new generation of catalyst systems.

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References

1. A. Rabis, P. Rodriguez, T.J. Schmidt, *ACS Catalysis* **2**, 864 (2012).
2. K. Sasaki, F. Takasaki, Z. Noda, S. Hayashi, Y. Shiratori, K. Ito, *ECS Transactions* **33**, 473 (2010).
3. A. Rabis, E. Fabbri, A. Foelske, M. Horisberger, R. Koetz, T.J. Schmidt, *ECS Transactions* **50**, accepted