Pt/Magnetic Fe Oxide Nanoparticles for ORR Electrocatalysis Synthesized by Gas-Diffusion Electrocrystallization (GDEx)

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The oxygen reduction reaction (ORR) is the most common cathodic reaction in fuel cells, and while Pt is the best catalyst for the ORR, it is very expensive. One of the strategies to overcome this issue is to reduce the Pt loading while maintaining or increasing the electrocatalytic activity. Supporting Pt nanoparticles (Pt NPs) on carbon materials is the most applied strategy for this purpose. However, carbon is susceptible to corrosion during fuel cell operation, leading to the detachment and aggregation of Pt NPs and loss of activity.[1] Metal oxides are a more stable alternative due to their inertness in harsh oxidative environments. Besides, metal oxides can also promote the ORR by enhancing the Pt NP dispersion, increasing Pt stability and resistance to poising. Reducible metal oxides (i.e., TiO_2, CeO_2, Fe_3O_4) can also form strong metal-support interactions with Pt.[2] For instance, in Pt NPs, supported on magnetic iron oxides (Fe_2O_3, Fe_3O_4), the charge transfer from Fe atoms to Pt atoms facilitates the adsorption of O_2 and the dissociation of the O=O bond, and the desorption of OH* from Pt sites enhancing the ORR activity.[3]

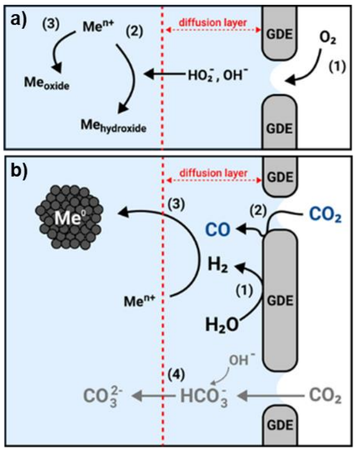

Fig. 1. Schematic illustration of the GDEx process. a) O_2-GDEx, b) CO_2-GDEx.

We recently reported an electrochemical method called gas-diffusion electrocrystallization (GDEx) for synthesizing metal-based NPs. In GDEx, reactive species are produced by reducing a gas in an electrochemical cell using a gas diffusion electrode as a cathode. These species react with metal ions in solution to produce NPs. The nature of the NPs depends on the nature of the reactive species. When O_2 is reduced (O_2-GDEx, Fig.1a), H_2O_2 and OH^- are produced, and metal (hydro)oxide NPs are formed. If CO_2 is reduced (CO_2-GDEx, Fig. 1b), CO and H_2 are produced, and metallic nanoparticles are synthesized. O_2-GDEx has already been used to synthesize magnetic Fe oxides, Mn-Co oxides and hydroxides and Zn-Cu hydroxychloride compounds,[4] while the synthesis of noble metals (Pt, Pd, Rh) has been performed using CO_2-GDEx.[5] This work combines both methods to synthesize Pt supported on Fe oxides (a mixture of Fe_2O_3 and Fe_3O_4) NPs. Using solutions containing Fe^{2+} and Pt^{4+} ions, iron oxide nanoparticle agglomerates were first synthesized using O_2-GDEx. Next, the feeding gas was changed to CO_2, and the reduction of Pt^{4+} ions was carried out using CO_2-GDEx to produce Pt/magnetic Fe oxide nanomaterials. The iron oxide nanoparticle agglomerates serve as a support for the Pt nanoparticles produced. The materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The Fe^{2+}/Fe^{3+} ratio was determined by $KMnO_4$ titration. The electrocatalytic activity towards ORR was evaluated in alkaline media, as Fe oxides are unstable in acidic conditions.

Overall, the GDEx process has shown to be a versatile technology for the synthesis of catalytic Pt materials for ORR with improved catalytic activity and stability and lower Pt loading than benchmark materials.

References:

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