Oxygen Electroreduction in Alkaline Media on Pd/C Catalysts
Prepared by Electrodeposition on Various Carbon Nanomaterials

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There have been multitude of studies on trying to enhance the electrocatalytic activity and stability of Pd-based catalysts for the oxygen reduction reaction (ORR) [1]. In this work surfactant free Pd/C catalysts were prepared by electrodeposition. Deposition was carried out by applying potential steps between -0.25 (or 0) and 0.85 V vs SCE to electrochemically deposit Pd on various carbon nanomaterials (carbon nanotubes, graphene nanosheets, graphene nanoplatelets and Vulcan carbon black; designated as CNT, GNS, GNP, CB, respectively). The obtained catalysts were characterised using cyclic voltammetry and the rotating disc electrode method in alkaline solution. Furthermore, catalysts were studied with scanning electron microscopy (SEM). Deposition of Pd was carried out in 1 mM H₂PdCl₄ and 0.05 M H₂SO₄ solution stepping between aforementioned potentials with step durations of 250 ms and 3 s respectively with 500 iterations.

Deposited Pd electroactive surface area varied greatly depending on the support material, with CNTs deposited at higher overpotential showed Pd surface areas of 0.19 cm² and GNS 1.17 cm². Particles on the surface of CNTs were agglomerated, and the surface of CNTs was mostly not covered, most of the metal was deposited on the defects and tips of the CNTs. To improve the deposition on the CNT surface an electrochemical activation was used, where the CNTs were cycled between 0.1-1.6 V vs RHE. The activation process improved the electrochemically accessible surface area to 0.4 cm². While the agglomeration remained, more individual Pd particles on the surface could be observed. Another attempt to improve the deposition on the surface of CNTs was to mix CNT with another carbon material. Mixture of GNP and CNT when depositing at higher overpotential showed metal particles deposited on the CNT surface and the material displayed larger electrochemical surface area and higher ORR activity than same materials when studied separately. Similarly, to CNTs activation process was applied, but when depositing on the activated CNT and GNP mixture loss in the electrochemical surface area was observed. Similar loss was also observed when trying to activate GNP separately, which could be due to lowering of the conductivity of the graphene.

While all of the processes improved the specific activity of the CNT based Pd/C catalyst for O₂ reduction it still remained inferior to that of GNS based catalyst. The influence of overpotential showed difference of 1.5-2-fold in electrochemical surface area. For all of the catalysts the ORR proceeded through the 4-electron pathway. Tafel slopes were typical to those reported for carbon-supported Pd nanoparticles.

Reference