Oxygen reduction on AgPd nanocatalysts prepared by galvanic exchange

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In this work galvanic exchange was employed to deposit Pd on silver nanoparticles and nanowires to enhance their electrocatalytic activity towards the oxygen reduction reaction (ORR).[1] The concentration of Pd ions in the exchange bath was varied resulting in four AgPd/C catalyst materials with varied Pd content. Ag nanowires (AgNW, 30 nm diameter, Blue Nano, USA) were exchanged at two different Pd precursor concentrations. Ag nanoparticles were synthesized using silver nitrate with citrate as capping agent and reduced with $NaBH_4$. Varying amounts of Ag/C material was dispersed in 2 mM H_2PdCl_4 solution and insoluble AgCl was removed with 0.2 M NH_4OH solution. Diluted AgNW suspension was pipetted onto GC electrode and the galvanic exchange process and cleaning was carried out directly on the rotating electrode. MP-AES was used to determine the Pd/Ag ratio and metal content in the AgPd/C materials. For AgPd/C the molar ratio of the 4 obtained catalysts varied from 88.5% Ag to 18.1% Ag depending on the exchange bath. TEM studies revealed that the spherical shape was retained only for the highest Ag content and at 79% Ag the particles were hollowed out becoming half-moon shaped. Further lowering the Ag content resulted in destruction of the Ag particles resulting in smaller porous larger particles. Similar effect was also observed on AgPdNW, where hollow nanowires with spherical Pd particles growing on top of the nanowire like structure were observed. XRD studies revealed alloying to some degree as we can observe the blending of Ag(111) and Pd(111) XRD peaks (Figure 1a). During ORR the activity enhancement was observed when comparing with Ag/C catalyst (Figure 1b), however, commercial Pd/C outperformed the AgPd/C counterparts, most likely due to the particle size as the Ag seeds of ~10 nm in diameter were used. Whilst the AgPd alloy did not show improvement in activity, the stability of the prepared catalyst increased resulting in drop of ESCA of only 21% for AgPd/C_2 compared to the 56% of the commercial Pd/C catalyst.

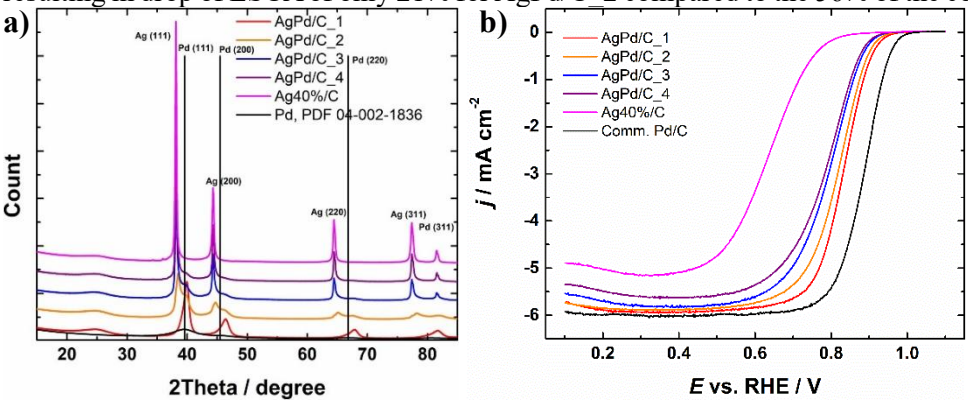

Figure 1. (a) XRD patterns of AgPd/C catalysts. (b) Comparison of ORR results for AgPd/C catalysts in O_2-saturated 0.1 M KOH.

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References

1. M. Lüsi, H. Erikson, H.-M. Piirsoo, J. Aruväli, A. Kikas, V. Kisand, A. Tamm, K. Tammeveski, *Appl. Surf. Sci.* 2023, **636**, 157859.