Identical Location TEM Combined with 3D Tomography of Functionalized Carbon for PEMFC

Yu, K.[1,2], Li, C.[3], Yang, F.[3], Xie, J.[3] and Ferreria, P.[1,2]

[1] TMI-University of Texas at Austin, United States, [2] International Iberian Nanotechnology Laboratory, United States, [3] Mechanical Engineering-Indiana University Purdue University Indianapolis, United States

Proton Exchange Membrane Fuel Cell (PEMFCs) are promising energy conversion devices due to their high energy density, low operating temperature and high efficiency [1]. One of the main obstacles for PEMFC development is the degradation of platinum group metal (PGM) catalysts which consists of Pt or Pt-alloy nanoparticles (i.e. 2-5 nm in diamete) supported on the surface of carbon particles (i.e. 40-60 nm in diameter) during the fuel cell operations. However, the degradation mechanisms of Pt or Pt-alloy nanoparticles are yet a source of debate. In this regard, transmission electron microscopy (TEM) is a powerful tool to provide both direct and indirect evidence to understand the degradation mechanisms of PEMFC.

In this work, Identical Location TEM (IL-TEM) combined with 3D scanning transmission electron microscope (STEM) was used to determine particle size distributions and the morphology of Pt nanoparticles supported on two different kinds of carbons, namely pristine carbon (Vulcan XC72) and NH_2-functionalized carbon (NH_2-functionalized Vulcan XC72).

In non-cycled NH_2-functionalized carbon, the TEM images show that Pt nanoparticles exhibit a more uniform distribution and smaller sizes. Subsequently, gold TEM grids were cycled between 0.6 and 1.0 V (vs hydrogen reduction potential reversible hydrogen electrode (RHE)) in 0.1 HClO4 liquid electrolyte for 1000 cycles. The IL-TEM images revealed that the Pt nanoparticles, as well as the pristine carbon, only suffered minor changes, which matched well with the electrochemical active surface area (ECSA) under Rotation Disk Electrode (RDE) test. On the other hand, the Pt nanoparticles on the NH2-functionalized carbon showed significant changes. From the 2D IL-TEM images, the Pt particles increased in size and agglomerated on the surface of NH_2-functionalized carbon.

To better understand the Pt distributions and morphologies on unfunctionalized and NH_2-functionalized carbon and the changes in carbon shape during durability tests, IL-TEM combined with 3D STEM tomography was obtained. Under these conditions, interparticle distances were compared, which revealed that for the case of NH2-functionalized carbon the changes were more significant. One of the explanations was that Pt nanoparticles were initially attached onto the NH_2 functional groups on the surface of the carbon black, then, these NH_2 functional groups were oxidized, consequently, these Pt nanoparticles lost anchoring points and incline to move around over the carbon surfaces. As the cycling potentials were relative high, the degradation mechanism, Ostwald ripening, would not dominate, rather, the surface migration of nanoparticles over the carbon surface is most likely the dominant mechanism.

In summary, IL-TEM combined with 3D-STEM were used to study the degradation mechanisms of Pt nanoparticles in unfunctionalized and functionalized carbon supports. Although the functionalized carbon showed better initial Pt distribution and higher ECSA, the functionalized groups were oxidized during cycling, leading to the motion of Pt nanoparticles and consequent deterioration of ECSA.

Reference

[1] Kocha, S. S. Principles of MEA preparation. In Handbook of Fuel Cells – Fundamentals, Technology and Applications, ed. 1; Vielstich, W., Lamm, A., Gasteiger, H. A., Eds.; Wiley: Chichester, UK, 2003; Vol.3, 538