Oxygen Evolution on Model Well-Characterised Mass-Selected Nanoparticles of RuOx - DTU Orbit (11/08/2019)

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In recent years, hydrogen production from polymer electrolyte membrane (PEM) electrolysis has attracted increasing interest in the development of a clean/ CO2 free technology for energy storage [1]. The majority of the efficiency losses are at the anode [2], where oxygen is evolved, according to the reaction: 2H2O \rightarrow O2 + 4H+ + 4e-. The most active and widely used catalysts for the oxygen evolution reaction (OER) are RuOx based materials. However, RuOx corrodes under reaction conditions. Moreover, Ru is very expensive and scarce [3]. In the current investigation, we focus on the evaluation of (a) oxygen evolution activity and (b) corrosion of well defined, mass selected Ru nanoparticles as a function of size and shape. We adapt a methodology previously used in our laboratory to study to investigate the oxygen reduction reaction [4]. The size selected electrocatalysts are prepared using an ultra-high-vacuum (UHV) compatible technique where nanoparticles are aggregated in a magnetron sputter source. This technique has distinct advantages, as it results in a high degree of control over critical parameters such as particle size, coverage and density [5]. By investigating such well-defined catalysts, we can improve our understanding of the relationship between catalyst structure and reactivity. The catalysts are formed from a ruthenium target, deposited under vacuum directly onto a glassy carbon or Au(111) electrode and then oxidized in furnace at 400 °C under 1 bar oxygen. The structure and composition are tested ex-situ before and after annealing using X-ray Photoelectron Spectroscopy (XPS), high resolution Transmission Electron Microscopy (HR-TEM) and Scanning Electron Microscopy (SEM). Electrochemical activity and stability are tested ex-situ in a Rotating Ring Disk Electrode set-up [6]. Furthermore, Electrochemical Scanning Tunnelling Microscopy (EC-STM) is used to directly observe the catalyst dissolution under reaction conditions. The EC-STM images are acquired in Ar saturated 0.05 M H2SO4, while the potential is scanned at a scan rate of 2 mV/s. The metallic and pre-oxidized nanoparticles show distinct behaviour from each other, under OER conditions. The metallic nanoparticles disappear from view, as the potential is raised (Figure 1a), due to dissolution, while the pre-oxidised particles (Figure 1b) exhibit no evidence of corrosion in the same potential range. These microscopic data correlate closely with the activity data. The observed activity is significantly higher than the state-of-the-art reported in literature [7], [8]. If this activity could be replicated in an electrolyser, the precious metal loading could be lowered by one order of magnitude. [1] H. Dau, C. Limberg, T. Reier, M. Risch, S. Roggan, and P. Strasser, ChemCatChem, vol. 2, no. 7, pp. 724–761, Jun. 2010. [2] A. Marshall, B. Berresen, G. Hagen, M. Tsyplin, and R. Tunold, Energy, vol. 32, no. 4, pp. 431–436, Apr. 2007. [3] P. C. K. Vesborg and T. F. Jaramillo, RSC Adv., vol. 2, no. 21, p. 7933, 2012. [4] F. J. Perez-Alonso, D. N. McCarthy, A. Nierhoff, P. Hernandez-Fernandez, C. Strebel, I. E. L. Stephens, J. H. Nielsen, and I. Chorkendorff, Angew. Chem. Int. Ed. Engl., vol. 51, no. 19, pp. 4641–3, May 2012. [5] S. Murphy, R. M. Nielsen, C. Strebel, M. Johansson, and J. H. Nielsen, Carbon N. Y., vol. 49, no. 2, pp. 376–385, Feb. 2011. [6] M. Vukovic, J. Chem. Soc. Faraday Trans., vol. 86, no. 22, pp. 3743–3746, 1990. [7] R. Forgie, G. Bugosh, K. C. Neyerlin, Z. Liu, and P. Strasser, Electrochem. Solid-State Lett., vol. 13, no. 4, p. B36, 2010. [8] Y. Lee, J. Suntivich, K. J. May, E. E. Perry, and Y. Shao-horn, J. Phys. Chem C Lett., vol. 3, p. 394, 2012. [Formula]