Development of Non-Platinum Catalysts for Intermediate Temperature Water Electrolysis - DTU Orbit (27/07/2019)

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Water electrolysis is recognized as an efficient energy storage (in the form of hydrogen) supplement in renewable energy production. However, industrial alkaline water electrolyzers are rather ineffective and space requiring for a commercial use in connection with energy storage. The most effective modern water electrolyzers are based on polymeric proton-conducting membrane electrolytes (PEM), e.g. Nafion®, a perfluorocarbon-sulfonic acid polymer. These electrolyzers work at temperatures up to around 80 °C, and, in extreme cases, up to 130-140 °C. The most developed PEM electrolyzers are at the stage of commercial development. However, there is a great challenge for their widespread commercialization: high cost and low abundance of the electrocatalytic materials (Pt, IrO2) and use of Ti or other expensive construction materials. On the cathode side, the most active catalyst is Pt exhibiting the best compromise in metal-hydrogen bond strength1,2. Due to economic reasons there is a huge interest in replacing Pt by cheaper alternatives and much effort have been made in finding novel catalysts for Hydrogen Evolution Reaction (HER)3,4. Many anhydrous proton conductors have been investigated as electrolytes for the intermediate temperature applications, such as CsH2SO4, KHSO45. The most successful systems have been developed with CsH2PO4 (solid acid fuel cells (SAFCs) and Sn0.9In0.1P2O7 electrolytes6,7. While developing materials for the promising medium temperature electrolysis systems it is important to simulate conditions of those presented in the assembled operational electrolyzer. In this work a molten KH2PO4 will be used as an electrolyte while screening performance of various transition metals and their carbides at higher temperature (Figure 1). In this work will be shown that coatings of transition metal carbides not only improve the stability of pure metals but also enhance electrocatalytic efficiency of materials towards HER and Oxygen Evolution Reaction (OER) at intermediate temperatures (Figure 2). The increase of the electrocatalytic activity of tungsten carbide in the electrochemical hydrogen reduction between 120 and 150 °C was recently demonstrated to be several times more intensive than for platinum8. Tests were performed at 260 °C to confirm the reported tendency. As was foreseen, at 260 °C in molten KH2PO4WC demonstrated better performance than Pt as an electrocatalyst for hydrogen evolution reaction (HER) (Figure 3). 1 J.K.. Nørskov et al. J. Electrochem. Soc., 252:J23, 2005. 2 J. Greeley, T.F. Jaramillo, J. Bonde, I. Chorkendorff, J.K. Norskov, Nat. Mater., 5:909-913, 2006. 3 N. Armaroli, V. Balzani ChemSusChem, 4:21-36, 2011. 4 I.E.L. Stephens, I Chorkendorff, Angew. Chem. Int. Ed. 50: 1476-1477, 2011 5 T. Norby, Nature, 410:877-878, 2001. 6 H. Muroyama, K. Katsukawa, T. Matsui, K. Eguchi, J Electrochem Soc, 158(9): B1072-B1075, 2011 7 P. Heo, T. Y. Kim, J. Ha, K. H. Choi, H. Chang, S. Kang, Journal of Power Sources, 198:117–121, 2012. 8 A.V. Nikiforov et al. Int. J. Hydrogen Energy 37:18591–18597, 2012. [Formula]