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Borohydride oxidation reaction mechanisms and poisoning effects on Au, Pt and Pd bulk electrodes: from model (low) to direct borohydride fuel cell operating (high) concentrations.

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Abstract

The borohydride oxidation reaction (BOR) was characterized on the three most-studied noble metals (Au, Pt and Pd) in a range of $NaBH_4$ concentration and temperature that enables to bridge model studies of the BOR (low concentration) to more practical ones, relevant to the direct borohydride fuel cell (DBFC) operation. BOR mechanistic insights were unveiled using the complementary techniques of rotating disk electrode cyclic voltamperometry, rotating ring-disk electrode measurements of the BH_3OH^- production and differential electrochemical mass spectrometry detection of H_2 escape. When the concentration of sodium borohydride are brought to DBFC-like operating conditions, the H_2 escape is more severe and the poisoning effect of the metal surfaces by the BOR intermediates (BH_{ads} or $BH_{3,ads}$) is more significant, and stronger on Pt surfaces compared to Au and Pd ones. Even at high $NaBH_4$ concentrations, Pd exhibits promising BOR kinetics, making of this material an interesting candidate for DBFC anode electrocatalysis. These data enabled to complement our previous kinetic model and to confirm the BH_3 species oxidation pathways for $NaBH_4$ concentrations of 5 mM and 50 mM. However, this model is incomplete for high borohydride concentrations; it does not take into account possible local pH variations and cannot explain the origin of the important reduction currents measured at high potential on the Au ring electrodes. Finally, it is shown that the BOR mechanism at Pd electrodes must take into account PdH formation and oxidation.