Elucidation of adsorption processes at the surface of Pt(331) model electrocatalysts in acidic aqueous media

Abstract:

The Pt(331) surface has long been known to be the most active pure metal electrocatalyst for the oxygen reduction reaction (ORR) in acidic media. Its activity is often higher than those known for the Pt-based alloys towards ORR, being comparable with the most active Pt3Ni(111), Pt3Y or Pt5Gd, and being more active than e.g. polycrystalline Pt3Ni. Multiple active sites at this surface offer adsorption energies which are close to the optimal binding energy with respect to the main ORR intermediates; nevertheless, the exact location of these sites is still not clear. Taking into account the unique surface geometry of Pt(331), some adsorbates (including some oxygenated ORR-intermediates) should also contribute to the electronic structure of the neighbouring catalytic centres. However, the experimental elucidation of the specific adsorption of oxygenated species at this surface appears to be a non-trivial task. Such information holds the keys to the understanding of the high activity of this material and would enable the rational design of nanostructured ORR catalysts even without alloying. In this work, the electrified Pt(331)/electrolyte interface has been characterised using cyclic voltammetry (CV) combined with potentiodynamic electrochemical impedance spectroscopy (PDEIS) in 0.1 M HClO4 solutions. The systems
were studied in the potential region between 0.05 V and 1.0 V vs. RHE, where the adsorption of *H, *OH and *O species is possible in both O2-free and O2-saturated electrolytes. Our CV and PDEIS results support the hypothesis that in contrast to Pt(111), many Pt(331) surface sites are likely blocked by *O species at the polymer electrolyte membrane fuel cell benchmark potential of 0.9 V (RHE). We propose a model illustrated by simplified adsorbate structures at different electrode potentials, which is, however, able to explain the voltammetric and impedance data, and which is in good agreement with previously reported electrocatalytic measurements.