

New bimetallic catalyst for oxygen diffusion cathode in the brine electrolysis process

Marian Chatenet*[#], Marc Aurousseau*, Robert Durand*, Françoise Andolfatto[‡]

* LEPMI (UMR 5631 CNRS-INPG), ENSEEG, BP 75, 38402 Saint Martin d'Hères Cedex, France

[‡] Centre de Recherches Rhône-Alpes, ATOFINA, BP 63, rue H. Moissan, 69493 Pierre-Bénite Cedex, France

[#] To whom correspondence should be addressed (chatenet@cems.umn.edu); present address: University of Minnesota, Department of Chemical Engineering and Materials Science, 151 Amundson Hall, 421 Washington Avenue SE, Minneapolis, MN 55455, USA

Abstract

A new Oxygen Reduction Reaction (ORR) bimetallic catalyst is physically and electrochemically characterised: carbon-supported silver-platinum, Ag-Pt/C (10-10 wt%). Its resistance toward corrosion in 11.1 M soda is compared to that of commercial Pt/C (E-Tek).

X-Ray Diffraction (XRD) and Scanning Transmission Electron Microscopy (STEM) coupled with X-Ray analysis reveal three types of bimetallic particles: *small* (diameter $d < 5 \cdot 10^{-9}$ m) and *medium* ones ($d \approx 10^{-8}$ m) exhibit a high platinum concentration (95 and 88 wt% Pt respectively), whereas *large* ones ($d > 2 \cdot 10^{-8}$ m) content more silver (44 to 65 wt% Pt). Neither particles-free zones nor agglomerates are detected on the carbon surface. However locally, particles seem to gather by type, groups of *small* ones being surrounded by *large* ones and reversibly. The platinum active area is classically determined by hydrogen-adsorption voltammetry held in alkaline medium in order to prevent any silver electrochemical dissolution during the voltammetry sweeps. Despite identical platinum loadings, the active area of platinum is about 3.5 times smaller for Ag-Pt/C than for 10 wt% Pt/C: 3.8 cm² of Pt compared to 13 cm² of Pt, for a 0.2 cm² (geometric) catalyst active layered RDE. The silver migration at the particles surface could be an explanation.

The bimetallic catalytic properties are investigated in alkaline media on polycrystalline materials (bimetallic bulk catalysts, whose platinum concentration correspond to those of Ag-Pt/C particles types: PtAg and AgPt for the *small* and *large* particles respectively) and carbon-supported nanoparticles. They are compared to those of pure platinum. The ORR mechanism, studied on rotating ring-disk electrode, involves 4 electrons per oxygen molecule on all carbon-

supported catalysts either in classical soda solution (1 M NaOH at 25 °C) or in industrial medium (11.1 M NaOH at 80 °C). The reaction has a first order with respect to oxygen, both in classical and industrial soda solutions. ORR kinetic parameters are slightly different for Pt/C and Ag-Pt/C, in favour of the bimetallic catalyst: in 1 M NaOH at 25 °C, the current density at -0.1 V/Hg-HgO corrected from the diffusion both in solution and in the active layer, $i_{.100}$, is -0.89 and -0.92 A m⁻² of Pt for Pt/C and Ag-Pt/C respectively. A temperature increase favours the ORR kinetics on both catalysts whereas the pH effect is slightly detrimental on the reaction kinetics. Finally, in industrial medium, the corresponding $i_{.100}$ values are -1.1 and -1.4 A m⁻² of Pt, which highlights the bimetallic catalyst competitiveness to Pt/C. The results, confirmed for bulk materials, exhibit silver beneficial influence on the electrochemical behaviour of all bimetallic catalysts in industrial soda solution.

Ageing tests performed in industrial medium both in open-circuit and polarisation conditions reveal a better stability for all bimetallic catalysts. STEM imaging and XRD data show that whereas Pt/C is subjected to particles aggregation and losses via carbon corrosion, which decreases the active area of platinum, Ag-Pt/C is not deteriorated from exposure to the highly corrosive soda solution.

Finally, Ag-Pt/C stability and good activity toward ORR make this new promising catalyst useful in an air-cathode in the brine electrolysis process.

Key words: oxygen reduction, silver-platinum, concentrated alkaline media, corrosion