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## Short Communication

# Reply to the “Comment on the paper ‘The role of HBF<sub>4</sub> in electro-catalysis: Arsenic contamination and anion adsorption’ by A.L. Santos, R. Nagao, C.P. Oliveira, R.B. de Lima, H. Varela [J. Electroanal. Chem. 660 (2011) 147–152]”

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## ABSTRACT

This is a Reply to recent comment by M. Schell to our previously published article: Reply to the “Comment on the paper ‘The role of HBF<sub>4</sub> in electro-catalysis: arsenic contamination and anion adsorption’ by A.L. Santos, R. Nagao, C.P. Oliveira, R.B. de Lima, H. Varela [J. Electroanal. Chem. 660 (2011) 147–152]”

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We have recently reported an experimental investigation on the influence of different amounts of HBF<sub>4</sub> on the Pt|HClO<sub>4</sub>(aq) and Pt|HClO<sub>4</sub>(aq), HCOOH systems. [1] Following the previous work by Feliu and co-workers [2] on the presence of arsenic contamination in as-received HBF<sub>4</sub>, we used this chemical from two different suppliers and characterized it in terms of the amount of arsenic contamination by Hydride Generation Atomic Absorption Spectroscopy (HGAAS). The systems were studied by means of *in situ* nanogravimetry with the electrochemical quartz crystal nanobalance (EQCN), and in spite of the similar voltammetric profiles, the presence of arsenic was reflected in dramatic variations in the mass change vs. potential profiles, due to the deposition/dissolution of arsenic prior to the surface oxidation. Finally, the effect of As-contaminated HBF<sub>4</sub> on the electro-oxidation of formic acid was rationalized in terms of: (a) the enhancement of the electro-oxidation current at low potentials, and (b) the inhibition at high potentials. The former effect was unambiguously attributed to the arsenic-assisted electro-oxidation of formic acid, whereas the current decrease at high potential was suggested to result from anion adsorption.

In his comment [3] on our paper [1], Schell argues that we have misinterpreted some of his arguments and thus wrongly referred to his ideas. In this reply we address these criticisms.

The discussion given in Santos et al. [1] is based on our interpretation of the previous reports by Schell and co-workers. Of course,

if our interpretation does not strictly reflect the authors' ideas, this can cause misinterpretation of their papers. In some sense, it seems we extrapolated some of Schell's conjectures and conclusions to a broader context. Specifically, concerning the particular role we attributed to fluoroboric acid, it was deduced from the observation that the catalytic enhancement caused by fluoroboric acid was actually due to the presence of arsenic as an impurity.

Schell obtained similar behavior with fluoroborate in the oxidation of formic acid and the evidence is strong that it was caused for the same reason, arsenic poisoning [4,5]. If one was unaware of the presence of arsenic, it would be reasonable to believe that fluoroborate induced a catalytic mechanism. Schell has developed a theory for a catalytic mechanism induced by anions [6,7]. Besides small concentrations, we achieved effects with large concentrations of fluoroboric acid. These results and the interpretation of Schell and co-workers previous work led us to attribute to them the claim that fluoroborate anion primarily enhanced catalytic activity.

In spite of any misinterpretation, we emphasize that the main experimental findings presented in our paper [1] remain unchanged.

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