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## ACCEPTED MANUSCRIPT

## Faradaic Efficiency of Ethanol Oxidation to CO<sub>2</sub> at Metallic Nanoparticle/Short-Side-Chain PFSA Solid-State Electrolyte Interfaces Investigated by On-line DEMS

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#### **Abstract**

Ethanol has attracted attention as a renewable fuel for application in electrochemical reformers, for the production of hydrogen, and in fuel cells. The electro-oxidation of ethanol, however, faces a central drawback related to the difficulty for the C-C bond cleavage, which is required for its complete electro-oxidation to CO<sub>2</sub>. Thus, the efficiency has to be increased and this is the main challenge for the use of ethanol as a fuel in such devices. In this study, the ethanol electro-oxidation was studied at metallic nanoparticle/Aquivion® solid-state interfaces. The nanostructured electrocatalysts were formed by Pt/C, Rh/C, Sn/Pt/C, and Sn/(PtRh)/C nanoparticles, and the electrocatalysis was tested at temperatures ranging from 25 to 140 °C. Potentiostatic and potentiodynamic measurements showed a marked effect of the temperature on the electrocatalytic activity and, principally, on the stability, due to lower poisoning by adsorbed reaction intermediates above 100 °C. By using a new setup for coupling the solidstate electrolyte cell with a DEMS (Differential Electrochemical Mass Spectrometry) equipment, with a proper calibration, it was possible to determinate the faradaic efficiency of ethanol electrochemical oxidation to CO<sub>2</sub> at each studied condition. The results showed that the CO<sub>2</sub> current efficiencies (CCE) increased from approximately zero, at 25 °C, to 54.0, 44.1, 22.7, and 13.1% for Rh/C, Pt/C, Sn/(PtRh)/C (1:3), and Sn/Pt/C (1:3), respectively, at 120 °C, under potentiostatic conditions. The impact of the temperature was more prominent for Rh/C, and this

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