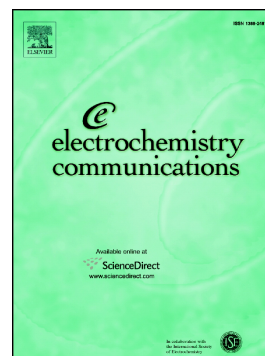


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Quantifying the turnover frequency for ethanol electro-oxidation on polycrystalline Pt in acid and alkaline media

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Abstract. The turnover frequency (TOF) is conventionally used to measure activity in catalysis but is rarely used in electro-catalysis, which uses the value of the interfacial current instead. Herein, a procedure to quantify the TOF for the ethanol oxidation reaction (EOR) in electro-catalysis is proposed and compared with the value observed in catalysis (Sapi et al., *Nano Lett.*, 14 (2014) 6727). The intrinsic TOF in an alkaline medium is $9.23 \text{ molecules}\cdot\text{site}^{-1}\cdot\text{s}^{-1}$, which is three times larger than the value obtained in an acidic medium, explaining the major differences observed between the interfacial currents recorded during cyclic voltammetry and chronoamperometry in the two media. In the future this methodology will be extended to single crystal surfaces and nanoparticles, assisting the development of electro-catalysts on a more fundamental theoretical basis.

1. Introduction

The nature of the support electrolyte plays an important role in the activity and selectivity of catalytic reactions [1-6] due to various interactions between the species found in the double layer and the active sites. Several papers describe the effects of ions on the ethanol oxidation reaction (EOR) [7-12] in electro-catalysis. In particular, adsorbed anions in acidic media, and non-covalent interactions between hydrated cations and adsorbed hydroxyl species in alkaline media, can influence the steps in the reaction.

Overall, there are advantages when EOR proceeds in alkaline rather than acidic media, which include [7,13]: first, significantly larger currents at a fixed interfacial potential; and second, a downward shift of the onset potentials of the Faradaic current. Based on these observations, the EOR in alkaline media has been selected as a promising reaction for use in fuel cells. However, other factors, such as the turnover frequency (TOF), are also considerably affected by the medium. The TOF quantifies the number of monolayers of the reactant that are consumed per unit time,

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