

Exploring the kinetic instabilities in the electro-oxidation of isopropanol

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The electro-oxidation of isopropanol (isopropyl alcohol, 2-propanol) on platinum proceeds with very high selectivity to acetone through a two-electrons process. The reversibility of the isopropanol ($\text{H}_3\text{C}-\text{HCOH}-\text{CH}_3$)/acetone ($\text{H}_3\text{C}-\text{CO}-\text{CH}_3$) pair is particularly appropriate for hydrogen transfer, and fuel cells operating with isopropanol present low crossover rates, and open circuit potential of 810 mV, which is considerably higher than 580 mV observed for methanol, under identical conditions.[1] Furthermore, isopropanol is non-toxic and often used for disinfection and cleaning. Mechanistically speaking,[2] acetone is also the main poisoning species, as no adsorbed CO, CO_{ad} , is detected and only very small amounts of CO_2 is observed at high potentials. Kinetic instabilities, namely self-organized potential oscillations, in the electro-oxidation of isopropanol on platinum and platinum-based catalysts, are often referred to as the cause of performance decrease and even a limiting factor to the wider use of this system. This is in contrast with our recent findings in several liquid fuels employed in fuels cell and also in electrochemical reformer to produce clean hydrogen. (see [3] and references therein). The main goal of this work is to understand the electrochemical oscillations observed in the electro-oxidation of isopropanol on platinum and then tune the reaction parameters in order engineer the oscillations towards the optimization of practical devices. A set of data exploring the effect of reaction temperature is given in Fig. 1. The voltametric signatures illustrate the effect of T on reaction rates along the sweep. In the range between 25 and 60 °C, and the oscillation frequency varied from c.a. 5×10^{-3} to 10^{-2} Hz, with the oscillatory activation energy (at constant current) around 25 $\text{kJ}\cdot\text{mol}^{-1}$. Interestingly, previous unreported mixed-mode oscillations depicted in Fig. 1(b) were found at 60 °C. From the fundamental perspective, the isopropanol/acetone system is very interesting as all electrochemical oscillators in this class involves CO_{ad} .

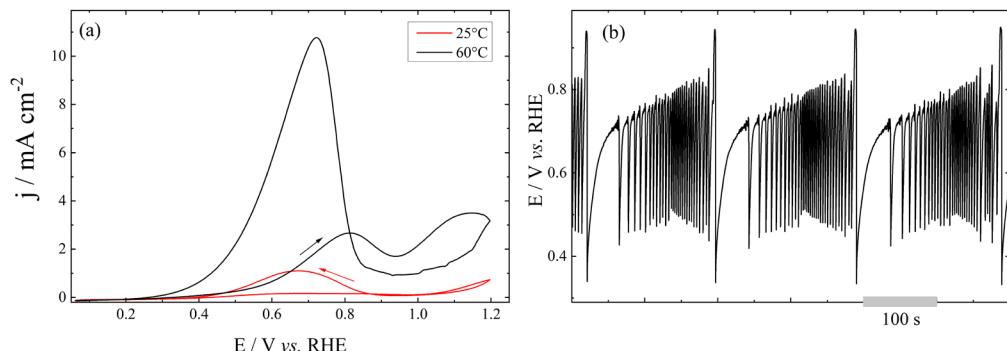


Figure 1: (a) voltammetric profiles of the electro-oxidation of isopropanol on Pt at 25 and 60 °C, and (b) potential oscillations recorded at $j = 0.4 \text{ mA cm}^{-2}$ and 60 °C. Electrolyte: aqueous solution containing $[\text{H}_2\text{SO}_4] = 0.1$ and $[\text{H}_3\text{C}-\text{HCOH}-\text{CH}_3] = 1 \text{ mol.L}^{-1}$.

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