
Near surface solution pH changes during alcohol/polyols electro-oxidation reactions studied by oscillations

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Electrochemical systems can depict self-organization phenomena such as oscillations. These systems provide precise control of boundary conditions with relative experimental simplicity and have become valuable for building models for the electrical double layer in systems away from thermodynamic equilibrium. Moreover, the electrochemical oxidation of alcohols and polyols are interesting to feed direct alcohol fuel cells or to provide both protons and electrons to H₂ production in electrolyzers. While these small organic molecules are oxidized in a wide pH range, oscillatory phenomena are commonly observed only in acidic media, the phenomenon being restricted for few molecules in neutral or alkaline media. Herein, the electrochemical oxidation of methanol, ethylene glycol, and glycerol were studied in unbuffered Na₂SO₄ solutions (pH 8.2). Regardless of the alcohol/polyol employed, the activity at low potential was addressed to the H⁺/H₂ pair and confirmed by online mass spectrometry experiments. Changes of the near surface solution pH (NSSpH) were estimated by mathematical modeling revealing changed up to 6.5 pH units and a 4 mm depletion layer after 100 s of polarization. NSSpH changes provide an acidic environment to alcohol/polyols oxidation as observed by means of the oscillation's features. Facilitating the mass-transport condition, the NSSpH becomes close to the bulk, in which both the low potential activity and the potential oscillations are no longer observed. Applying mathematical modeling to the galvanostatic time-series, it was possible to evaluate the changes in NSSpH and to conclude that the observed oscillations are due to the pH decrease triggered by the alcohol/polyol oxidation.

Acknowledgments:

FAPESP (2013/07296-2 and 2017/11986-5), CNPq (310550/2022-0) and CAPES