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PII: S1572-6657(18)30033-X
DOI: doi:10.1016/j.jelechem.2018.01.023
Reference: JEAC 3814

To appear in: *Journal of Electroanalytical Chemistry*

Received date: 15 September 2017
Revised date: 11 January 2018
Accepted date: 15 January 2018

Please cite this article as: Edwin Khoo, Martin Z. Bazant, Theory of voltammetry in charged porous media, *Journal of Electroanalytical Chemistry* (2018), doi:10.1016/j.jelechem.2018.01.023

Theory of voltammetry in charged porous media

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(Dated: January 9, 2018)

Abstract

We couple the Leaky Membrane Model, which describes the diffusion and electromigration of ions in a homogenized porous medium of fixed background charge, with Butler-Volmer reaction kinetics for flat electrodes separated by such a medium in a simple mathematical theory of voltammetry. The model is illustrated for the prototypical case of copper electro-deposition/dissolution in aqueous charged porous media. We first consider the steady state with three different experimentally relevant boundary conditions and derive analytical or semi-analytical expressions for concentration profiles, electric potential profiles, current-voltage relations and overlimiting conductances. Next, we perform nonlinear least squares fitting on experimental data, consider the transient response for linear sweep voltammetry and demonstrate good agreement of the model predictions with experimental data. The experimental datasets are for copper electrodeposition from copper(II) sulfate solutions in a variety of nanoporous media, such as anodic aluminum oxide, cellulose nitrate and polyethylene battery separators, whose internal surfaces are functionalized with positively and negatively charged polyelectrolyte polymers.

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