Modeling Bipolar Electrochemistry in Order to create a Basis for Computational Tribology Experiments

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引言：In the field of boundary lubrication, surfactant adsorption plays an important role. Recently, several experiments [1][2] focused on controlling adsorption behavior electrodynamically. In this context, Zhang [2] investigated the adsorption behavior of SDS (sodium dodecyl sulfate) on steel BPE (bipolar electrode). Here we aim on establishing a virtual model in order to reproduce Zhang’s experimental findings and furthermore to predict or validate related experiments. The first step is a complete model of BPE, explicitly including the full diffuse double layer (DDL) structure.

计算方法：Our 2d model electrochemical cell consists of working electrode WE, counter electrode CE, BPE and electrolyte. Inspired by Bazant [3], the full Poisson-Nernst-Planck (PNP) equation system is solved within the electrolyte domain

\[ \mathbf{N}_i = -D_i \nabla c_i - u_i z_i F c_i \nabla \phi \quad \text{(Nernst-Planck)} \]

\[ \nabla \cdot (-\varepsilon \nabla \phi) = \rho \quad \text{(Poisson)} \]

with conservation law \( \nabla \cdot \mathbf{N} = 0 \) and physics-coupling through charge density \( \rho = F \sum z_i c_i \).

Ion species \( H_3O^+, OH^-, Na^+, ClO_4^-, C_{12}H_{25}SO_4^- \) in aqueous solution correspond to Zhang’s setup.

Three governing surface reactions at the electrodes, namely the dissolution of iron and electrolysis of water, state the boundary conditions:

- Fe \( \rightarrow \) Fe\(^{3+}\) + 2e\(^-\) \quad \text{anodic}
- 6H\(_2\)O \( \rightarrow \) O\(_2\) + 4H\(^{3+}\) + 4e\(^-\) \quad \text{anodic}
- H\(_2\)O + 2e\(^-\) \( \rightarrow \) H\(_2\) + 2OH\(^-\) \quad \text{cathodic}

Those half-reactions lead to species flux at WE, BPE and CE governed by electrochemical kinetics.

Each reaction thus imposes boundary conditions given by the following flux expression related Butler-Volmer equation,

\[ \mathbf{N} = K_n \cdot c_R \cdot e^{\frac{-\xi}{RT}} - K_c \cdot c_{Ox} \cdot e^{\frac{-\xi}{RT}} \]

where \( K_n \) and \( K_c \) are the local surface concentrations of reductant and oxidant. The potential difference between solid electrode phase and liquid electrolyte phase is expressed as the overpotential \( \eta = \phi_s - \phi_l \), here the potential drop across the DDL stretching out to the \( \xi \)-plane at Debye length \( \lambda_D \). Methods to determine the potential at isolated BPE stem from [4].

结果：At the current stage, a qualitative steady state model with pseudo parameters including only one half-reaction has been solved.

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<td>( c_{\text{ini}} )</td>
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</table>

表 1. parameters

结论：Convergence is difficult to be guaranteed for this highly non-linear PNP system. Mesh-related deviations are likely to occur. In case those issues can be solved, present results promise the realization of [2] and extension to other problems.

参考文献: