Analysis of current at the surface of a rocking disk electrode

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Introduction: Surface and solution kinetics of a redox reaction can be reliably studied using hydrodynamic electrochemical methods. In this work, we introduce a novel electroanalytical tool, the rocking disk electrode, and compare it with the existing popular tool, the rotating disk electrode (RDE). For about half a century, the RDE has been applied to numerous fields including, but not limited to, measurement of diffusion coefficients, kinetic parameters, passivity, trace analysis, corrosion, homogeneous and heterogeneous catalysis, and electrocrystallization [1]. In this poster, we

- Compare the momentum and species transport near the surface of the RDE and the RoDE
- Contrast and analyze the current at the surface of the RDE and the RoDE

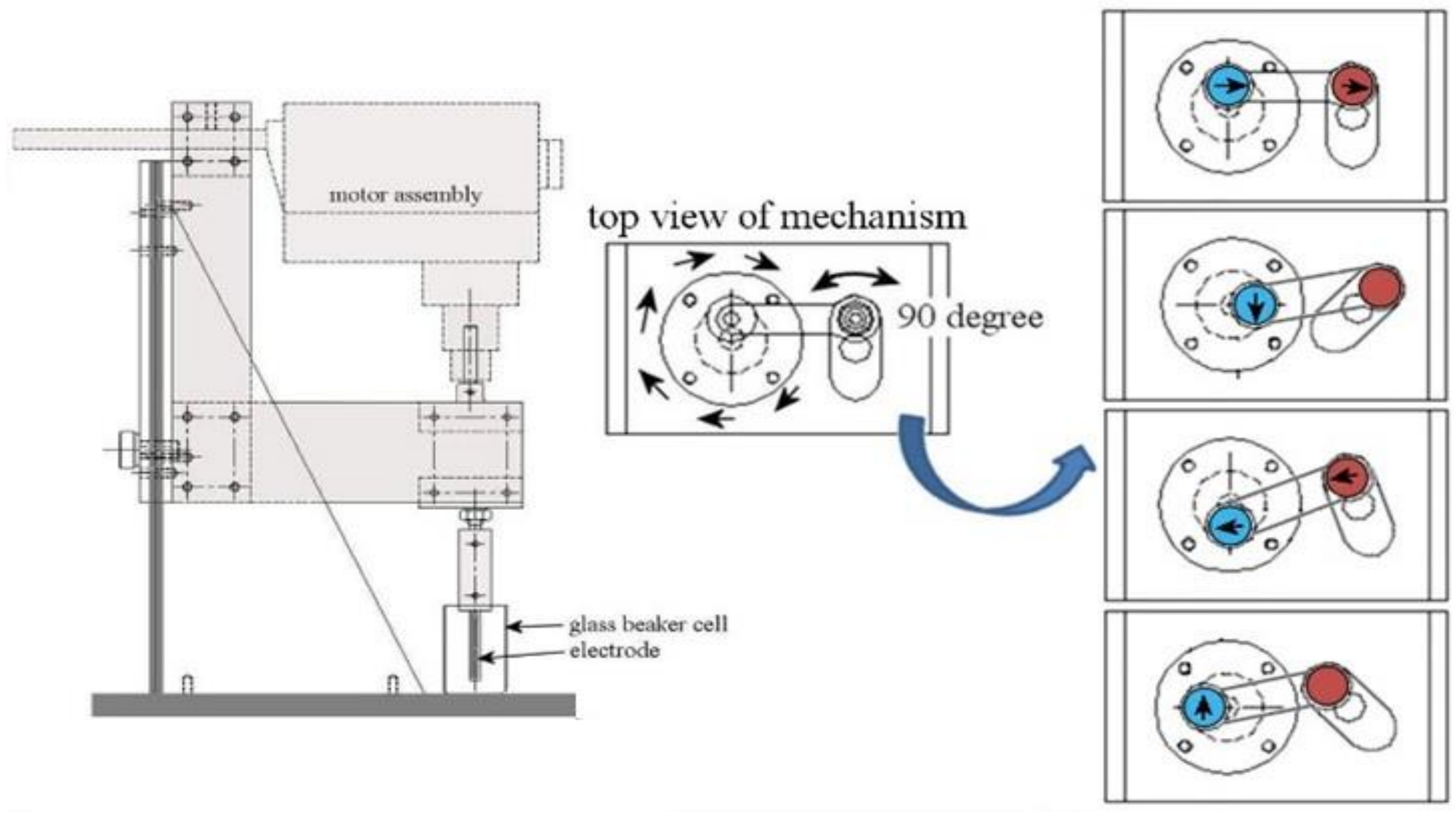

Figure 1. RoDE experimental set up showing the rocking mechanism [2]

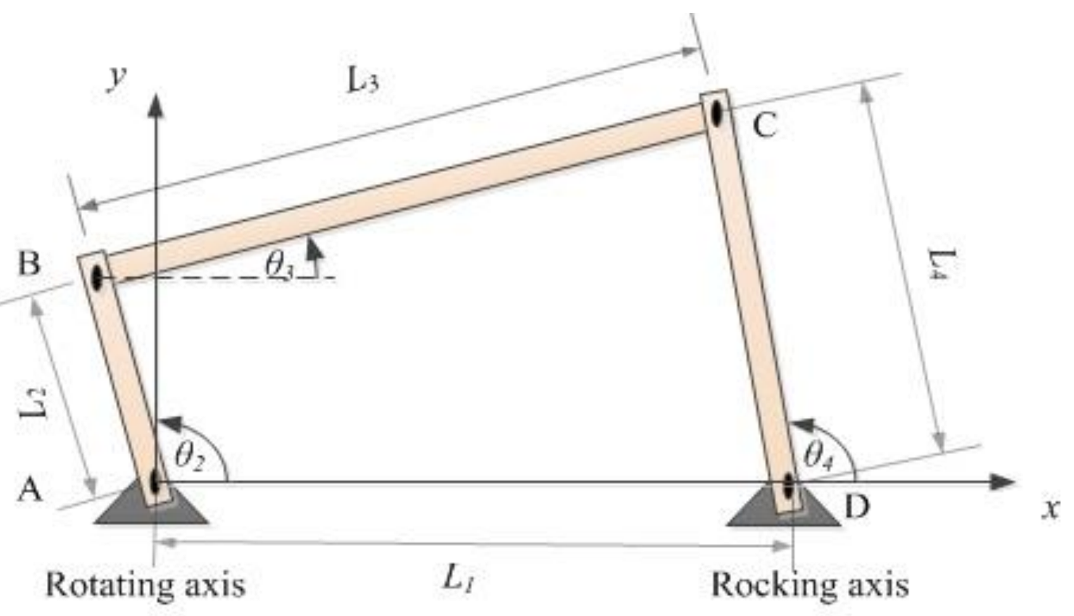

Figure 2. Four-bar mechanism

In the RoDE, a four-bar mechanism translates the rotating motion into a "rocking" motion. Here, by rocking we refer to the back-and-forth motion.

Computational Methods:

- Two dimensional (2D) axisymmetric model
- Laminar flow with a swirl flow and Transport of Diluted Species modules
- Mathematical model in the time domain:

$$\mathbf{u}\cdot\nabla\mathbf{u} = -\frac{1}{\rho}p + \nu\nabla^2\mathbf{u} \qquad ,\nabla\cdot\mathbf{u} = 0$$

$$\frac{\partial c_i}{\partial t} = -\nabla\cdot\mathbf{N}_i, i = O, R \qquad ,\mathbf{N}_i = -D_i\nabla^2 c_i + \mathbf{u}\cdot\nabla c_i$$

Here $\mathbf{u}$ represents the velocity vector, p is the pressure, ρ is the density and ν is the kinematic viscosity of the fluid. A sliding wall condition with a velocity corresponding to the rotation/rocking frequency is set along the walls of the electrode and a no-slip condition for the walls of the container. For the species transport, c_i is the concentration, $\mathbf{N}_i$ is the flux, D_i is the diffusion coefficient, and O and R represent the species undergoing oxidation and reduction respectively. We specify an inward flux at the electrode surface and a no flux condition at the other walls.

Results:

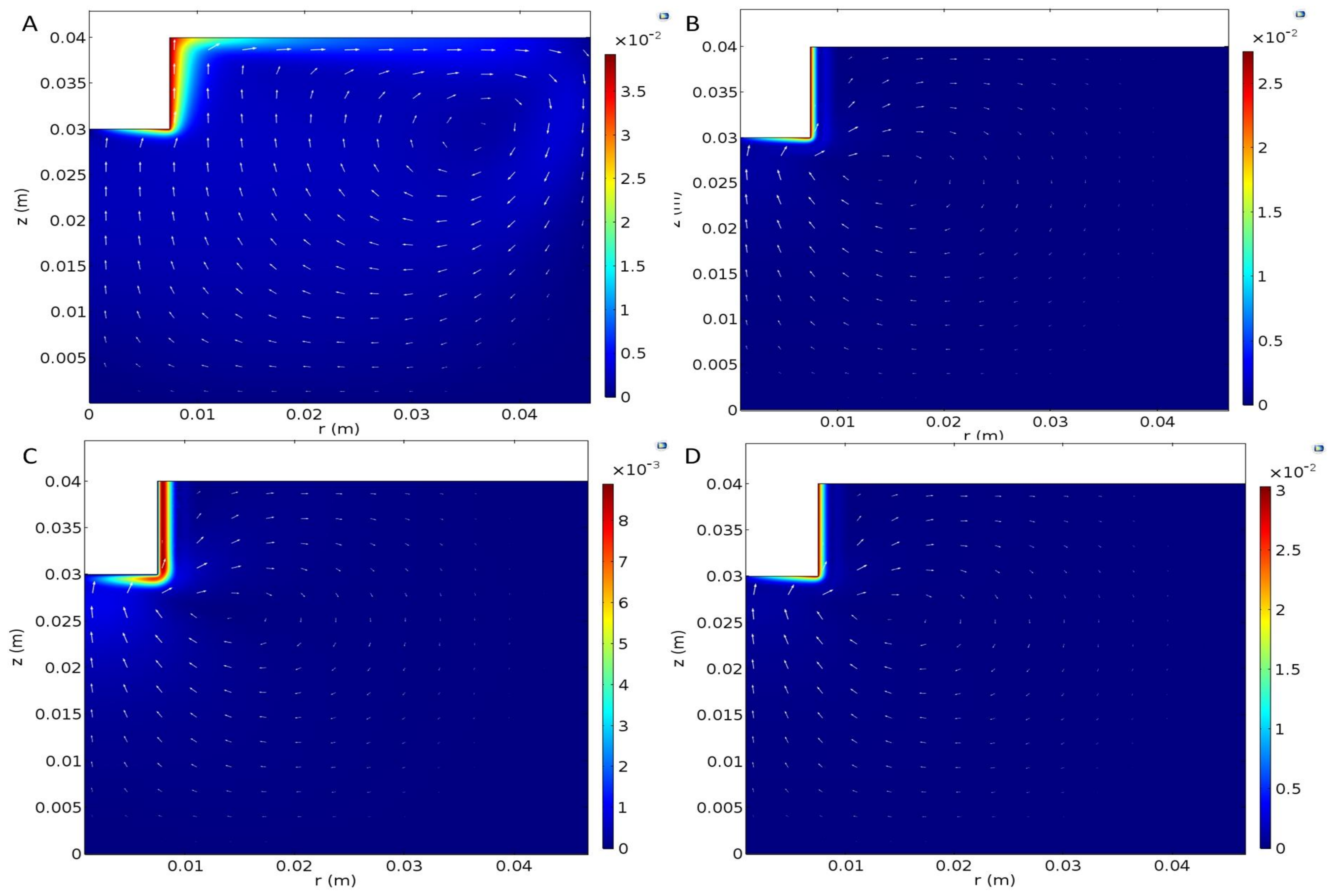

Figure 3. Flow pattern predicted by the 2D axisymmetric model at 50 rpm around the (A) RDE, (B),(C),(D) at the RoDE for max, min, -ve max rocking frequencies respectively

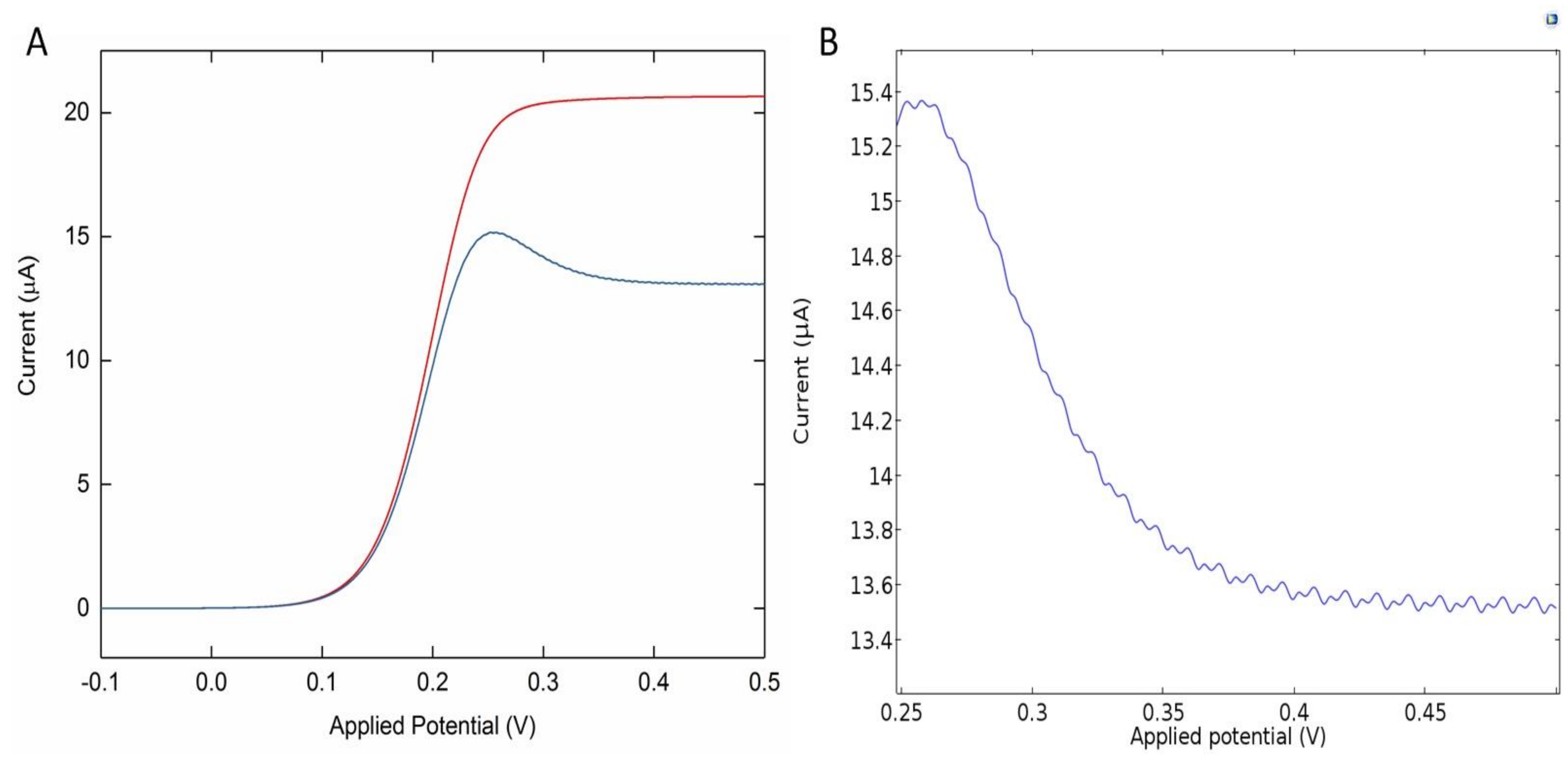

Figure 4. (A) Current at the surface of the RDE (red) and the RoDE (blue), (B) Current at the RoDE magnified to show the periodic behavior

The maximum magnitude of the velocity around the RDE was 3.9E-2 ms^{-1} and 3.0E-2 ms^{-1} around the RoDE. The current at the RoDE (Fig. 4) has a periodic behavior, which can be attributed to the motion of the electrode, because the current at the RDE shows no periodic behavior. Limiting currents at the surface of the RDE and the RoDE are 15.1 μA and 20.0 μA respectively.

Conclusions: COMSOL® allows us to easily couple the multiphysics of non-linear kinematics of the motion of the RoDE with fluid mechanics and species transport. The periodic behavior, seen in Fig. 4B for the current at the RoDE, shows that we can obtain more data points from a single RoDE experiment compared to the RDE. In the future:

- We will characterize the RoDE for more complex electrochemical reactions involving different reaction mechanisms
- We will investigate the hydrodynamics around a porous RoDE and explore the the electrochemical evaluation of such electrodes

References:

1. C.Deslouis,Flow modulation technique and EHD Impedance: a tool for electrode processes and hydrodynamic studies, Electrochemica Acta, 35, 1637-1648 (1990)
2. D. Ahn, Hydrodynamic Voltammetry at a Rocking Disc Electrode: Theory versus Experiment, Electrochemica Acta, 188, 837-844 (2016)

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