The Effect of Redox Cycling on the Fe^{3+} Reduction within the Microchannel Electrochemical Cells

Y. Li[1,2], W. Van Roy[1], P. M. Vereecken[1,2], and L. Lagae[1,2]

[1] IMEC vzw, B-3001, Leuven, Belgium
[2] Katholieke Universiteit Leuven, B-3001 Leuven, Belgium

Microchannel electrochemical cells have received considerable interests as a promising micro total analysis system (µTAS). When going from a macro system to a micro system, 3D semi-infinite diffusion field might be confined by the microchannel [1]. In addition, when the WE-CE are closely spaced, redox cycling can significantly influence the diffusion field [2].

Here we investigate the scan rate dependent redox cycling within microchannel electrochemical cells. The electrochemical cell consists of a PDMS microchannel (200 um wide x 20 um high) on top of a Pt micro-electrode array containing five pairs of 40 um x 800 um large electrodes (Fig. 1). A solution of 10mM $FeCl_3$ in 0.2M KCl was used as a model system. Rotating Disk Electrode (RDE) voltammetry was used as a benchmark. All the experiment and modeling were done in the stationary solution.

Fig. 2 shows the microchannel voltammograms for the facing WE-CE configuration (e.g., WE1-CE1): a sigmoidal like shape at v=5mV/s (Fig. 2 (a)) and a typical peak like shape at v=50mV/s (Fig. 2 (b)) [3]. The sigmoidal like shape response indicates the redox cycling [4].

Fig. 3 shows experimental and simulated plots of ΔU_p vs. $\log_{10}v$ at the facing and nonfacing WE-CE configurations (e.g., WE1-CE2). In the facing WE-CE configuration, the experimental ΔU_p increases with $\log_{10}v$ at the high scan rates (v>20mV/s), similar to the macroscopic (stationary RDE) experiment. However, at low scan rates (v<20mV/s), ΔU_p strongly decreases with scan rate. In the nonfacing WE-CE configuration, the experimental ΔU_p increases with scan rate over the entire measured range. Modeling of the facing WE-CE configuration without redox cycling fails to reproduce the experimental results – it shows increasing ΔU_p over the entire range (curve (5)). When redox cycling is switched on, the model is in excellent agreement with the measurements (curve (4)). For the nonfacing WE-CE configuration, modeling without redox cycling adequately reproduces the experimental trend. The stronger increase at high scan rates for the experimental data may have been caused by the iR drop associated with air bubbles.

Fig.4 (a) and (c) show the modeled Fe^{3+} concentration profiles at 5mV/s for facing WE-CE. Without redox cycling the depletion layer extends to the channel sidewall. This is a typical thin layer behavior [1] [3]. After activating the redox cycling, Fe^{2+} is converted back into Fe^{3+}, and a steep concentration gradient is restored (Fig. 4 (c)). While at the nonfacing case, the semi-infinite diffusion dominates the both cases and it is only slightly influenced by the redox cycling (Fig. 4 (b) and (d)).
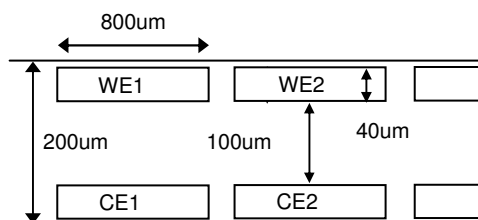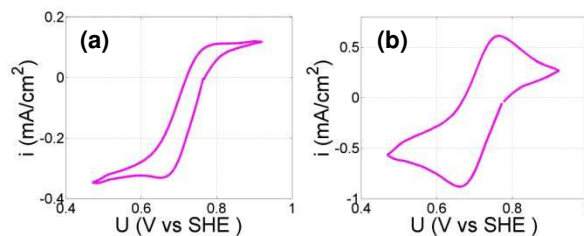

Fig. 2. 10mM $FeCl_3$ voltammograms of the microchannel electrochemical cells (a) sigmoidal like at 5mV/s and (b) peak like at 50mV/s.

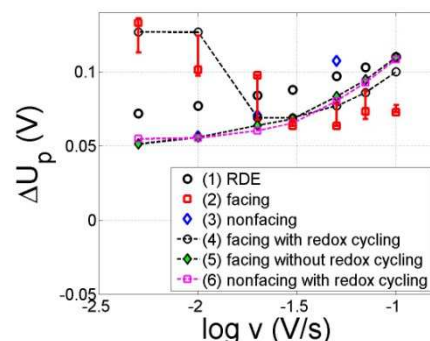Fig. 3. The plot of ΔU_p and $\log_{10}v$ of 10mM $FeCl_3$: (1) RDE measurement (2) facing WE-CE measurement (3) nonfacing WE-CE measurement (4) facing WE-CE with redox cycling modeling (5) facing WE-CE without redox cycling modeling (6) nonfacing WE-CE with redox cycling modeling.
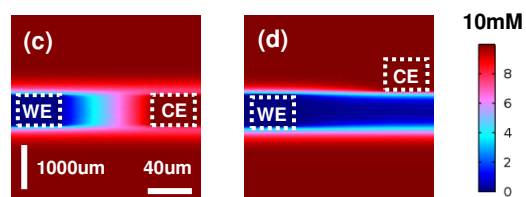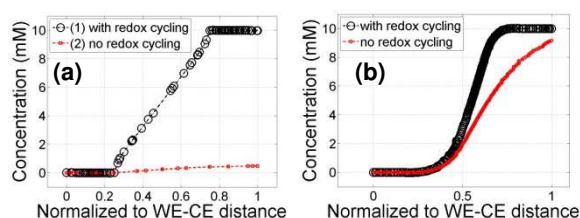

Fig. 4. Modeled Fe^{3+} concentration profile of 5mV/s (a) for the facing WE-CE along the distance to WE (b) for the nonfacing WE-CE along the distance to WE (c) for the facing WE-CE with redox cycling at the channel bottom (d) for the nonfacing WE-CE with redox cycling at the channel bottom (unequal x- and y-scales).

[1] R. A. Clark, et. al., Anal. Chem., **70**, 1119 (1998).
[2] P. M. Lewis, et. al., Anal. Chem., **82**, 1659 (2010).
[3] J. S. Rossier, et. al.,, Anal. Chem., **71**, 4294 (1999).
[4] M. Rahimi, et, al., Anal. Chem., **83**, 7555 (2011).

Fig. 1. Schematics of the microelectrode array.