

Flow-Through Electrochemical Surface Plasmon Resonance (SPR): Detection of Intermediate Reaction Products

SPR is sensitive to various processes taking place on or near a sensor chip. The SPR sensor chip can also simultaneously serve as a working electrode for electrochemical measurements. Combining electrochemical with SPR measurements has led to the development of Electrochemical SPR (EC-SPR). To date, EC-SPR has been used in the analysis of trace metal ions, detection of surface bound redox species, electrochemical polymerization and biosensing. These studies are mainly focused on adsorption/desorption processes or conformation changes in the adsorbed species. EC-DualFlow™ is a novel two channel flow-through EC-SPR technology with precision sample delivery control, which can measure both the electrochemical and SPR signals simultaneously. More importantly, it allows one to monitor the electrochemical, or/and SPR signals at different locations along the flow path, which opens the door to many new applications. For example, one can generate an electrochemical reaction at an upstream location and detect the reaction products at a downstream location. This unique capability makes it possible to separate the proton and electron transfer processes, as well as the reaction intermediates and final products.

Recently, Huang et al.[1] describes a study of reaction intermediates of hydroquinone-quinone (HQ-BQ) using EC-SPR enabled by the EC-DualFlow™ module. HQ-BQ system has been widely studied as one of the most classical organic redox reactions, and electrochemistry of quinones is also important for understanding biological electron transfer processes such as the photosynthesis, oxidative phosphorylation, cytotoxic functions and paradoxically antitumor activity. Huang et al. have investigated the redox reaction of hydroquinone-benzoquinone (HQ-BQ) system in acetonitrile.

In their work, a potential step was applied to the working electrode (position 1) in the presence and absence of HQ and BQ, and the SPR signals at positions 1, 2 and 3 were monitored as a function of time (FIG. 1). FIG. 2 shows the current at position 1 and the SPR signals at the three positions after stepping the potential to -0.75 V for 2 s and then back to 0 V. In the absence of HQ and BQ, only a small (2 mDeg) SPR shift was detected, which is attributed to the double layer charging (green lines).

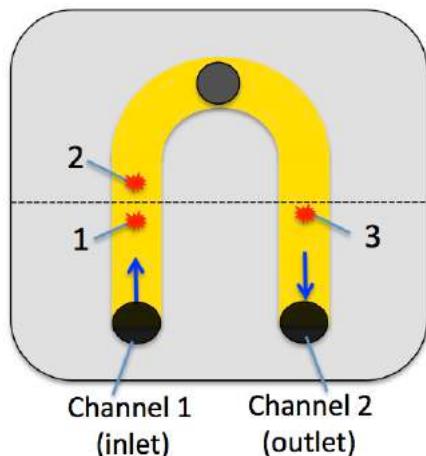


FIG. 1 A schematic drawing of the flow channels and the gold-coated sensing chip (top view). The two channels are connected into a U-shape. The WE for each channel is located at position 1 and 3. The RE is located at the turn of the U-shaped flow stream. The CE (not shown) are positioned in the flow channels above each WE. The solution flows into the cell through channel 1 and exits through channel 2. Position 2 and 3 are at downstream locations. For 100 μ L/min flow rate, it takes 0.1 s and 5 s for a sample to flow from position 1 to positions 2 and 3, respectively.

FIGs. 2a and 2b show the electrochemical current and SPR signals at position 1, respectively. The electrochemical current signal at position 1 is due to the reduction of HQ-BQ. The simultaneously

recorded SPR signal shows a large drop immediately after stepping the potential to -0.75 V for 2 seconds, because the newly generated BQ^- has an index of refraction smaller than the electrolyte. The SPR signal returns to the baseline immediately after the potential is stepped back to 0 V because BQ^- is carried downstream by the flow.

At position 2 (FIG. 2c), the SPR behavior is different. The signal shows only a small negative peak when the potential is stepped to -0.75 V. However, it turns into a larger positive peak after the potential is stepped back to 0 V. The positive peak is due to the transformation of the short-lived radical BQ^- carried by the flow into HQ and BQ at position 2, which becomes more disperse by the time it reaches position 3 (FIG. 2d).

The radical lifetime is a measure of the time a radical stays in the excited state before decaying to the ground state by combining with an electron. For first-order kinetics, the lifetime of radicals is the time that takes for the number of excited molecules to decay to $1/e$ or 36.8% of the initial concentration. In this case, the lifetime was found to be ~0.02 s, by measuring the signal attenuation at different positions. This work demonstrates that EC-SPR is a powerful tool for detecting and measuring reaction intermediates, and has potential to be used for studying reaction kinetics. It also demonstrates the importance of fast SPR detection time in EC-SPR with the novel dual channel flow cell designed by Biosensing Instrument Inc.

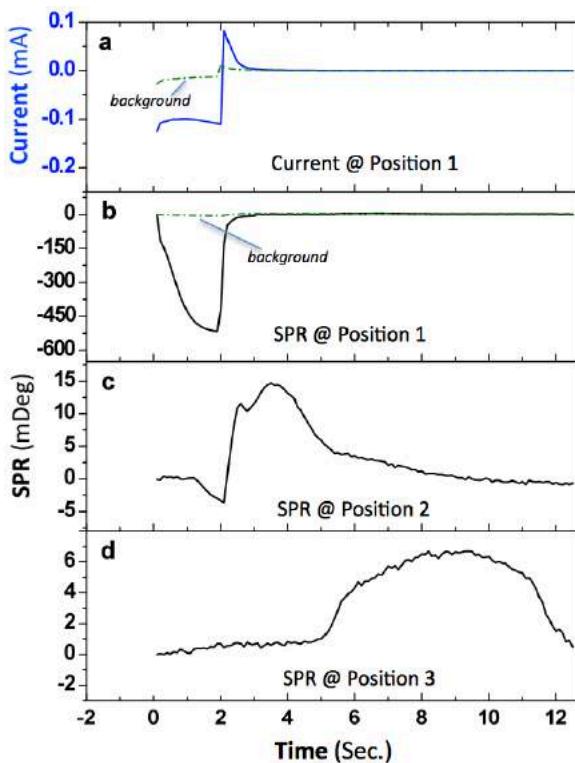


FIG. 2 Characterization of BQ^- with EC-SPR (Potential: -0.75 V, 2 s) at positions 1, 2 and 3 of the sensing chip. (a) Current of the HQ-BQ and solvent (0.1 M Bu_4NPF_6 in acetonitrile), (b) SPR signal of the HQ-BQ and solvent (0.1 M Bu_4NPF_6 in acetonitrile) at position 1, (c) SPR signal of the HQ-BQ at position 2, (d) SPR signal of the HQ-BQ at position 3. Flow rate = 100 $\mu\text{L}/\text{min}$.

References

- [1] X. Huang, S. Wang, X. Shan, X. Chang, N.J. Tao, 649, 37-41(2010).