Lecture #10

Electrochemistry of micro-disk electrode. Limiting stage of electrochemical reaction.

The large impact of ultramicroelectrodes (UME) is rooted in their ability to support very useful extensions of electrochemical methodology into previously inaccessible domains of time, medium, and space. That is, UMEs allow one to investigate chemical systems on time scales that could not previously be reached, in media that could not previously be employed, or in microstructures where spatial relationships are important on a distance scale relevant to molecular events.

It is not meaningful to try to impose a potential step on a time scale shorter than the cell time constant. In fact, the full establishment of a potential step requires ~5R_uC_{dl}, and the added time for taking data normally implies that the step must last at least 10R_uC_{dl}, and often more than 100R_uC_{dl}. To a large extent, the size of the electrode controls the cell time constant and, therefore, the lower limit of experimental time scale.

The cell time constant expresses as follows:

$$R_u C_{dl} = \frac{r_o C_{dl}^o}{4k}$$

Even though R_u rises inversely with r_0, C_{dl} decreases with the square; hence R_uC_{dl} scales with r_0. This is an important result indicating that smaller electrodes can provide access to much shorter time domains.

Consider, for example, the effect of electrode size in a system with C_{dl}^o = 20 μF/cm^2 and k = 0.013 Ω^{-1} cm^{-1} (characteristic of 0.1 M aqueous KCl at ambient temperature). With r_0 = 1 mm, the cell time constant is about 30 μs and the lower limit of time scale in step experiments (defined as a minimum step width equal to 10R_uC_{dl}) is about 0.3 ms. This result is consistent with the general experience that experiments with electrodes of "normal" size need to be limited to the millisecond time domain or longer. However, with r_0 = 5 μm the cell time constant becomes about 170 ns, so that the lower limit of time scale drops to about 1.7 μs. Before UMEs were understood and readily available, the microsecond regime was very difficult to reach in electrochemical studies.

UMEs even allow access to the nanosecond domain, although not yet with routine ease or convenience. To reach it, one must reduce the electrode size further and work with solutions having high conductivity. For example, by using a disk UME with r_0 = 0.5 μm and by working in 1 M H_2SO_4, one can, in principle, achieve a cell time constant below 1 ns, so that the lower limit of time scale could be smaller than 10 ns [1].

The difference in surface area between macroelectrodes and microelectrodes causes differences in diffusion profiles of electroactive species from the bulk electrolyte to the electrode-electrolyte interface. In macroelectrodes, the planar surface leads to a semi-infinite diffusion field (Figure 1, top). In microelectrodes with a disk surface, however, the diffusion field is hemispherical (Figure 1, bottom).

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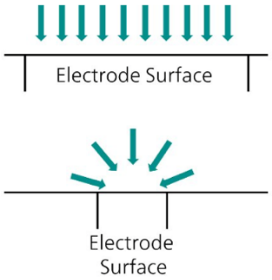

Figure 1. Illustrations of the diffusion profile (green arrows) of electroactive species. Top: the planar diffusion profile from a macroelectrode. Bottom: the hemispherical diffusion profile from a micro size disk electrode [2].

The different diffusion profiles are responsible for the differences in electrochemical behavior of the microelectrodes compared to macroelectrodes [3], as shown below (Figure 2, 3). It is also worth noticing the large difference of the measured currents between the macroelectrodes (peak currents at ±1.5 mA) and microelectrodes (limiting currents at ±50 nA) due to the large difference in surface area between the two electrode types.

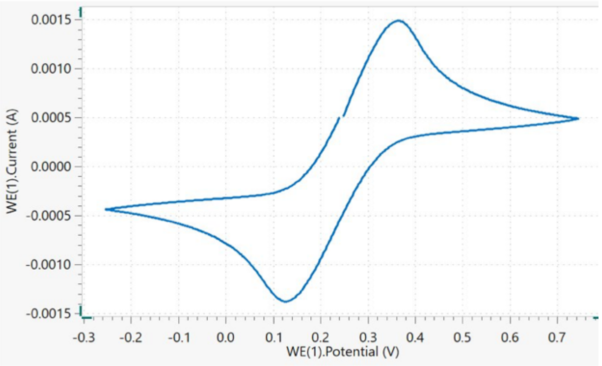

Figure 3. The cyclic voltammogram of a ferri/ferro solution at 100 mV/s with a 3 mm diameter gold electrode.

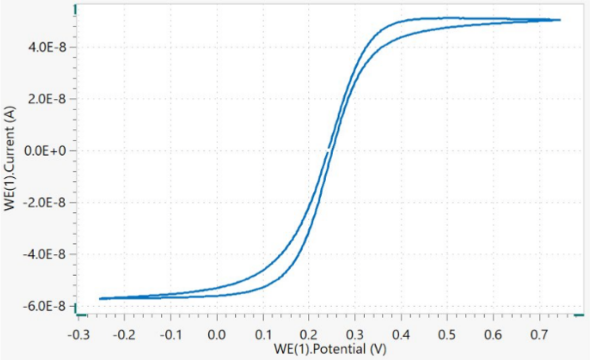

Figure 4. The cyclic voltammogram of a ferri/ferro solution at 100 mV/s with a 10 µm diameter gold electrode.

The current measured at microelectrodes typically ranges from pA to nA, i.e., orders of magnitude smaller than the current measured at macroelectrodes. The small currents observed at microelectrodes reduce or eliminate the ohmic drop (ΔE_{ohmic}) defined as the product of the current (i) and the electrolyte resistance between the reference and working electrode, called uncompensated resistance (R_{u}).

References

1. Bard, Allen J., Larry R. Faulkner, and Henry S. White. Electrochemical methods: fundamentals and applications. John Wiley & Sons, 2022.
2. https://www.metrohm.com/en/applications/application-notes/autolab-applikationen-anautolab/an-ec-030.html
3. Derek Plechter. Why Microelectrodes? Microelectrodes Theory Appl. 1991, 3–16.

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