# Lecture #10

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

Goal

*This lecture introduces the fundamental concepts and analytical advantages of microdisk electrodes in electrochemical research. Students will learn how their unique diffusion properties differ from macroelectrodes, how steady-state currents are established, and how to identify and analyze the limiting stage of electrochemical reactions under various conditions.*

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:

$$R_uC_{dl} = \frac{r_oC_{dl}^o}{4k}$$

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).

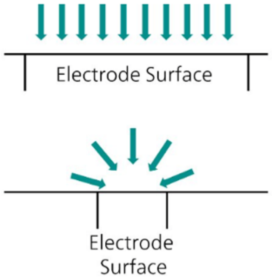

Figure 1. Illustrations of the diffusion profile (green arrows) of electroactive species. Top: the planar diffusion profile from a macroelectrode. Bottom: the hemispherical diffusion profile from a micro size disk electrode [2].

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.

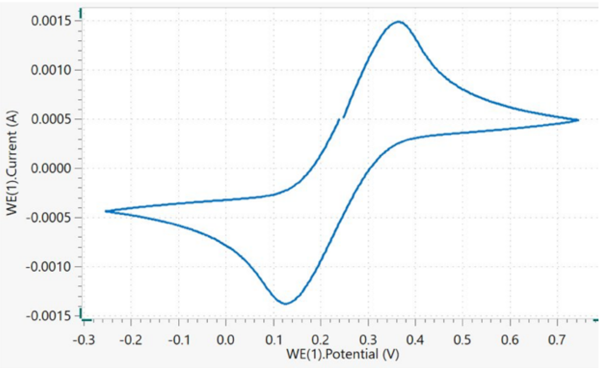

Figure 3. The cyclic voltammogram of a ferri/ferro solution at 100 mV/s with a 3 mm diameter gold electrode.

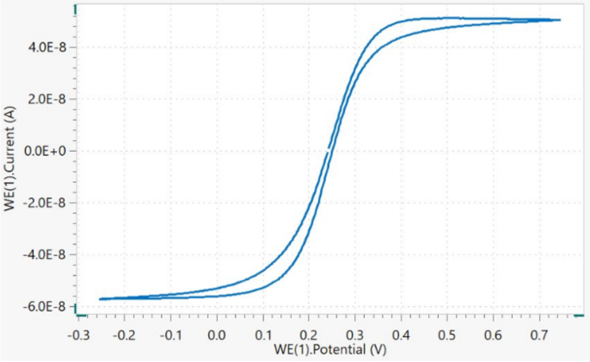

Figure 4. The cyclic voltammogram of a ferri/ferro solution at 100 mV/s with a 10 μm diameter gold electrode.

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 ($\Delta E_{\text{ohmic}}$) defined as the product of the current ($i$) and the electrolyte resistance between the reference and working electrode, called uncompensated resistance ($R_{\text{u}}$).

## Learning Outcomes

*By the end of this lecture, students will be able to:*

1. *Explain the physical and electrochemical characteristics of microdisk electrodes compared to conventional electrodes (related to LO 1.2 and 1.3).*
2. *Describe how radial diffusion affects steady-state current and sensitivity in microelectrode systems (related to LO 1.3 and 2.1).*
3. *Identify and analyze the limiting stage of electrochemical reactions—whether controlled by kinetics, mass transfer, or charge transfer (related to LO 2.3).*

## Questions and Self-study Assignments

1. *Describe the main advantages of microdisk electrodes in electrochemical research.*
2. *Explain how diffusion profiles differ between planar and microdisk electrodes.*
3. *Derive an expression for the steady-state diffusion-limited current at a microdisk electrode.*

4. *Discuss how to experimentally determine the limiting stage of an electrochemical reaction.*
5. *Review one scientific paper applying microelectrodes for studying fast kinetics or biological systems and summarize the key findings.*

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.