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Electrochemical Methods for the Micro- and Nanoscale

www.electrochemical-methods.org

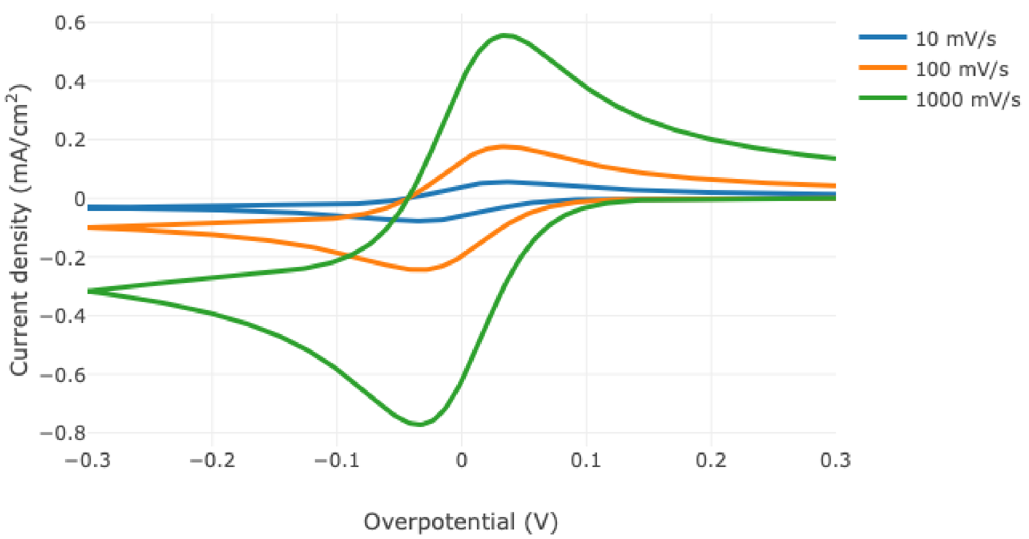
Solutions to the tasks: Chapter 5 – Classical methods

Task 5.1 (Cyclic voltammetry – simulation)

We use the great and simple-to-use web app from Peter M. Attia (https://petermattia.com/cyclic_voltammetry_simulation/cvwebapp.html) to solve this task. However, many other simulation tools would do the job either.

The simulator deals with an "EC mechanism," coupling an electrochemical and a chemical reaction. We turn the chemical reaction off by providing $k_c = 0$. The web app considers the reduction as the forward reaction, so we have to apply the initial concentration of O instead of R (and the scan direction flips accordingly).

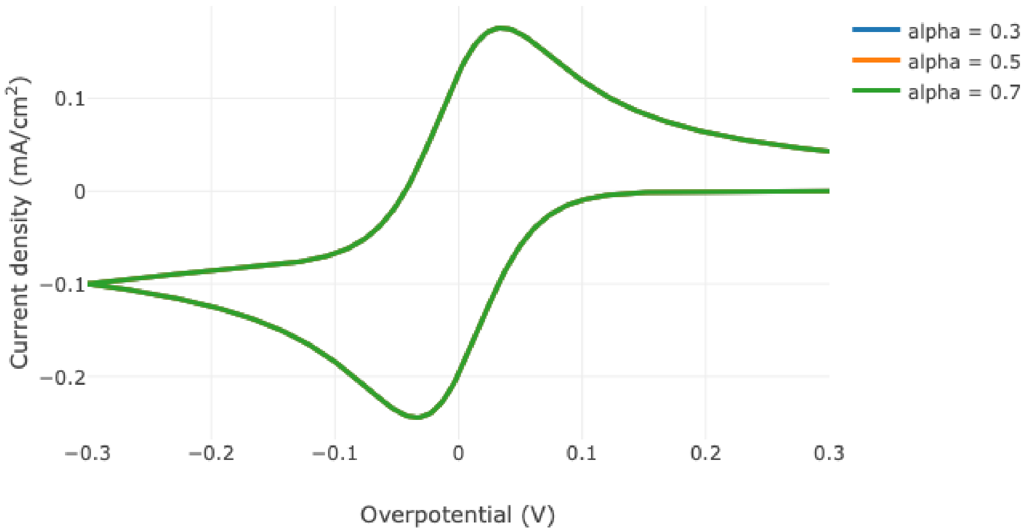
1. The influence of the scanrate was investigated for a reversible system with $k_0 = 1\,\mathrm{cm\,s^{-1}}$ at 10, 100 and 1000 $\mathrm{mV\,s^{-1}}$.



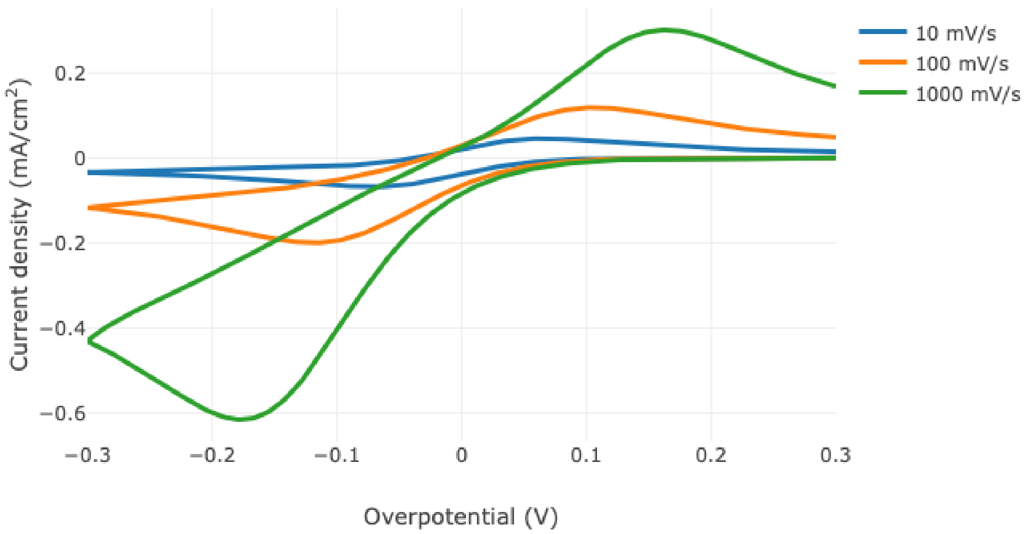
For all investigated scanrates, the system is reversible. The reversibility parameter Λ was 507, 160, and 51 for increasing scanrates. Accordingly, the peak potential and separation do not depend on the scanrate.

Closer analysis shows a growing peak current density with the square root of scanrate (the web app shows the current density values when hovering over the plot).

2. Different symmetry factor α does not influence the outcome as the system is reversible, here for a scanrate of $100\,\mathrm{mV\,s^{-1}}$ with the curves for different α overlaying each other:

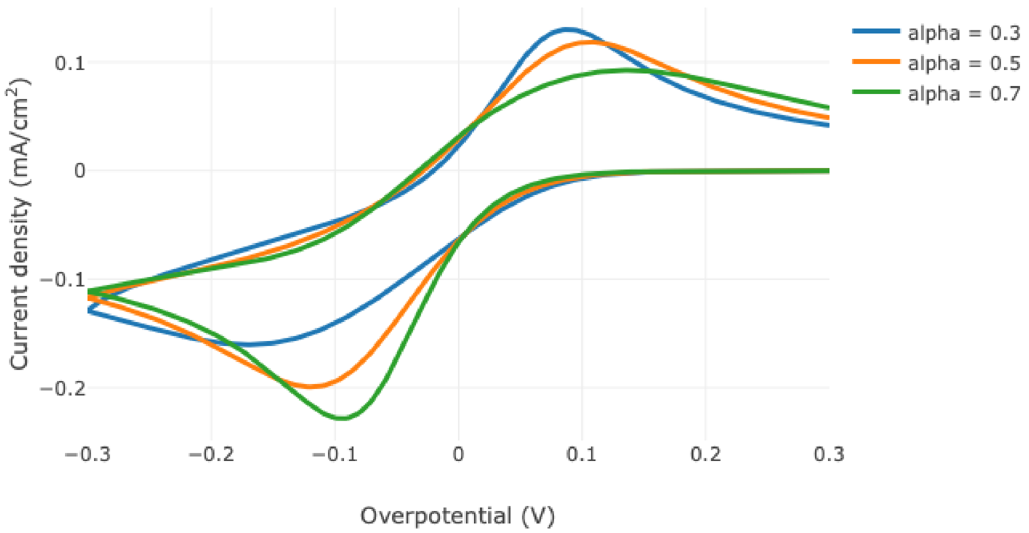


3. Choosing $k_0 = 1 \times 10^{-3}\,\mathrm{cm\,s^{-1}}$ turns the system quasi-reversible. The reversibility parameter Λ was 0.51, 0.16, and 0.051 for increasing scanrates.



The peak position moves away from zero overpotential, and the peak separation grows with increasing scanrate. Closer analysis shows a growing peak current density with the square root of scanrate. Overall the peak current density is slightly lower than in case of the reversible system analyzed before.

In the quasi-reversible system, the symmetry factor α influences the curve shape, here for a scanrate of $100\,\mathrm{mV\,s^{-1}}$:



Task 5.2 (Influence of the double layer capacity on voltammetry)

Additionally to the faradaic current distributions from the redox process, the charging/discharging of the double layer capacity contributes to the measured current. For a scanrate of $100\,\mathrm{mV\,s^{-1}}$ and a double layer capacity of $c_{\mathrm{dl}} = 20\,\mathrm{\mu F\,cm^{-2}}$ the contribution is:

$$i_{\mathrm{c}} = c_{\mathrm{dl}} \cdot \frac{\mathrm{d}E}{\mathrm{d}t} = 20\,\mathrm{\mu F\,cm^{-2}} \times 100\,\mathrm{mV\,s^{-1}} = 0.002\,\mathrm{mA\,cm^{-2}}$$

Comparing the current densities of charging the double layer capacity to the values from Task 5.1 shows that the double layer capacity plays a minor role for CVs investigating redox-active species in the electrolyte. In contrast, the double-layer capacity largely contributes to the signal for higher scanrates like in fast-scan cyclic voltammetry (FSCV) or when measuring the surface reaction of the electrode material itself.

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