

Appendix B: Effect of current density on response time τ

The response time τ can be calculated for the stage where an electrical current is suddenly applied and when an electrical current is suddenly stopped (i.e. transition to OCV). In this appendix, we will show that the time scale for the voltage response, τ , is not equal in these two cases. Fig. B1 shows an example of the response time τ as a function of the current density j , for chronopotentiometric stages when a current density is suddenly applied or when a current density is suddenly stopped.

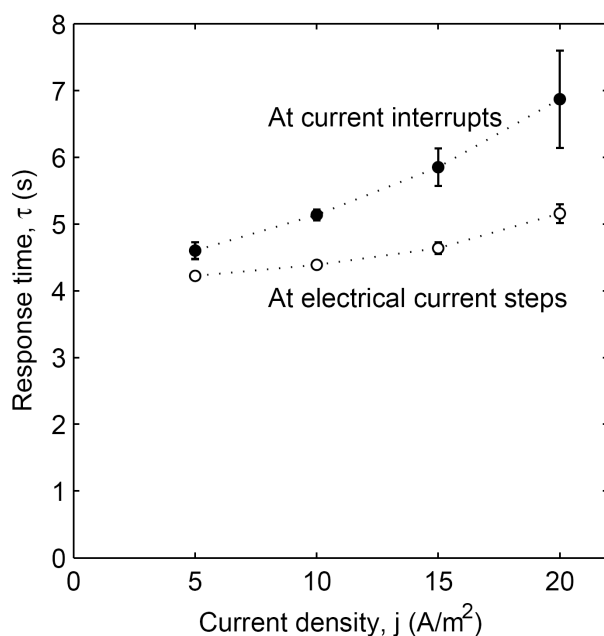


Figure B1: Experimentally derived time scale τ versus current density j , for chronopotentiometric stages when a current density is suddenly applied or when a current density is suddenly stopped, for a flow rate of 50 ml/min.

Fig. B1 shows that τ increases with increasing current density for stages when the current is interrupted, while τ is less dependent on the current density for stages when the current is suddenly applied. Moreover, the response time τ is in general larger for stages when

the current is interrupted compared to stages when the current is applied, as also demonstrated for the example in Fig. B1. Both effects can be explained when analyzing the derivative of the electromotive force as generated by each membrane, and regarding the local concentrations at the membrane-water interface. The electromotive force is given by the Nernst equation, corrected for activity coefficients and average permselectivity:

$$E = \alpha \frac{R \cdot T}{z \cdot F} \cdot \ln \left(\frac{\gamma_{c,m} \cdot c_{c,m}}{\gamma_{d,m} \cdot c_{d,m}} \right) \quad (\text{eq. B1})$$

In which E is the electromotive force (V), α is the permselectivity (-), R is the universal gas constant (8.314 J/(mol·K)), z is the valence of the ions (-), F is the Faraday constant (96485 C/mol), $c_{s,m}$ is the concentration at the interface between the seawater and the membrane (M) and $c_{r,m}$ is the concentration at the interface between the river water and the membrane (M). γ are the corresponding molar activity coefficients.

The derivates for the transient series of E to time t (in s) is:

$$\frac{\partial E}{\partial t} = \alpha \frac{RT}{zF} \frac{\partial \ln \left(\frac{\gamma_{c,m} \cdot c_{c,m}}{\gamma_{d,m} \cdot c_{d,m}} \right)}{\partial t} \quad (\text{eq. B2})$$

The temporal changes in activity coefficients are an order of magnitude smaller than that of the concentrations. Therefore, the activity coefficients are assumed steady. In other words, the activity coefficients are not neglected for the calculation of E, but assumed stationary for each individual compartment. This yields:

$$\frac{\partial E}{\partial t} \approx \alpha \frac{RT}{zF} \frac{\partial \ln \left(\frac{c_{c,m}}{c_{d,m}} \right)}{\partial t} \quad (\text{eq. B3})$$

Applying the chain rule and quotient rule for differentiating yields:

$$\frac{\partial E}{\partial t} \approx \alpha \frac{RT}{zF} \frac{c_{d,m}}{c_{c,m}} \frac{\partial \left(\frac{c_{c,m}}{c_{d,m}} \right)}{\partial t} \quad (\text{eq. B4})$$

$$\frac{\partial E}{\partial t} \approx \alpha \frac{RT}{zF} \frac{c_{d,m}}{c_{c,m}} \left(\frac{c_{d,m} \frac{\partial c_{c,m}}{\partial t} - c_c \frac{\partial c_{d,m}}{\partial t}}{c_{d,m}^2} \right) \quad (\text{eq. B5})$$

$$\frac{\partial E}{\partial t} \approx \alpha \frac{RT}{zF} \frac{1}{c_{c,m} \cdot c_{d,m}} \left(c_{d,m} \frac{\partial c_{c,m}}{\partial t} - c_c \frac{\partial c_{d,m}}{\partial t} \right) \quad (\text{eq. B6})$$

In practical cases, the derivative of the concentrations in the concentrated stream has an opposite sign to that in the diluted stream. Hence, this equation is easier to interpret as:

$$\frac{\partial E}{\partial t} \approx \alpha \frac{RT}{zF} \frac{1}{c_{c,m} \cdot c_{d,m}} \left(c_{d,m} \frac{\partial c_{c,m}}{\partial t} + c_{c,m} \frac{-\partial c_{d,m}}{\partial t} \right) \quad (\text{eq. B7})$$

Furthermore, the mixing conditions (i.e. flow rate and compartment geometry) in the concentrated and diluted compartment can be assumed equal. In that case, the concentration profile in the diffusive boundary layer of the concentrated stream is symmetrical to that in the diluted stream, and therefore the ionic transport (both by diffusion and due to the electrical field) is equal in magnitude. In other words, $\partial c_{c,m}/\partial t = -\partial c_{d,m}/\partial t = \partial c/\partial t$. That simplifies eq. B7 to:

$$\frac{\partial E}{\partial t} \approx \alpha \frac{RT}{zF} \frac{1}{c_{c,m} \cdot c_{d,m}} (c_{d,m} + c_{c,m}) \frac{\partial c}{\partial t} \quad (\text{eq. B8})$$

Because the sum of the diluted and concentrated solutions is constant (because equal mixing conditions were assumed), the only terms of interest are:

$$\frac{\partial E}{\partial t} \propto \frac{1}{c_{c,m} \cdot c_{d,m}} \frac{\partial c}{\partial t} \quad (\text{eq. B9})$$

This shows that the voltage response, after a sudden change in electrical current, is inversely proportional to the product of the diluted and concentrated concentrations. As a consequence, $\partial E/\partial t$ is largest when the diluted concentration (c_d) becomes very small, which occurs in practical cases when no electrical current is allowed for a while (OCV). In other words, the electromotive force E is more sensitive for the same change in concentration during the transition to OCV than during the transition towards a stage with an electrical

current. This explains why τ is larger when the electrical current is interrupted, compared to the τ when an electrical current is suddenly applied.

A larger change in current density increases the concentration change that is induced near the membrane-water interface. Therefore, τ increases for increasing current density at stages when the current is interrupted. The larger current density implies a larger ion transport, and therefore the concentrations near the membrane-water interface do have a larger change over time. In other words, the factor $\partial c/\partial t$ in eq. B9 is larger when the current density increases.

However, when the current density suddenly starts, the response time τ is not strongly affected. This is caused by two counteracting effects. The factor $\partial c/\partial t$ increases for larger current densities, but the larger ion transport rate decreases the factor $\frac{1}{c_{c,m} \cdot c_{d,m}}$ in eq. B9 for larger current densities. As these factors have a counteracting effect, the time scale τ is rather independent of the current density for stages when an electrical current is suddenly applied.