IV. Transport Phenomena

Lecture 19: Transient Diffusion

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In this lecture we show how to use simple scaling arguments to approximate the solution to transient diffusion problems, which arise in electrochemical energy systems. In each case, we will also briefly mention the related results from exact solutions to the diffusion equation to show how well the scaling analysis works. For further reading, see Bard & Faulkner, *Electrochemical Methods.*

1 Response to a Current Step

1.1 Sand's Time

Suppose we have a cell and we turn on the current at time $t = 0$, $I(t) = I\theta(t)$, where $\theta(t)$ is the Heaviside step function, and I is above the limiting current, we observe the concentration profiles indicated in Fig. 1. This current can be sustained for an amount known as 'Sand's time', which occurs when $c(x = 0) \to 0$ and $V \to 0$.

This is solved in 2009 previous notes and in Bard & Faulkner, *Electrochemical Methods.* Here we give a simple scaling analysis for t_{sand}:

Since $\Delta x \sim \sqrt{Dt}$ and the $A \sim Ft \sim \Delta x \Delta c$, and thus $\Delta c \sim \frac{Ft}{\sqrt{Dt}} = c_0$ at t_{sand}.

$$F\sqrt{\frac{t_{sand}}{D}} \sim c_0, F = \frac{I}{neA}$$

$$t_{sand} \sim \left(\frac{c_0 neA}{I}\right)^2 D$$

The exact solution to the diffusion equation is $t_{sand} = \frac{\pi}{4} D \left(\frac{c_0 n e A}{I} \right)^2$. Scaling arguments are very powerful!
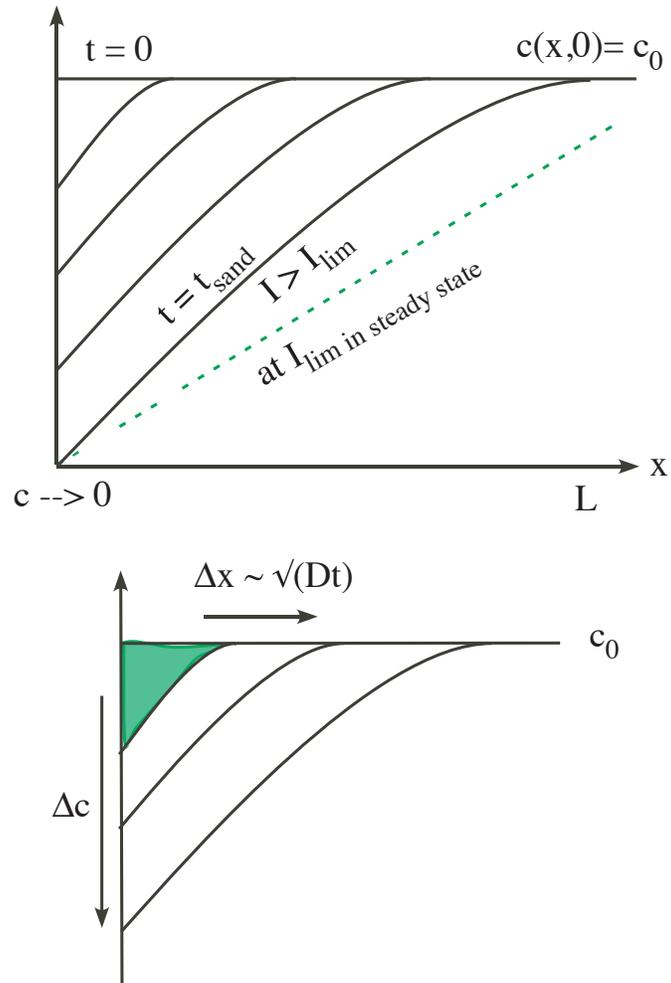
Figure 1: Top: We display how the concentration as a function of space progresses in time after we turn on a constant current $I > I_{lim}$ at $t = 0$. t_{sand} is the point in time beyond which the current I cannot be sustained anymore. since the concentration gradient cannot be maintained anymore once $c(x = 0) = 0$. Bottom: This is a magnified version of the top figure. The shaded region is the total amount of material transportedl and grow as Ft. The area of the shaded region, A, is proportiona to $\Delta c \Delta x$.

1.2 Chronopotentiometry (Voltage vs time at constant current)

Our scaling analysis implies $\frac{c(0)}{c_0} \sim 1 - \sqrt{\frac{t}{t_{sand}}}$ for $I > I_{lim}$. Both the Nernst equilibrium voltage and the activation overpotential tend to have logarithmic dependence $\Delta V \sim \ln \frac{c(0)}{c_0} \sim \ln \left(1 - \sqrt{\frac{t}{t_{sand}}}\right)$ as $c(0) \rightarrow 0$, for $I > I_{lim}$.
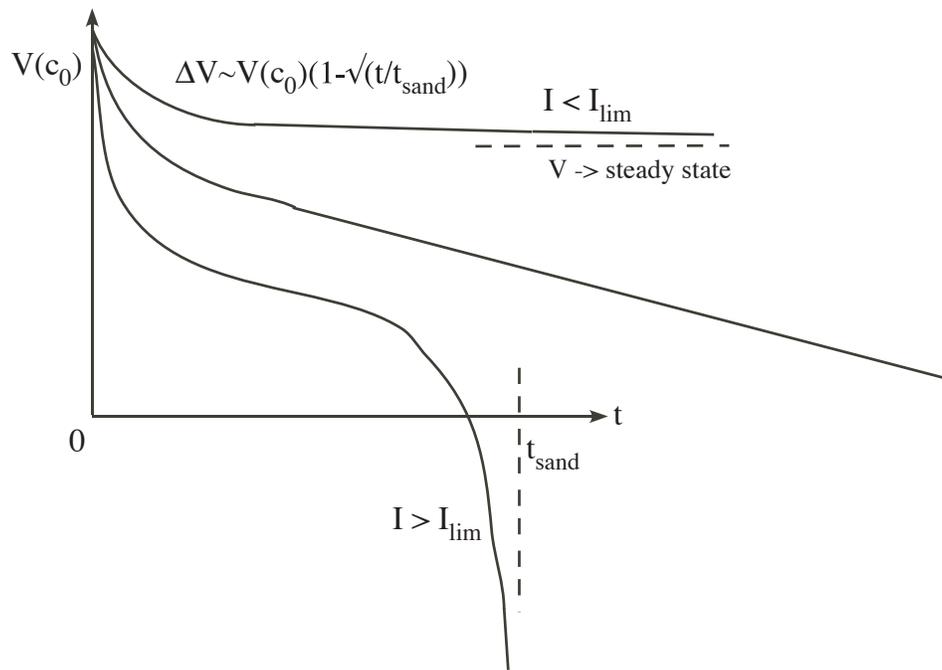

Figure 2: $V(t)$ for values of suddenly applied $I < I_{lim}$, $I = I_{lim}$ and $I > I_{lim}$ respectively. For small times, $\Delta V \sim V(c_0) \left(1 - \sqrt{\frac{t}{t_{sand}}}\right)$. For large times, $I < I_{lim}$ leads to a steady state voltage; $I = I_{lim}$ leads to a voltage hitting 0; and $I > I_{lim}$ diverges logarithmically at Sand's time.

1.3 Galvanostatic Intermittent Titration Technique (GITT)

Batteries can be tested by small slow current pulses, and the relaxation is fitted to Sand's solution of the diffusion equation to infer the diffusivity $D(c_0)$ vs state of charge c_0. In Fig. 3, we show the input current pulses and the voltage response. The dashed curves indicate the open-circuit voltage and the voltage response for some fixed $I > 0$ respectively. The two curves

form an envelope that bounds the actual function $V(It)$. The zigzag curves have a $\sqrt{\frac{t}{t_{sand}}}$ or $1 - \sqrt{\frac{t}{t_sand}}$ dependence as the V jumps back and forth between the OCV dashed curve to the $I > 0$ dashed curve.
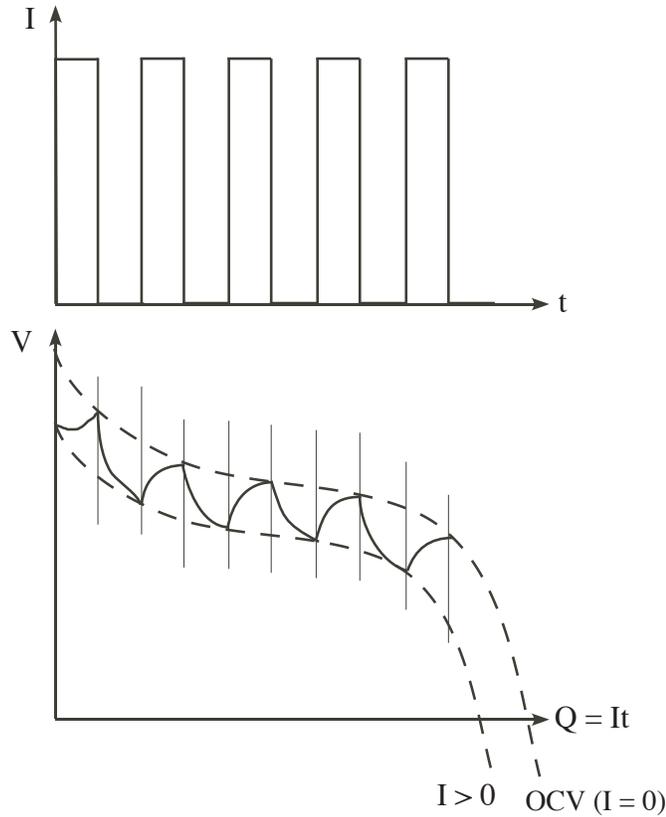

Figure 3: GITT: The dashed curves indicate the open-circuit voltage and the voltage response for some fixed $I > 0$ respectively.

2   Response to a Voltage Step

2.1   Cottrell Equation

For linear response, this is like a sudden concentration step at the electrode surface.

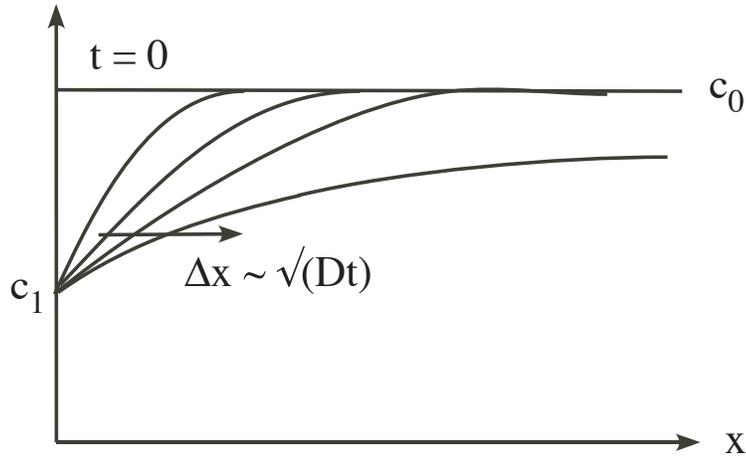We have the following boundary conditions:

Figure 4: If we fix the concentration at the boundary to be c_1, we observe how the current responds in time.

$$
\begin{aligned}
c(x,0) &= c_0 \\
c(0,t) &= c_1 \\
\frac{\partial c}{\partial t} &= D\frac{\partial^2 c}{\partial x^2}
\end{aligned}
$$

By scaling analysis, we have

$$
F = \frac{I}{neA} = D\frac{\partial c}{\partial x}(0,t) \sim D\frac{c_0 - c_1}{\sqrt{Dt}}
$$

Thus,

$$
I(t) \sim neA\Delta c\sqrt{\frac{D}{t}}
$$

The exact solution is given by:

$$
\begin{aligned}
\frac{c(x,t) - c_1}{c_0 - c_1} &= erf\left(\frac{x}{2\sqrt{Dt}}\right) \\
F &= D\frac{\partial c}{\partial x}(0,t) \\
&= \Delta c\frac{2}{\sqrt{\pi}}\frac{1}{2\sqrt{Dt}}
\end{aligned}
$$

where $erf(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-x^2} dx$. Thus, we obtain the *Cottrell Equation*:

$$I(t) = neA\Delta c \sqrt{\frac{D}{\pi t}}$$

Again, this result is the same as the one obtained from scaling analysis except for a factor of $\sqrt{\pi}$.

2.2   Potentiostatic Intermittent Titration Technique (PITT)

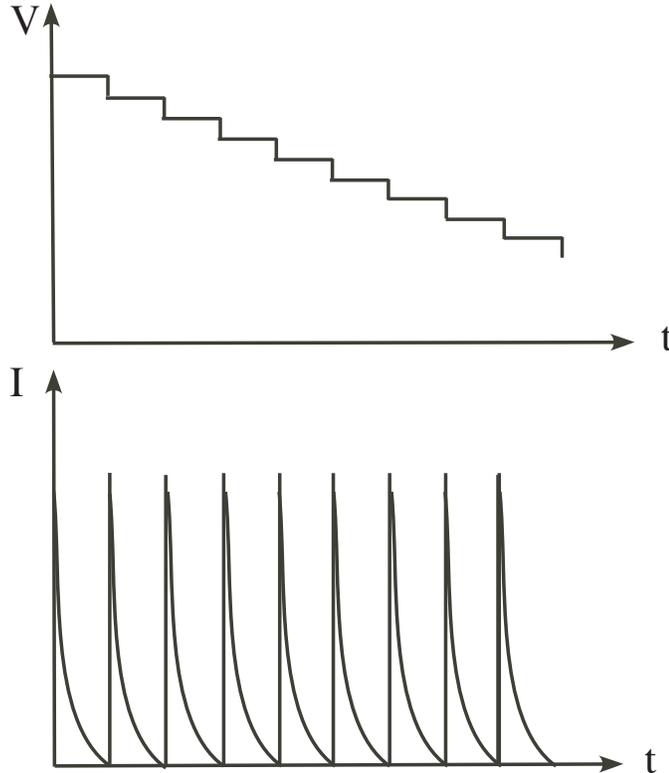We can characterize a battery by slow small voltage steps to infer $D(c_0)$.

Figure 5: The input voltage steps and current response, which goes as $\sqrt{\frac{D}{t}}$, are shown for PITT. $D(c_0)$ can be inferred from such measurements.

10.626 Electrochemical Energy Systems

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