

700

Lecture #17 of 20+

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The Double Layer

Chapter 13

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(UPDATED) 702

Q: What's in this set of lectures?

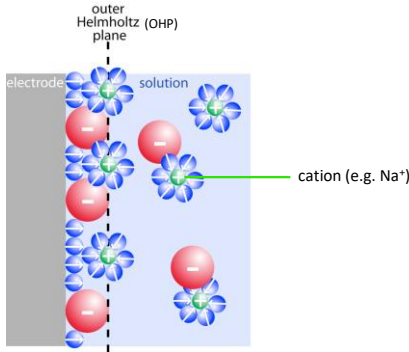
A: B&F Chapter 13 main concepts:

- Section 1.2.3: Double layer structure
- Sections 13.1 & 13.2: Gibbs adsorption isotherm, Electrocapillar(it)y, Surface excess, Lippmann's equation, Point of Zero Charge
- Section 13.3: Models: Helmholtz, Gouy–Chapman (Poisson–Boltzmann), Gouy–Chapman–Stern
- Section 13.5: Specific adsorption

702

... cations have strongly coordinated waters that exchange slowly...

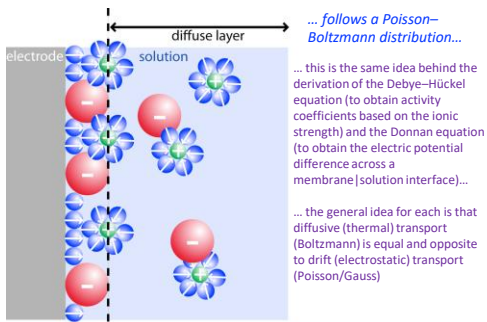
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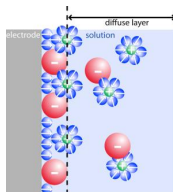
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... the (second) layer of solution extending from the OHP that has a composition perturbed from bulk is called the diffuse layer

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Notice particularly the following:

- 1) A layer of *oriented waters* covers the surface...
... water orientation (O or H) is dictated by the surface charge
- 2) Anions shed their primary hydration layers and directly adsorb onto the surface. This is called "specific adsorption"...
... with F^- being an exception
- 3) In general, cations do not specifically adsorb; their primary hydration layers are too strongly attached (by the ion-dipole interaction) to be shed at room temperature. This is an example of "nonspecific adsorption"...
... with $(CH_3)_4N^+$ being an exception

708

... now put it all together, and what do we have? 715
 ... recasting the difference in electric potential ($d\phi$) as the change in applied potential (dE)...

... we have the **electrocapillary equation** (B&F pp. 537–538)...

Recall $\bar{\mu} = \mu + zF\phi$

$$-d\gamma = \sigma^M dE + \sum_i \Gamma_i d\mu_i$$

the **surface tension** (units: energy/area, typically J m^{-2} or N m^{-1} ... these are identical)

$$\left(\gamma = \frac{\partial G}{\partial A} \right)$$

715

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the **surface excess concentration** of species i (units: moles/area), and sometimes called the **Gibbs surface excess**

716

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Recall $\bar{\mu} = \mu + zF\phi$

$$-d\gamma = \sigma^M dE + \sum_i \Gamma_i d\mu_i$$

the **chemical potential** of species i

... but where is the electric potential (ϕ) term?

717

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 Recall $\bar{\mu} = \mu + zF\phi$

$$-d\gamma = \sigma^M dE + \sum_i \Gamma_i d\mu_i$$

↑
 the change in potential between the WE and the RE

718

... now put it all together, and what do we have? 719
 ... recasting the difference in electric potential ($d\phi$) as the change in applied potential (dE)...

... we have the **electrocapillary equation** (B&F pp. 537–538)...

$$-d\gamma = \sigma^M dE + \sum_i \Gamma_i d\mu_i$$

... so measurement of the **surface tension** (γ) of a variable-area electrode as a function of its **potential** (E) is a direct way to get at its surface charge (density), σ^M . This is called **Lippmann's Equation**:
 (this means at constant chemical potential of all species)

We want to know this...
 ... or better yet, q^M
 ... or better yet, q^2

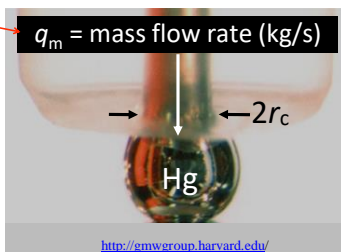
$$\sigma^M = - \left(\frac{d\gamma}{dE} \right)_{\mu_i}$$

Key Point: Measuring γ is easy if the electrode is a liquid...

719

... thus, our window into the double layer structure is the dropping mercury electrode (DME)... Seriously! 720

B&F used "m," but IUPAC prefers q_m



<http://gmwgroup.harvard.edu/>

... since drop moves slowly, $F_\gamma \approx F_{(g)gravity}$ (recall that $F_g = mg = (q_m t_{max})g$)

... and just before dropping...

$$t_{max} = \frac{2\pi r_c}{q_m g} \gamma$$

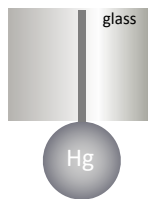
↑ acceleration due to gravity

(... recall that γ has units of $N m^{-1}$)

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... now, in a *dropping mercury electrode*, as the name implies...

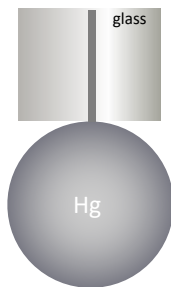
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... now, in a *dropping mercury electrode*, as the name implies...

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722

... now, in a *dropping mercury electrode*, as the name implies...

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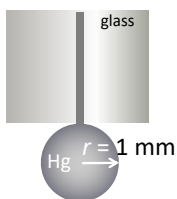


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... what do we measure during this process?

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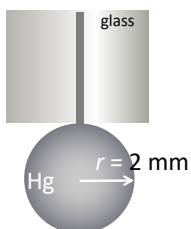


... suppose the electrode is at a potential where $\sigma^M = q^M/A = 25 \mu\text{C}/\text{cm}^2$
... what is the surface charge, q^M ?

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... what do we measure during this process?

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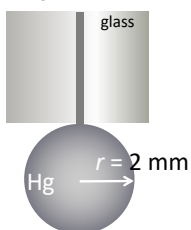


$$\begin{aligned} q^M &= (25 \times 10^{-6} \text{ C/cm}^2)(4\pi r^2) \\ &= (25 \times 10^{-6} \text{ C/cm}^2)4\pi(0.1)^2 \\ &= (25 \times 10^{-6} \text{ C/cm}^2)(0.126 \text{ cm}^2) \\ &= 3.14 \times 10^{-6} \text{ C} = \mathbf{3.14 \mu\text{C}} \end{aligned}$$

725

... what happens as the electrode grows?

726



... so even though the *potential is constant*,
... and even though *no Faradaic electrochemistry* is occurring,
... the Hg droplet grows (*surface area increases*),
... and thus current flows to its surface...
... and this current is proportional to q^M

726

... what happens as the electrode grows?



727

... after it falls, off, the current drops to a small value...

... and then the process repeats...

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... okay, so let's do an experiment... scan the potential (E) while we measure the current in 0.1 M HCl...

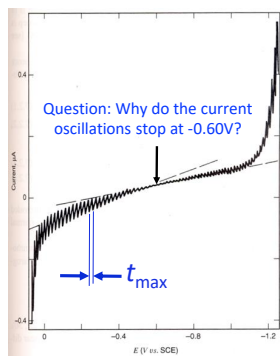


Figure 7.1.5 Residual current curve for 0.1 M HCl. The sharply increasing currents at potentials more positive than 0 V and more negative than -1.1 V arise from oxidation of mercury and reduction of H^+ , respectively. The current between 0 V and -1.1 V is largely capacitive. The PZC is near -0.6 V vs. SCE. (From L. Meites, "Polarographic Techniques," 2nd ed., Wiley-Interscience, New York, 1965, p. 101, with permission.)

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 7.1.5

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728

... okay, so let's do an experiment... scan the potential (E) while we measure the current in 0.1 M HCl...

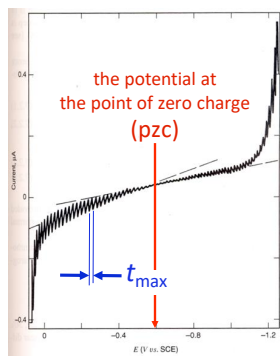


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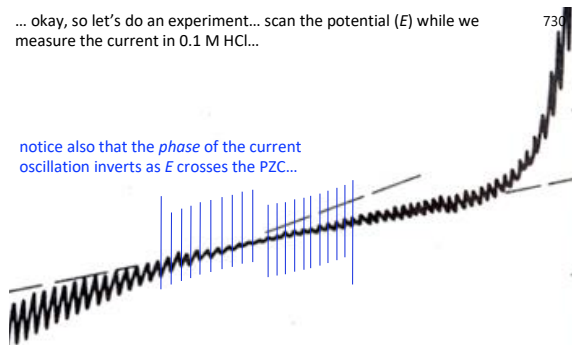
Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 7.1.5

729

729

... okay, so let's do an experiment... scan the potential (E) while we measure the current in 0.1 M HCl...

notice also that the *phase* of the current oscillation inverts as E crosses the PZC...



Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 7.1.5

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... a linear scan voltammogram acquired with a DME (and therefore called a *polarogram*)

... DMEs are "self-cleaning"

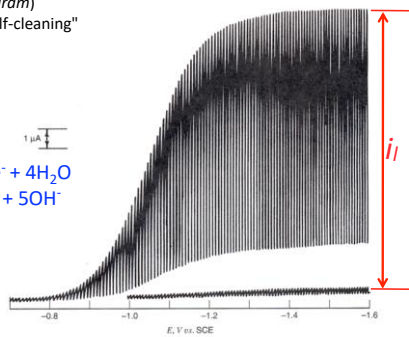
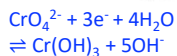


Figure 7.1.4 Polarogram for 1 mM CrO_4^{2-} in deaerated 0.1 M NaOH, recorded at a DME.

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... look familiar? ... It's just this:

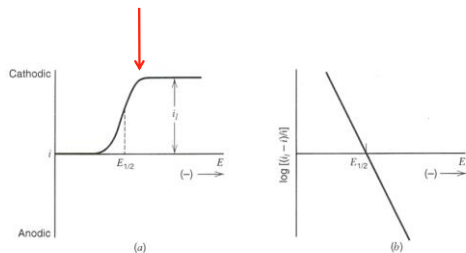
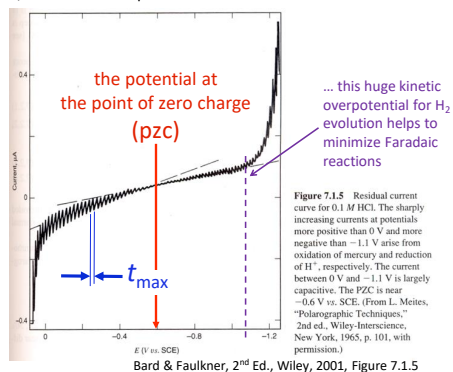


Figure 1.4.2 (a) Current-potential curve for a Nernstian reaction involving two soluble species with only oxidant present initially, (b) $\log[(i_l - i)/i]$ vs. E for this system.

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... okay, now going back to the case of 0.10 M HCl, let's measure the drop time, t_{max} , as a function of potential...

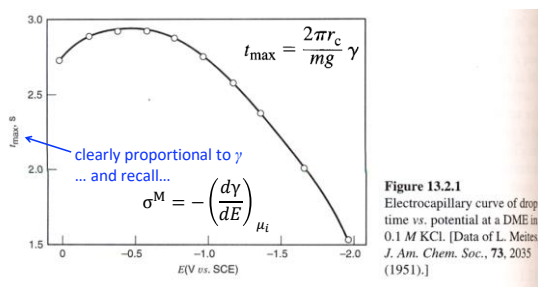


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... take the t_{max} versus E data and make a plot... and voila!...

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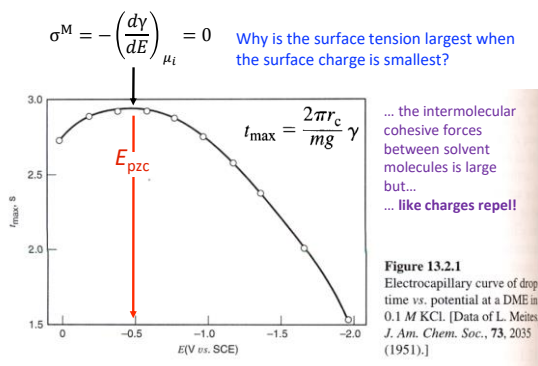


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... take the t_{max} versus E data and make a plot... and voila!...

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... here's what the C vs. E data actually look like as a function of concentration, for aqueous KF at a DME...

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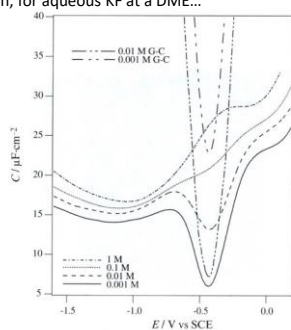


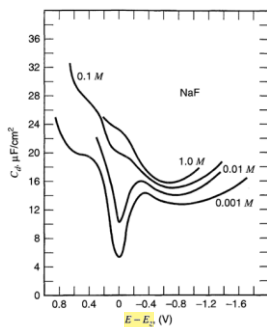
Fig. 5.13 Capacity of a mercury electrode in a KF solution ($pzc = -0.433V$) with the respective Gouy-Chapman capacity [Paolo Galletto, EPFL thesis].

H.H. Girault, *Analytical and Physical Electrochemistry*, EPFL Press, 2004, Figure 5.13

739

... data for aqueous NaF from B&F is qualitatively similar...

740



Flat? ... Eh; not really.

Why were both of these measured using fluoride salts?

In order to minimize specific adsorption!

Figure 13.3.1 Differential capacitance vs. potential for NaF solutions in contact with mercury at 25°C. [Reprinted with permission from D. C. Grahame, *Chem. Rev.*, **41**, 441 (1947). Copyright 1947, American Chemical Society.]

Grahame, *Chem. Rev.*, 1947, 41, 441

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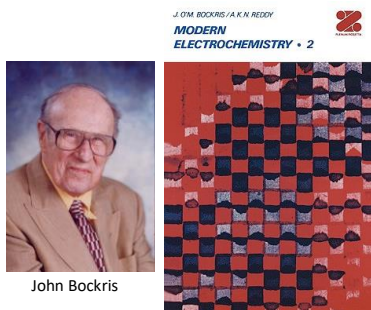
For the purposes of this class, we want to understand the microscopic origin of the *most prominent features* of these C_d vs. E data:

- A minimum in C_d exists at the pzc.
- C_d is quasi-constant at potentials well positive and well negative of the pzc.
- This quasi-constant C_d is larger when E is (+) of pzc than when it is (-) of pzc.
- C_d increases with salt concentration at all potentials, and the "dip" near the pzc disappears.

741

... do you want to understand the details of C_d away from the pzc?
Do you want to understand *the hump*? There is a book for that...

742



John Bockris

Bockris, *J. Chem. Educ.*, 1983, 60, 265

742

743

Three traditional models for double layer structure:

- 1) Helmholtz
- 2) Gouy–Chapman (GC)
- 3) Gouy–Chapman–Stern (GCS)

... let's take a look at each of these...

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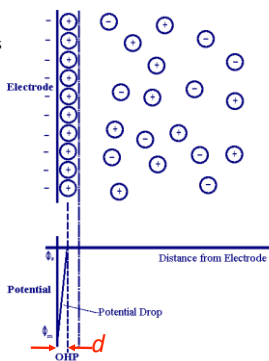
Models of Electrical Double Layer:

744

1) **The Helmholtz Model:** this is the simplest possible model. It postulates that ions (anions *and* cations) occupy a plane located a distance, d , from the electrode surface, and that the effective "dielectric constant" operating in the double layer is potential independent:

$$C_d = \frac{\epsilon\epsilon_0}{d}$$

... for a parallel plate capacitor, C is independent of E because the permittivity of the capacitor, $\epsilon\epsilon_0$, and its spacing, d , are both independent of applied potential...



<http://www.cartage.org.lb/>

744

... the Helmholtz model says that the electrical double layer acts like, and looks like (*rare in EChem*), a parallel plate capacitor... 745

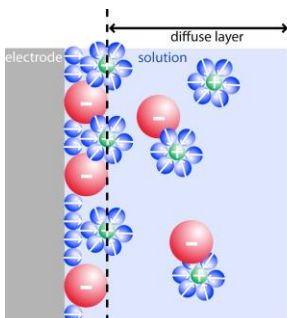
$$C_d = \frac{\epsilon\epsilon_0}{d}$$

... C_d is therefore independent of E because the permittivity of the capacitor, $\epsilon\epsilon_0$, and its spacing, d , are both independent of applied potential...

... Question: What value for C_d do we calculate by plugging in to this model the known "dielectric constant" (permittivity = IUPAC) of water?

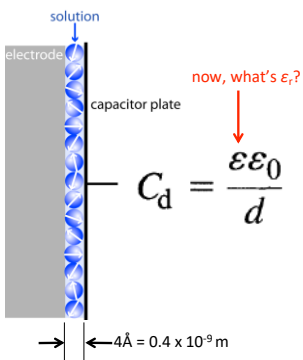
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... recall, here's what the double layer really looks like... 746



746

... and here's what the double layer looks like in the Helmholtz approximation... 747



747

... first, what's ϵ_r for water? Well, that depends... *can it rotate?* (BRIEFLY) 748

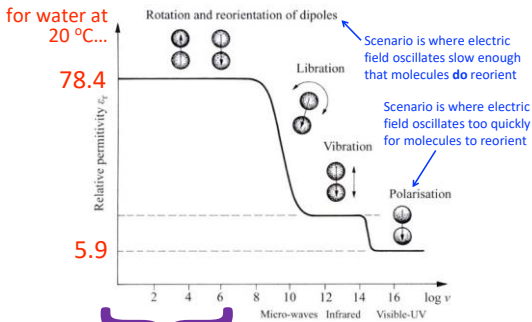
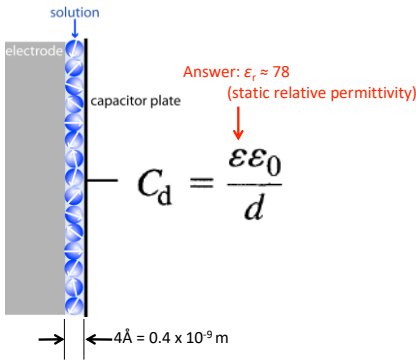


Fig. 1.7 Variation of the relative permittivity of water as a function of the applied electric field. *Electrochemical impedance spectroscopy range*

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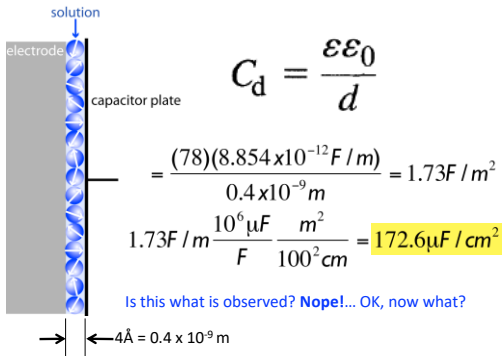
... and here's what the double layer looks like in the Helmholtz approximation... 749



749



... and here's what the double layer looks like in the Helmholtz approximation... 750



750



... now, what if the water dielectric is saturated, and thus fixed? 751

... so that water cannot rotate...

$$C_d = \frac{\epsilon_r \epsilon_0}{d}$$

$$C = \frac{(6)(8.854 \times 10^{-12} \text{ F/m})}{0.4 \times 10^{-9} \text{ m}} = 0.133 \text{ F/m}^2$$

$$0.133 \text{ F/m} \frac{10^6 \mu\text{F}}{\text{F}} \frac{\text{m}^2}{100^2 \text{ cm}^2} = 13.3 \mu\text{F/cm}^2$$

... much more reasonable!



751

... if the Helmholtz model is correct, we'd get this exactly: (BRIEFLY) 752

$$\sigma^M = -\left(\frac{d\gamma}{dE}\right)_{\mu_i} \quad C_d = \left(\frac{\partial \sigma^M}{\partial E}\right)$$



752

... here are electrocapillary data for various electrolytes... (BRIEFLY) 753

... hey, you can already see that the Helmholtz Model fails a little...

... mostly on the left...

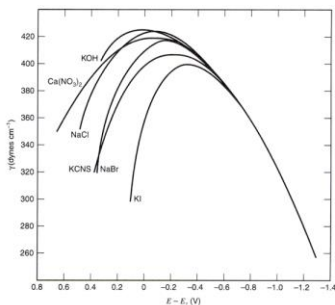


Figure 13.2.2 Electrocapillary curves of surface tension vs. potential for mercury in contact with solutions of the indicated electrolytes at 18°C. The potential is plotted with respect to the PZC for NaF. [Reprinted with permission from D. C. Grahame, *Chem. Rev.*, 41, 441 (1947). Copyright 1947, American Chemical Society.]



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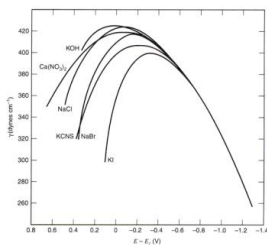


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(BRIEFLY) 754

Notwithstanding, notice particularly the following:

- the γ vs. E parabola is independent of salt...
... at potentials negative of the pzc...
- ... but strongly dependent on salt positive of pzc...
- ... and pzc itself depends on the electrolyte...
... we'll get to this shortly...

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