Scaling Analysis of Energy Storage by Porous Electrodes

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May 14, 2012

1 Theoretical Capacity

The maximum theoretical capacity occurs as $\epsilon_i \to 0, \epsilon_p \to 0 \Rightarrow \epsilon_a \to 1$, where ϵ_i, ϵ_p, and ϵ_a are the volume fractions of inactive material, pores, and active material in the electrode respectively. First we define the volumetric energy density

$$\mathcal{E} = \frac{\text{energy}}{\text{volume}} = \epsilon_a \mathcal{E}_a \qquad (1.1)$$

where $\mathcal{E}_a$ is the maximum theoretical volumetric energy density of the active material. Our analysis below is very general and applies to a wide range of energy storage devices. For example, we consider the fundamental scalings for a battery and or (super)capacitor.

Battery

We consider a porous electrode with an active material containing ions of charge (ze) at a concentration c_s. By dimensional analysis, we obtain an approximation for the energy density of the battery:

$$\mathcal{E}_a = (ze)c_s V \ [=] \ \frac{charge}{ion} * \frac{ion}{volume} * \frac{energy}{charge} \ [=] \ \frac{energy}{volume}. \qquad (1.2)$$

where V is a representative voltage (energy/charge). This may be taken as the open circuit voltage, but in practice would be less than this limit.

(Super)capacitor

Here we consider the model where we have a porous charged electrode with double layers forming and storing charge. Then the "active" area lies along the interface between the inactive material and pores at a characteristic width λ,

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which may be the Debye length in the case of thin double layers, or may be a characteristic ion size in the case of ionic liquids. Then, we can define the "active area" as

$$\epsilon_a = \lambda a_p. \tag{1.3}$$

where a_p is the area density of the pore [=] surface area of pore per total volume.

Assuming a linear response (i.e. that the capacitance of the double layer does not depend on the voltage), we can approximate the stored charge per area as the capacitance per area of the double layer times a characteristic voltage.

$$q_s = C_s V \approx \frac{\varepsilon}{\lambda} V \tag{1.4}$$

where ε is the dielectric constant in the pores. We qualitatively compare this stored charge per area in electrolyte solutions and ionic liquids in Table 1.

electrolyte solution	$\lambda \approx \lambda_D$ (larger)	larger ε
ionic liquid	$\lambda \approx$ ion size (smaller)	smaller ε

Table 1: Comparison of capacitance parameters for electrolyte solutions and ionic liquids.

Then, again by dimensional analysis, the energy density of the active material can be approximated by

$$\mathcal{E}_a = \frac{q_s V}{\lambda} \; [=] \; \frac{\frac{charge}{area} * \frac{energy}{charge}}{length} \; [=] \; \frac{energy}{volume}. \tag{1.5}$$

Substituting in the expression for q_s above,

$$\mathcal{E}_a = \frac{\varepsilon V^2}{\lambda^2}. \tag{1.6}$$

2 Balance of Electrodes

Consider the system of an anode and cathode electrode separated by a "separator" as in Figure 1. Now, we note that if it is desired that the system be rechargeable, we want $\mathcal{E}_A L_A \approx \mathcal{E}_C L_C$, where $\mathcal{E}_A$ and $\mathcal{E}_C$ are the energy densities of the anode and cathode respectively. Thus, the same total amount of energy can be stored in each electrode. If this balance is not approximately satisfied, there will be wasted volume in the electrode with more total energy capacity. Assuming this balance is satisfied, we can write the total energy stored per system volume as

$$\mathcal{E} = \frac{\mathcal{E}_C L_C}{L_C + L_S + L_A} \approx \frac{\mathcal{E}_A L_A}{L_C + L_S + L_A}. \tag{2.1}$$
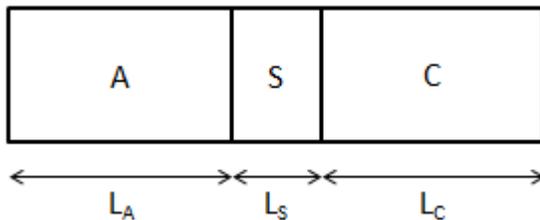
Figure 1: Model electrode system with an anode, A, cathode, C, and separator, S, and associated lengths.

Using the first definition, and dividing through by $\mathcal{E}_A L_C$,

$$\frac{\mathcal{E}}{\mathcal{E}_A} = \frac{(\mathcal{E}_C/\mathcal{E}_A)}{1 + \frac{L_S}{L_C} + \frac{L_A}{L_C}} \tag{2.2}$$

$$= \frac{(\mathcal{E}_C/\mathcal{E}_A)}{1 + \frac{L_S}{L_C} + \frac{\mathcal{E}_C}{\mathcal{E}_A}}. \tag{2.3}$$

A plot of this relationship is found in Figure 2.

3   Optimization of Electrode Thickness

Here we begin by assuming the electrodes are reasonably well balanced and analyze the effects of the thickness of a given electrode. We note that this is likely a very reasonable assumption for supercapacitor in which the two electrodes may be two identical porous materials. For simplicity, we consider a "half-system" – a single electrode with ϵ_i, ϵ_a, ϵ_p, length L, and half of a separator with length L_S. Intuitively we see that a large value of L is good for energy density, but adversely affects transport, limiting power density. Define

$$\mathcal{E} = \frac{energy}{total\ volume} = \frac{\epsilon_a \mathcal{E}_a L}{L + L_S} \tag{3.1}$$

where $cale_a$ is the energy density of the active material, and (assuming dissipative power)

$$\mathcal{P} = \frac{power}{total\ volume} = \frac{\sigma E^2 L}{L + L_S} = \frac{\sigma(V/L)^2 L}{L + L_S} \tag{3.2}$$

where the factors of $L/(L + L_S)$ account for the fact that energy/power density come only from the electrode. We again assume that σ is a function of the porosity, ϵ_p,

$$\sigma = \sigma_p f(\epsilon_p) \tag{3.3}$$

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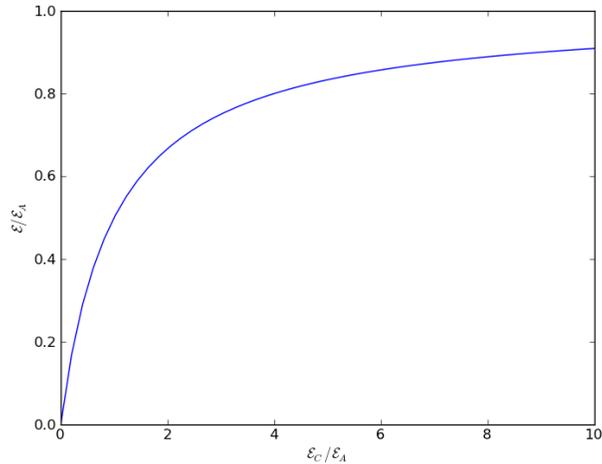
Figure 2: Ratio of total energy density per anode energy density compared to the ratio of cathode/anode energy densities. To the left of 1 is the case with a large cathode (low cathode energy density) and right of 1, the anode is large.

where σ_p is the conductivity in the pores and $f(\epsilon_p)$ is a factor reflecting the microstructure (next section).

Also, define the following dimensionless variables:

$$\tilde{\mathcal{E}} = \frac{\mathcal{E}}{\mathcal{E}_a} \tag{3.4}$$

$$\tilde{\mathcal{P}} = \frac{\mathcal{P}}{\sigma_p \left(\frac{V}{L_S}\right)^2} \tag{3.5}$$

$$\tilde{L} = \frac{L}{L_S}. \tag{3.6}$$

We choose L_S as the length scale for the non-dimensional power, because we will optimize electrode length. The dimensionless power density can be rewritten as

$$\tilde{\mathcal{P}} = \frac{\frac{\sigma(V/L)^2 L}{L+L_S}}{\sigma_p \left(\frac{V}{L_S}\right)^2} \tag{3.7}$$

$$= \frac{f(\epsilon_p)\tilde{L}}{\tilde{L}^2(1+\tilde{L}} \tag{3.8}$$

$$= \frac{f(\epsilon_p)}{\tilde{L}(1+\tilde{L})}. \tag{3.9}$$

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Similarly,

$$\tilde{\mathcal{E}} = \frac{\mathcal{E}}{\mathcal{E}_a} = \frac{\epsilon_a \tilde{L}}{1 + \tilde{L}} \Rightarrow \epsilon_a = \tilde{\mathcal{E}}(1 + \tilde{L}^{-1}). \tag{3.10}$$

Now, noting that $\epsilon_p + \epsilon_i + \epsilon_a = 1$, we can substitute this into the power expression to relate the dimensionless energy and power densities:

$$\boxed{\tilde{\mathcal{P}}\tilde{L}(1 + \tilde{L}) = f\left(1 - \epsilon_i - \tilde{\mathcal{E}}(1 + \tilde{L}^{-1})\right)}. \tag{3.11}$$

This is the *dimensionless Ragone relation*, which should collapse experimental data over large classes of porous electrode energy storage systems.

Also, we note that the energy density is maximized when the pore volume fraction goes to zero (maximizing $\epsilon_a = 1 - \epsilon_i$). Then

$$\tilde{\mathcal{E}}_{max} = \frac{(1 - \epsilon_i)\tilde{L}}{1 + \tilde{L}}. \tag{3.12}$$

And the power density is maximized as $\epsilon_a \to 0$, or $\epsilon_p \to \epsilon_i - 1$. Then, using the Wiener upper bound for the function f (below)

$$\tilde{\mathcal{P}}_{max} = \frac{1 - \epsilon_i}{\tilde{L}(1 + \tilde{L})}. \tag{3.13}$$

These functions are plotted in Figure 3 and 4. We see that a value for $\tilde{L}$ of approximately 1 represents a good compromise between maximum obtainable power and energy density.

3.1 Conductivity Bounds

The effective conductivity can be determined numerically (or sometimes analytically) for a particular microstructure, but it is not widely appreciated in electrochemistry that there are rigorous mathematical bounds on its possible values. Assuming that ions can only pass through the pores, the maximum conductance for any *anisotropic pore structure* is given by the Wiener upper bound,

$$f(\epsilon_p) \le f_W(\epsilon_p) = \epsilon_p \quad \text{(anisotropic)} \tag{3.14}$$

which is attained by straight parallel pores (resistors in parallel), aligned with the current. The maximum conductance for any *isotropic 3D pore structure* is given by the Hashin-Shtrikman upper bound

$$f(\epsilon_p) \le f_{HS}(\epsilon_p) = \frac{2\epsilon_p}{3 - \epsilon_p} \quad \text{(3D isotropic)} \tag{3.15}$$

which is attained by a random core-shell microstructure with non-conducting cores and conducting shells. *These formulae provide rigorous bounds on the*
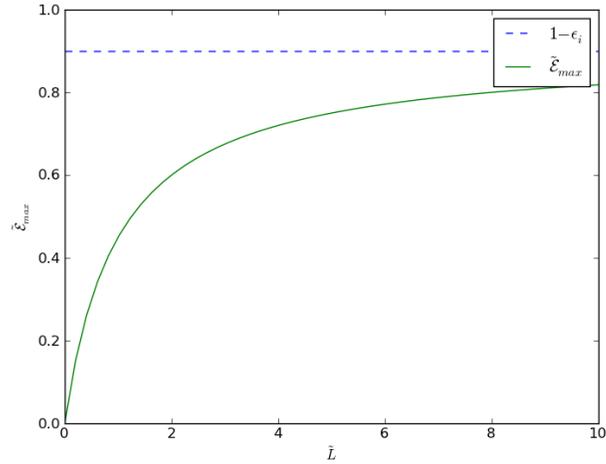
Figure 3: The maximum dimensionless energy density as a function of the dimensionless length with $\epsilon_i = 0.1$. Note that it approaches a theoretical limit as $\tilde{L} \to \infty$.
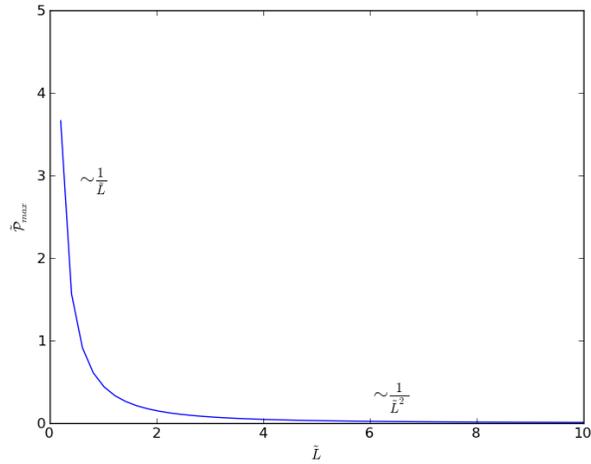
Figure 4: The maximum dimensionless power density as a function of the dimensionless length with $\epsilon_i = 0.1$. Here, low values of $\tilde{L}$ maximize the objective.
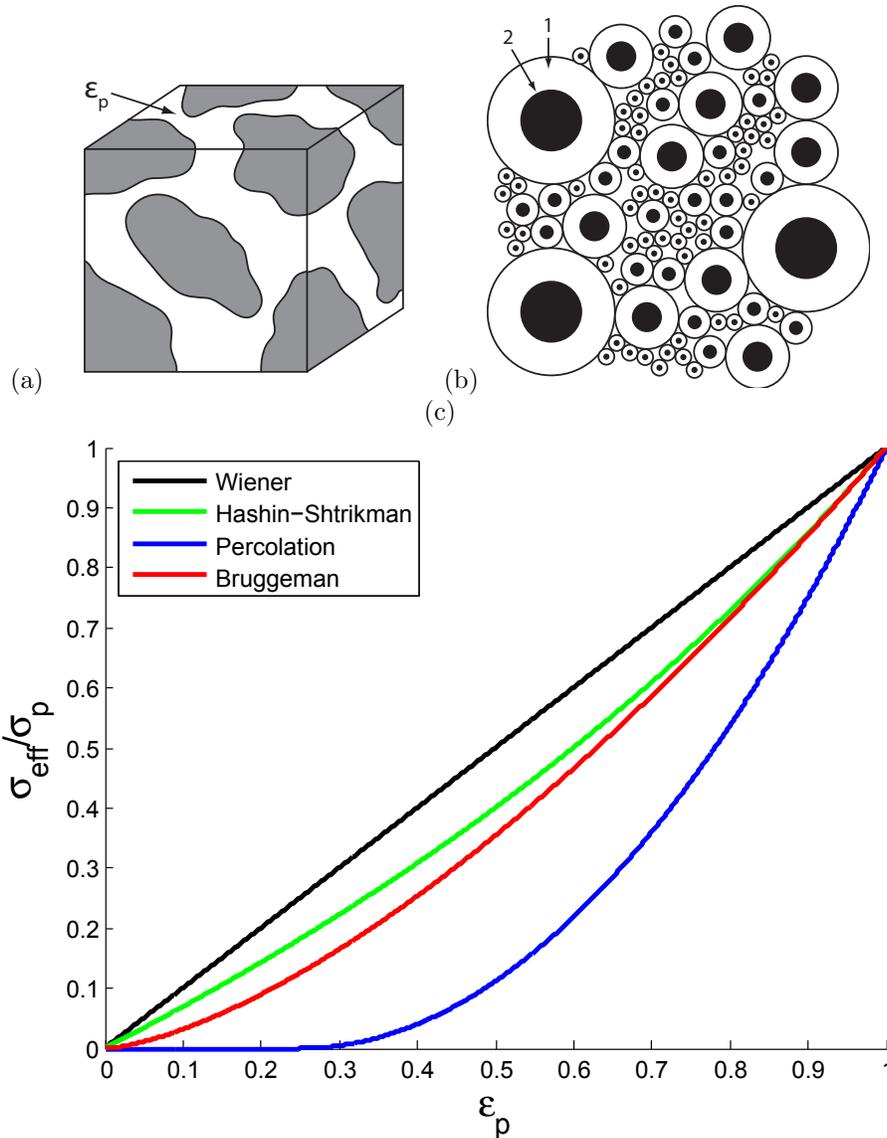
Figure 5: (a) Typical porous volume. (b) Space-filling random core-shell microstructure which attains the Hashin-Shtrikman upper bound on conductivity of isotropic two-phase microstructures. (c) Comparison of models of effective conductivity $\sigma/\sigma_0 = f(\epsilon_p)$ with conducting pores in a nonconducting matrix. The Wiener upper bound for anisotropic microstructure, attained by parallel stripes aligned with the current; the HS upper bound; the empirical Bruggeman relation used in electrochemistry, and a statistical percolation model in three dimensions. [Figures courtesy of Todd Ferguson]

Ragone relation, which can be exceeded only by changing the materials, and not by changing the porous microstructure.

It is interesting to note that the empirical Bruggeman relation

$$f_B(\epsilon_p) = \epsilon_p^{3/2} \quad \text{(Bruggeman)} \tag{3.16}$$

which is often used in electrochemistry, happens to be close to the HS upper bound in three dimensions, except at low porosity where it is smaller. Theoretically, this makes sense, since a liquid-soaked porous material has a percolating conducting phase similar to the optimal HS core-shell microstructure, except at low volume fraction, where pore-blocking occurs more easily and lowers the conductivity, as in statistical percolation models.

4   Optimization of Microstructure

Here, we suppose that we have a good electrode size balance (Section 2) and size (Section 3). Then, to eliminate length concerns, define

$$\bar{\mathcal{P}} = \tilde{\mathcal{P}}\tilde{L}(1 + \tilde{L}) \tag{4.1}$$

$$\bar{\mathcal{E}} = \tilde{\mathcal{E}}(1 + \tilde{L}^{-1}) \tag{4.2}$$

and the dimensionless Ragone relation (Equation 3.11), is simplified to

$$\bar{\mathcal{P}} = f\left(1 - \epsilon_i - \bar{\mathcal{E}}\right). \tag{4.3}$$

We can use the Wiener and Hashin-Shtrikman upper bounds to get feasible regions in the dimensionless Ragone Plot. The Hashin-Shtrikman bound (in 3 dimensions),

$$\bar{\mathcal{P}}_{HS} = \frac{2(1 - \epsilon_i - \bar{\mathcal{E}})}{2 + \epsilon_i + \bar{\mathcal{E}})}. \tag{4.4}$$

is the upper limit for isotropic microstructures, which is typically the case when a porous electrode is fabricated from powders and grains in a dense paste, without any spatial bias. The Wiener upper bound,

$$\bar{\mathcal{P}}_W = 1 - \epsilon_i - \bar{\mathcal{E}}, \tag{4.5}$$

is the upper limit for general anisotropic microstructures, attained by straight pores parallel to the current. The difference between these bounds quantifies the possible gain in going from isotropic to anisotropic microstructures, as shown in Figure 6.

5   Fixed Charging Time, τ

Any optimization of an energy storage system must take into account the typical time scale for charge or discharge, set by the desired application. Here we
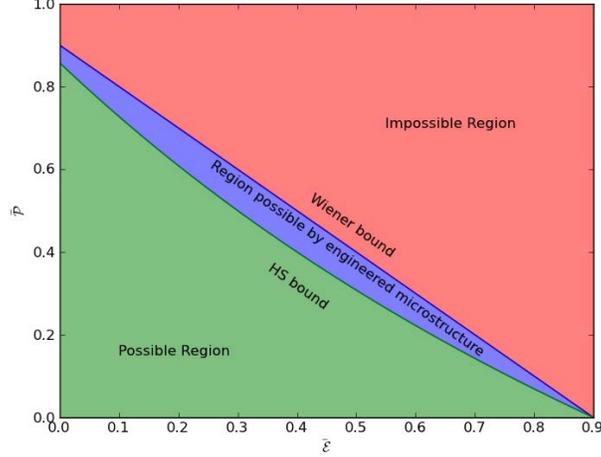
Figure 6: Dimensionless Ragone plot with theoretical bounds and $\epsilon_i = 0.1$.

continue with analysis of the length-optimized system in terms of $\bar{\mathcal{P}}$ and $\bar{\mathcal{E}}$. By definition, with charging time scale, τ, the power density and energy density are approximately related by

$$\mathcal{P} = \frac{\mathcal{E}}{\tau}. \tag{5.1}$$

Also, there is some $\bar{\tau}$ such that

$$\bar{\mathcal{P}} = \frac{\bar{\mathcal{E}}}{\bar{\tau}} = f(1 - \epsilon_i - \bar{\mathcal{E}}). \tag{5.2}$$

In the anisotropic (Wiener) limit,

$$\frac{\bar{\mathcal{E}}}{\bar{\tau}} = 1 - \epsilon_i - \bar{\mathcal{E}}. \tag{5.3}$$

Solving for $\bar{\mathcal{E}}$ and denoting this as the Wiener limit, $\bar{\mathcal{E}}_W$, we see that

$$\bar{\mathcal{E}} \leq \bar{\mathcal{E}}_W = \frac{1 - \epsilon_i}{1 + \bar{\tau}^{-1}} = (1 - \epsilon_i)\frac{\bar{\tau}}{1 + \bar{\tau}}, \tag{5.4}$$

which has the exact same shape as that of Figure 3, based on Equation 3.12. In the case of the power density, we see that

$$\bar{\mathcal{P}} = \frac{\bar{\mathcal{E}}}{\bar{\tau}} \leq \bar{\mathcal{P}}_W = \frac{\bar{\mathcal{E}}_W}{\bar{\tau}} = \frac{1 - \epsilon_i}{1 + \bar{\tau}}, \tag{5.5}$$

which is plotted in Figure 7. Thus, we see that to balance energy and power

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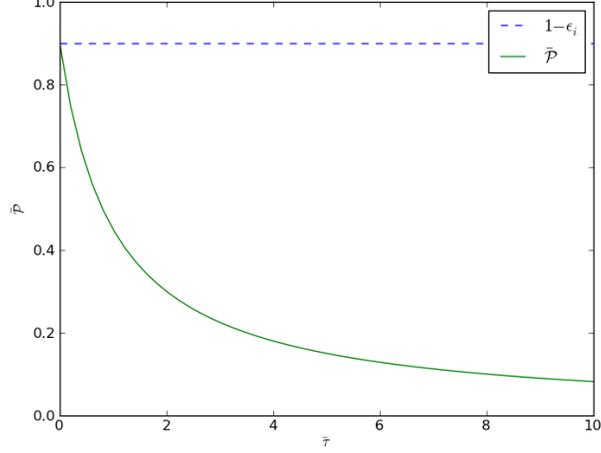
Figure 7: Length-adjusted power density, $\epsilon_i = 0.1$. Note it is maximized at high discharge rates.

density, we want $\bar{\tau} \approx 1$.

What is the dimensionless time, $\bar{\tau}$? By definition

$$\bar{\tau} = \frac{\bar{\mathcal{E}}}{\bar{\mathcal{P}}} = \frac{\tilde{\mathcal{E}}(1 + \tilde{L}^{-1})}{\tilde{\mathcal{P}}\tilde{L}(1 + \tilde{L})} = \frac{\tilde{\mathcal{E}}}{\tilde{\mathcal{P}}\tilde{L}^2} = \frac{\mathcal{E}/\mathcal{E}_a}{\frac{\mathcal{E}/\tau}{\sigma_p(V/L_S)^2}\left(\frac{L}{L_S}\right)^2} = \frac{\tau\sigma_p V^2}{\mathcal{E}_a L^2} = \frac{\tau}{\tau_{ref}} \qquad (5.6)$$

where

$$\tau_{ref} = \frac{\mathcal{E}_a L^2}{\sigma_p V^2}. \qquad (5.7)$$

We again consider two cases, and examine interpretations for τ_{ref} for batteries and supercapacitors.

Battery: Substituting in $\mathcal{E}_a$,

$$\tau_{ref} = \frac{\mathcal{E}_a L^2}{\sigma_p V^2} = \frac{zec_s L^2}{\sigma_p V} = \frac{L}{\sigma_p A}\frac{ALzec_s}{V}, \qquad (5.8)$$

where A is a representative cross sectional area of the electrode. Examining the first term, we see that it is a resistance, while the second term is a capacitance – the "pseudocapacitance" of a battery. Thus, we can interpret this τ_{ref} as an RC time.

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Supercapacitor: Substituting in $\mathcal{E}_a$,

$$\tau_{ref} = \frac{\varepsilon V^2}{\lambda^2} \frac{L^2}{\sigma_p V^2} = \frac{\varepsilon}{\sigma_p} \left(\frac{L}{\lambda} \right)^2 . \tag{5.9}$$

The first term here is known as a "relaxation time" of the electrolyte. In a perhaps more familiar interpretation of this term, we can substitute in a relation for σ_p and use the definition of the Debye length

$$\sigma_p = \frac{\sum_i (z_i e)^2 c_0 D}{k_B T} \tag{5.10}$$

$$\lambda_D^2 = \frac{\varepsilon k_B T}{\sum_i (z_i e)^2 c_0}, \tag{5.11}$$

so that

$$\sigma_p = \lambda_D^{-2} D \varepsilon \tag{5.12}$$

where we have assumed similar diffusivities for each species. Then, we have

$$\tau_{ref} = \frac{\varepsilon}{\sigma_p} \left(\frac{L}{\lambda} \right)^2 = \frac{\lambda_D^2}{D} \left(\frac{L}{\lambda} \right)^2 = \frac{L^2}{D} \left(\frac{\lambda_D}{\lambda} \right)^2 \tag{5.13}$$

which is a diffusion time through the electrolyte. Thus, for a supercapacitor, we interpret τ_{ref} as related to either the electrolyte relaxation time or a diffusion time through the electrolyte.

6   Optimal Electrode Thickness for a Given Time Scale

Because we have seen we want $\bar{\tau} \approx 1$, if we choose a characteristic discharging time, we can optimize over L. We note that $\bar{\tau}$ and $\bar{\mathcal{E}}$ have length scales "buried" in them, so we consider $\tilde{\mathcal{E}}$.

$$\tilde{\mathcal{E}} = \frac{\bar{\mathcal{E}}}{1 + \tilde{L}^{-1}} \leq \frac{\bar{\mathcal{E}}_W}{1 + \tilde{L}^{-1}} = \frac{1 - \epsilon_i}{(1 + \tilde{L}^{-1})(1 + \bar{\tau}^{-1})}. \tag{6.1}$$

Also, note that we can write $\bar{\tau}$ as

$$\bar{\tau} = \frac{\tau \sigma_p V^2}{\mathcal{E}_a L^2} = \frac{L_{RC}^2}{L^2} \tag{6.2}$$

where

$$L_{RC} = \frac{\tau \sigma_p V^2}{\mathcal{E}_a}. \tag{6.3}$$
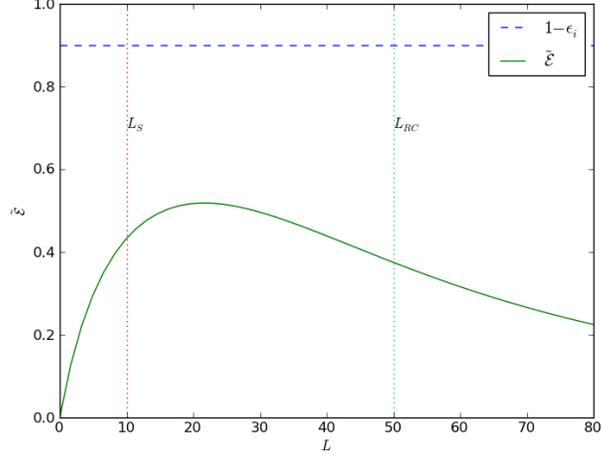
Figure 8: Dimensionless energy density as a function of length with $\epsilon_i = 0.1$, a specified τ, and $L_S < L_{RC}$. We see the energy density increases with L until L_S, at which point it approaches a maximum, then decays as it approaches and passes L_{RC}.

Now, because $\tilde{L}^{-1} \sim \frac{1}{L}$ and $\bar{\tau}^{-1} \sim L^2$, we see that we will have a maximum. A plot of this relationship is presented in 8. To the left of the graph is the case where L is small relative to the separator, so the energy density is low. To the right, we wee that, $L \gg L_{RC}$, so $\bar{\tau} \ll 1$. As we saw in Equation 5.4 and the shape of Figure 3, this leads to low energy density. Conceptually this can be interpreted that, in order to maintain a specified discharge time, ϵ_p must increase, leading to a decrease in ϵ_a and an associated decrease in the energy density. We see the effect of low and increasing L_{RC} in Figure 9. Thus, we can see that we want $L_{RC} \gg L_S$, and if $L_S \sim L$ ($\tilde{L} \sim 1$), we then desire that $\tau \gtrsim \frac{\mathcal{E}_a L_S^2}{\sigma_p V^2}$, or

$$\tau \gtrsim \begin{cases} \frac{zec_s L_S^2}{\sigma_p V} & \text{battery} \\ \frac{\varepsilon}{\sigma_p} \frac{L_S^2}{\lambda^2} & \text{supercapacitor} \end{cases} \tag{6.4}$$

$$= \tau_{RC}. \tag{6.5}$$

So we note that if $\tau < \tau_{RC}$, charging in the given time does not penetrate the full electrode, so energy density goes down. In other words, if the charging time is less than τ_{RC}, we find that the penetration distance (the effective thickness actually charged), L, of the charging is less than that of the electrode L_e (See Figure 10). Then, because

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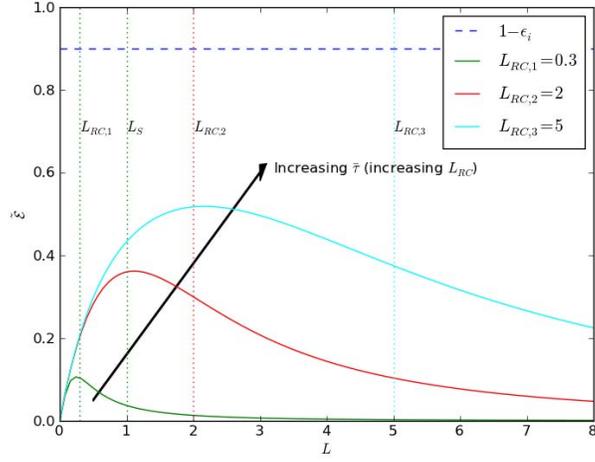
Figure 9: Dimensionless energy density as a function of length with $\epsilon_i = 0.1$ and increasing values of τ (increasing L_{RC}). We see that while $L_{RC} < L_S$, the maximum energy density remains low, but when $L_{RC} > L_S$, the maximum energy density gets closer to the theoretical limit of $1 - \epsilon_i$.
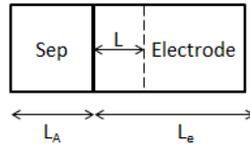
Figure 10: Schematic of the penetration length L, as compared to the full electrode length L_e, when $\tau < \tau_{RC}$.

$$\tau_{RC} = \hat{R}\hat{C}L_e^2, \tag{6.6}$$

$$L \sim \sqrt{\frac{\tau}{\hat{R}\hat{C}}}, \tag{6.7}$$

where $\hat{R}$ and $\hat{C}$ are the resistance and capacitance per length. We can relate the penetration length L to the charging time scale τ.

$$L = \begin{cases} L_e & \tau \gtrsim \tau_{RC} \\ \sqrt{\frac{\tau}{\hat{R}\hat{C}}} = \sqrt{\frac{\tau\sigma_p\lambda^2}{\varepsilon}} = \sqrt{D\tau} & \tau \ll \tau_{RC} \end{cases}. \tag{6.8}$$

Alternatively,

$$\frac{L}{L_e} = \begin{cases} 1 & \frac{\tau}{\tau_{RC}} > 1 \\ \sqrt{\frac{\tau}{\tau_{RC}}} & \frac{\tau}{\tau_{RC}} < 1 \end{cases}. \tag{6.9}$$

We can approximate this relationship with a scaling formula

$$\frac{L}{Le} \approx \frac{1}{1 + \sqrt{\frac{\tau_{RC}}{\tau}}} = \frac{\sqrt{\frac{\tau}{\tau_{RC}}}}{1 + \sqrt{\frac{\tau}{\tau_{RC}}}}, \tag{6.10}$$

which is simply an expression which has the right trends for $\tau \gg \tau_{RC}$ and $\tau \ll \tau_{RC}$.

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Spring 2014