Designing supercapacitor electrolyte via ion counting

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Note S1. Theoretical derivations

Let us consider a supercapacitor whose capacitance is "C" that is at a state of charge V(t)

at time 't". The charge stored in this device at this time is:

$$Q(t) = C \times V(t) \tag{1}$$

The number of electrons utilized for charging the device to a voltage V(t), $n_e(t)$ is then:

$$n_e(t) = Q(t) \times N_e = C \times V(t) \times N_e$$
(2)

where N_e is the number of electrons per Coulomb of charge and is equal to the reciprocal of the fundamental constant, Elementary charge 'e' (Table S1).

$$N_e = \frac{1}{e} \tag{3}$$

Table S1. Numerical values of constants used in this paper.¹

Quantity	Symbol	Value	Unit
Elementary charge	e	1.602176487 x 10 ⁻¹⁹	Coulomb
Avogadro's constant	N _A	6.02214179 x 10 ²³	mole ⁻¹

From the number of electrons transferred, the number of positive (n_+) and negative ions (n_-) utilized for charging the device to a voltage V(t) can be calculated as:

$$n_{+}(t) = \frac{n_{e}(t)}{z_{+}} = \frac{C \times V(t) \times N_{e}}{z_{+}}$$
(4)

$$n_{-}(t) = \frac{n_{e}(t)}{z_{-}} = \frac{C \times V(t) \times N_{e}}{z_{-}}$$
(5)

where z_+ and z_- are the valences of the positive and negative ions (i.e. electrons transferred per ion), respectively.

Now, moles of electrolyte present in the device at a fully discharged state is:

$$m^0 = c^0 \times v_{electrolyte} \tag{6}$$

where c^0 is the initial concentration of the electrolyte and $v_{electrolyte}$ is the volume of electrolyte in the device.

Moles of positive (m^{0}_{+}) and negative (m^{0}_{-}) ions present in the electrolyte at fully discharged state are:

$$m_{+}^{0} = z_{-} \times m^{0} = z_{-} \times c^{0} \times v_{electrolyte}$$
⁽⁷⁾

$$m_{-}^{0} = z_{+} \times m^{0} = z_{+} \times c^{0} \times v_{electrolyte}$$
(8)

The number of positive $(n^{0}_{+,electrolyte})$ and negative ions $(n^{0}_{-,electrolyte})$ present in the electrolyte at a fully discharged state (i.e., at V(t) = 0) can be calculated as:

$$n^{0}_{+,electrolyte} = m^{0}_{+} \times N_{A} = z_{-} \times c^{0} \times v_{electrolyte} \times N_{A}$$
⁽⁹⁾

$$n_{-,electrolyte}^{0} = m_{-}^{0} \times N_{A} = z_{+} \times c^{0} \times v_{electrolyte} \times N_{A}$$
(10)

where N_A is the Avogadro's constant (Table S1).

The number of positive $(n_{+,electrolyte}(t))$ and negative $(n_{-,electrolyte}(t))$ ions remaining in the electrolyte when the device is at a charged state are then:

$$n_{+,electrolyte}(t) = n_{+,electrolyte}^{0} - n_{+}(t) = z_{-} \times c^{0} \times v_{electrolyte} \times N_{A} - \left(\frac{C \times V(t) \times N_{e}}{z_{+}}\right)$$
(11)

$$n_{-,electrolyte}(t) = n_{-,electrolyte}^{0} - n_{-}(t) = z_{+} \times c^{0} \times v_{electrolyte} \times N_{A} - \left(\frac{C \times V(t) \times N_{e}}{z_{-}}\right)$$
(12)

Now, moles of positive $(m_+(t))$ and negative $(m_-(t))$ ions remaining in the electrolyte at the charged state are:

$$m_{+}(t) = \frac{n_{+,electrolyte}(t)}{N_{A}} = z_{-} \times c^{0} \times v_{electrolyte} - \left(\frac{C \times V(t) \times N_{e}}{z_{+} \times N_{A}}\right)$$
(13)

$$m_{-}(t) = \frac{n_{-,electrolyte}(t)}{N_{A}} = z_{+} \times c^{0} \times v_{electrolyte} - \left(\frac{C \times V(t) \times N_{e}}{z_{-} \times N_{A}}\right)$$
(14)

Moles of electrolyte at the charged state is:

$$m(t) = \frac{m_+(t)}{z_-} = \frac{m_-(t)}{z_+} = c^0 \times v_{electrolyte} - \left(\frac{C \times V(t) \times N_e}{z_+ \times z_- \times N_A}\right)$$
(15)

The concentration of the electrolyte at the charged state (i.e., the effective concentration of the electrolyte when the device is charged to V(t)), is then:

$$c(t) = \frac{m(t)}{v_{electrolyte}} = c^0 - \left(\frac{C \times V(t) \times N_e}{z_+ \times z_- \times v_{electrolyte} \times N_A}\right)$$
(16)

Now, we can calculate the electrolyte utilization factor $(\eta(t))$ defined in the manuscript (*the ratio of the number of positive (or negative) ions required to charge the device to a voltage V to the number of positive (or negative) ions present in the electrolyte at a fully discharged state*) as follows:

$$\eta(t) = \frac{n_+(t)}{n_{+,electrolyte}^0} \times 100 = \frac{n_-(t)}{n_{-,electrolyte}^0} \times 100 = \frac{C \times V(t) \times N_e}{z_+ \times z_- \times c^0 \times v_{electrolyte} \times N_A} \times 100$$
(17)

The device capacitance can be expressed as a function of the volumetric capacitance $(C_{sp,v})$ of the electrode system and the total volume of electrode in the device $(v_{electrode})$.

$$C = \frac{C_{sp,v} \times v_{electrode}}{4} \tag{18}$$

Also, as defined in the manuscript, the electrolyte-to-electrode volume ratio (Γ) is,

$$\Gamma = \frac{v_{electrolyte}}{v_{electrode}}$$
(19)

From eqs. (17), (18) and (19), $\eta(t)$ can be written as:

$$\eta(t) = \frac{C_{sp,v} \times V(t) \times N_e}{4 \times z_+ \times z_- \times c^0 \times \Gamma \times N_A} \times 100$$
(20)

Critical electrolyte concentration (c^{*}) and critical volume ratio (Γ^*) are calculated from eq. (20), at $\eta(t) = 100$ as follows:

$$c^{*}(\Gamma) = \frac{C_{sp,v} \times V_{rated} \times N_{e}}{4 \times z_{+} \times z_{-} \times \Gamma \times N_{A}}$$
(21)

$$\Gamma^{*}(c^{0}) = \frac{C_{sp,v} \times V_{rated} \times N_{e}}{4 \times z_{+} \times z_{-} \times c^{0} \times N_{A}}$$
(22)

Critical electrolyte volume $(v_{electrolyte}^{*})$ is then,

$$v_{electrolyte}^{*}(c^{0}) = \Gamma^{*}(c^{0}) \times v_{electrode}$$
(23)

Combining (16), (17) & (20), the effective concentration of the electrolyte at a charged state V(t) can be expressed in terms of the initial electrolyte concentration and the utilization factor as:

$$c^{\text{charged}}(t) = c^0 \left(1 - \frac{\eta(t)}{100} \right)$$
(24)

The derivations shown in this section are for the general case wherein all the ions are present in the solvated state when the supercapacitor device is fully discharged and counter-ion adsorption is the primary charge storage mechanism. However, desolvation of ions has been shown to occur, especially in nanoporous carbons, and other charge storage mechanisms such as ion-exchange and co-ion desorption have been demonstrated during supercapacitor operation.² One can take the above generic theoretical treatment and adapt it to specific cases. Next, we show the modifications for two specific cases with desolvated ions present in the pores, namely, counter ion adsorption and ion exchange mechanism.

Note S1-B. Counter-ion adsorption with desolvated ions in the pores

Here, we describe how the equations derived in the previous section can be modified for the cases of supercapacitor mechanisms that involve desolvated ions. Firstly, in the cases where desolvated ions are present in the pores, the concentration of the electrolyte at fully discharged state (V = 0) will be lower than the initial concentration of the electrolyte that was filled in the device (c^0). This concentration, $c^{0,'}$, can be determined if the in-pore ion population at fully discharged state is known for a given carbon electrode – electrolyte system (see, for example Table 1 in Grey et al paper²).

$$c^{0,'} = \frac{m^{0,'}}{v_{electrolyte}} = \frac{m^0 - m^{0,in-pore}}{v_{electrolyte}}$$
(B.1)

where $m^{0,2}$ is the effective moles of electrolyte present in the bulk after in-pore adsorption of the desolvated ions, m^0 is the moles of the electrolyte present just before filling the device (and before the desolvated ions are adsorbed into the pores), given by

$$m^0 = c^0 \times v_{electrolyte} \tag{B.2}$$

And $m^{0,\text{in-pore}}$ is the moles of the electrolyte corresponding to the desolvated ions present in the pores at a fully discharged state and $v_{\text{electrolyte}}$ is the volume of the electrolyte filled into the device. Equations 6 – 10 can accordingly be modified as:

$$m^{0,'} = c^{0,'} \times v_{electrolyte} \tag{B.3}$$

$$m_{+}^{0,'} = z_{-} \times m^{0,'} = z_{-} \times c^{0,'} \times v_{electrolyte}$$
 (B.4)

$$m_{-}^{0,'} = z_{+} \times m^{0,'} = z_{+} \times c^{0,'} \times v_{electrolyte}$$
 (B.5)

$$n_{+,electrolyte}^{0,'} = m_{+}^{0,'} \times N_{A} = z_{-} \times c^{0,'} \times v_{electrolyte} \times N_{A}$$
(B.6)

$$n_{-,electrolyte}^{0,'} = m_{-}^{0,'} \times N_A = z_+ \times c^{0,'} \times v_{electrolyte} \times N_A$$
(B.7)

For the specific case of counter-ion adsorption with desolvated ions in the pores, Equations 11 and 12 that calculate the number of positive $(n'_{+,electrolyte}(t))$ and negative ions $(n'_{-,electrolyte}(t))$ remaining in the electrolyte when the device is at a charged state then become:

$$n'_{+,electrolyte}(t) = n^{0,'}_{+,electrolyte} - n_{+}(t) = z_{-} \times c^{0} \times v_{electrolyte} \times N_{A} - \left(\frac{C \times V(t) \times N_{e}}{z_{+}}\right)$$
(B.8)

$$n_{-,electrolyte}^{'}(t) = n_{-,electrolyte}^{0,'} - n_{-}(t) = z_{+} \times c^{0} \times v_{electrolyte} \times N_{A} - \left(\frac{C \times V(t) \times N_{e}}{z_{-}}\right)$$
(B.9)

Note that the number of net positive $(n_+(t))$ and negative $(n_-(t))$ required for charging the device to a voltage of V(t) is still the same and is dictated by the requirement of maintaining charge neutrality.

Equations 13 – 17 and Equation 20, can accordingly be modified as:

$$m'_{+}(t) = \frac{n'_{+,electrolyte}(t)}{N_{A}} = z_{-} \times c^{0,'} \times v_{electrolyte} - \left(\frac{C \times V(t) \times N_{e}}{z_{+} \times N_{A}}\right)$$
(B.10)

$$m'_{-}(t) = \frac{n'_{-,electrolyte}(t)}{N_{A}} = z_{+} \times c^{0,'} \times v_{electrolyte} - \left(\frac{C \times V(t) \times N_{e}}{z_{-} \times N_{A}}\right)$$
(B.11)

$$m'(t) = \frac{m'_{+}(t)}{z_{-}} = \frac{m'_{-}(t)}{z_{+}} = c^{0,'} \times v_{electrolyte} - \left(\frac{C \times V(t) \times N_{e}}{z_{+} \times z_{-} \times N_{A}}\right)$$
(B.12)

$$c'(t) = \frac{m'(t)}{v_{electrolyte}} = c^{0, -1} \left(\frac{C \times V(t) \times N_e}{z_+ \times z_- \times v_{electrolyte} \times N_A} \right)$$
(B.13)

$$\eta'(t) = \frac{n_{+}(t)}{n_{+,electrolyte}^{0,'}} \times 100 = \frac{n_{-}(t)}{n_{-,electrolyte}^{0,'}} \times 100 = \frac{C \times V(t) \times N_{e}}{z_{+} \times z_{-} \times c^{0,'} \times v_{electrolyte} \times N_{A}} \times 100$$
(B.14)

$$\eta'(t) = \frac{C_{sp,v} \times V(t) \times N_e}{4 \times z_+ \times z_- \times c^{0,'} \times \Gamma \times N_A} \times 100$$
(B.15)

The critical values are then:

$$c^{*'}(\Gamma) = \frac{C_{sp,v} \times V_{rated} \times N_e}{4 \times z_+ \times z_- \times \Gamma \times N_A}$$
(B.16)

$$\Gamma^{*,'}(c^{0,'}) = \frac{C_{sp,v} \times V_{rated} \times N_e}{4 \times z_+ \times z_- \times c^{0,'} \times N_A}$$
(B.17)

$$v_{electrolyte}^{*}(c^{0,'}) = \Gamma^{*,'}(c^{0,'}) \times v_{electrode}$$
(B.18)

The electrolyte concentration at a charged state can then be expressed in terms of utilization factor as:

$$c^{\text{charged,'}}(t) = c^{0,'} \left(1 - \frac{\eta'(t)}{100} \right)$$
 (B.19)

Note S1-C. Ion exchange as the primary charging mechanism with desolvated ions in the pores

Grey et al demonstrated that, in addition to the normal view of counter ion adsorption during charging, two other mechanisms namely the ion exchange mechanism and the co-ion desorption mechanism exist during supercapacitor operation.²⁻⁴ One or more of these three mechanisms have been shown to exist within a given supercapacitor system depending on the carbon type and electrolyte composition.² We next show the modification in the theoretical framework for the case where desolvated ions are present in the carbon pores at a fully discharged state and the primary charging mechanism is ion exchange. In this case, there are two key points of note from Grey et al paper.³

i. The in-pore ion population at a fully discharged state (0 V), m^{0,in-pore} is a function of the electrolyte concentration for a given carbon type and electrolyte.

$$m^{0,in-pore} = h\left(c^{0}\right) \tag{C.1}$$

As a specific example, they showed that for Kuraray YP-50F carbon with PEt_4 -BF₄/ACN electrolyte, the in-pore cation and anion populations vary linearly with the electrolyte concentration and the populations of the two ions were equal within the pores at all concentrations studied.

ii. The in-pore ion populations of the cations and anions are functions of the cell voltage (V(t)) and electrolyte concentration (c(t)), which can be generically represented as follows:

$$m_{+}^{in-pore}(t) = p(V(t), c(t))$$
 (C.2)
 $m_{-}^{in-pore}(t) = q(V(t), c(t))$ (C.3)

We now incorporate the above points into the theoretical framework. At a fully discharged state (i.e., V = 0), the effective moles of electrolyte present in the bulk after in-pore adsorption of the desolvated ions, $m^{0,'}$ is

$$m^{0,'} = m^0 - m^{0,in-pore}$$
 (C.4)

where m⁰ is the moles of the electrolyte present just before filling (i.e., before the desolvated ions are adsorbed into the pores), given by

$$m^0 = c^0 \times v_{electrolyte} \tag{C.5}$$

where c^0 is the initial electrolyte concentration that was filled into the device and $v_{electrolyte}$ is the volume of the electrolyte filled into the device. And $m^{0,in-pore}$ is the moles of the electrolyte corresponding to the desolvated ions present in the pores at a fully discharged state, given by equation (C.1).

Also, the moles of cations and anions present in the bulk (and contributing to the electrolyte conductivity) at a fully discharged state are

$$m_{+}^{0,'} = z_{-} \times m^{0,'}$$
 (C.6)

$$m_{-}^{0,'} = z_{+} \times m^{0,'}$$
 (C.7)

The effective electrolyte concentration in the device at a fully discharged state, c^{0,'}, is then:

$$c^{0,'} = \frac{m^{0,'}}{v_{electrolyte}} = \frac{m^0 - m^{0,in-pore}}{v_{electrolyte}}$$
(C.8)

When the device is at a charged state V(t), the moles of electrolyte that are adsorbed in the pores and unavailable to contribute to the bulk electrolyte conductivity in the device is

$$m^{in-pore}(t) = \frac{m_{+}^{in-pore}(t)}{z_{-}} = \frac{m_{-}^{in-pore}(t)}{z_{+}}$$
(C.9)

where $m_{+}^{\text{in-pore}}(t)$ and $m_{-}^{\text{in-pore}}(t)$ are given by equations (C.2) and (C.3).

As a side note, to maintain charge neutrality it should follow that

$$\frac{p(V(t),c(t))}{z_{-}} = \frac{q(V(t),c(t))}{z_{+}}$$
(C.10)

The moles of electrolyte at a charged state V(t) can then be calculated as:

$$m^{\text{charged},'}(t) = m^{0} - m^{\text{in-pore}}(t) = m^{0} - \frac{m_{+}^{\text{in-pore}}}{z_{-}} = m^{0} - \frac{p\left(V(t), c^{\text{charged},'}(t)\right)}{z_{-}}$$
(C.11)

Thus, the effective electrolyte concentration at a charge state is

$$c^{\text{charged,'}}(t) = \frac{m^{\text{charged,'}}(t)}{v_{\text{electrolyte}}} = \frac{1}{v_{\text{electrolyte}}} \left(m^0 - \frac{p\left(V(t), c^{\text{charged,'}}(t)\right)}{z_-} \right)$$
(C.12)

It must be noted that while the expression for the effective electrolyte concentration at charged state reduced to a simple analytical expression in the previous cases, in the present case it is an implicit function, which may or may not reduce to an analytical form. This will depend on the functions that provide the in-pore ion population (i.e., functions p and q in this case). If it does not reduce to an analytical form, numerical methods must be used to calculate the effective electrolyte concentration, and subsequently the electrolyte conductivity at a given state of charge.

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Note S2. Importance of volumetric specific capacitance (C_{sp.v}, F/cm³) of the electrode

While reporting supercapacitor material and device performance characteristics, it is important to present true metrics. Gravimetric (C_{sp,g}, F/g) and volumetric (C_{sp,v}, F/cm³) specific capacitances are the commonly used metrics for evaluating the performance of the carbon material in supercapacitors.⁵⁻¹⁰ Typically in supercapacitor literature, the reported specific capacitances are based on the amount of activated carbon in the electrode⁶ and do not take into account the amounts of binder and conductive carbon additives which account for a non-trivial portion of the electrode (typically, 15-20 wt.%). Gogotsi and Simon have outlined the problems in extrapolating the active material performance to device level performance values.¹¹ A more useful metric for the performance of the electrode and device is the volumetric capacitance (C_{sp,v}) based on the total volume of the electrode in the device. C_{sp,v} can be used across devices of different sizes and is helpful in optimizing various processes involved in device manufacture at different scales: carbon synthesis, electrode fabrication, current collector development, electrode lamination onto the current collector, electrode ("jelly roll") assembly, terminal welding, electrolyte production, device assembly and finally electrolyte filling and sealing the device. Table S2 compares devices at three different scales fabricated with the same activated carbon. The volumetric capacitances and the time constants are quite similar across the scales, which was achieved through process optimizations at every scale and demonstrates excellent process scale-up.

Table S2. Performance values for supercapacitors of different sizes fabricated with the same carbon material and electrode fabrication process. The electrolyte was 1.5 M tetraethylammonium tetrafluoroborate (TEATFB) in acetonitrile, filled to the highest volume ratios.

Cell size	Electrode volume, v _{electrode} (cm ³)	C (F)	ESR (mΩ)	Time constant, $\tau = C \times ESR (s)$	Volumetric capacitance, C _{sp,v} (F/cm ³)
Button cell	0.05	1.13	1330	1.50	90.4
D cell	23.2	503	3.00	1.51	86.7
Large cell	129.7	2830	0.53	1.50	87.3

Note S3. Relationship between the device capacitance (C) and volumetric specific

capacitance (C_{sp,v}) of the electrode

The capacitance of a supercapacitor (C) can be expressed in terms of the capacitances of the positive (C₊) and negative (C₋) electrodes as:

$$\frac{1}{C} = \frac{1}{C_{+}} + \frac{1}{C_{-}}$$
(25)

$$C = \frac{C_{+}C_{-}}{C_{+}+C_{-}}$$
(26)

The capacitances of the individual electrodes can be expressed in terms of their specific capacitances as:

$$C_{+} = C_{sp,v,+} \times v_{electrode,+}$$
(27)
$$C_{-} = C_{sp,v,-} \times v_{electrode,-}$$
(28)

where $C_{sp,v,x}$ and $v_{electrode,x}$ are the volumetric specific capacitance and electrode volume of the respective electrodes. For a symmetric electrode system wherein the positive and negative electrodes are identical,

$$C_{sp,\nu,+} = C_{sp,\nu,-} = C_{sp,\nu}$$
(29)

$$v_{electrode,+} = v_{electrode,-} = \frac{v_{electrode}}{2}$$
(30)

where $v_{\text{electrode}}$ is the total volume of electrode in the device.

Combining equations (26) through (30),

$$C = \frac{C_{sp,v} \times v_{electrode}}{4} \tag{31}$$

For an asymmetric electrode system, wherein the positive and negative electrodes comprise activated carbons of different pore structure and pore size distribution tuned to optimize the performance, the device capacitance doesn't reduce to a simple form as shown in eq. (31), as the volumes of the positive and negative electrodes may not be the same. However, one can calculate an average volumetric capacitance ($C_{sp,v}$) of a given positive electrode – negative electrode combination from the from the actual measurement of capacitance of the electrode assembly in a small form factor cell (e.g. button cell). This can then be combined with the total volume of the electrode assembly to calculate device capacitance for devices of any size using eq. (31).

Note S4. Electrolyte conductivity

The electrolyte conductivity is a function of concentration and temperature. As all experiments and discussions in this paper pertain to room temperature conditions (25°C), the conductivity (σ , mS/cm) of the TEATFB / acetonitrile electrolyte was measured in the concentration range 0 to 1.5 M range and the data was fit to the following equation:

$$\sigma = a_1 \times c + a_2 \times c^2 + a_3 \times c^3 + a_4 \times c^4 \tag{32}$$

where $a_1 = 71.36$, $a_2 = -7.78$, $a_3 = -41.54$ and $a_4 = 20.35$.

Note S5. Jelly roll characteristics and electrolyte saturation volume

The electrode assembly in cylindrical supercapacitors is typically wound spirally in the form of a jelly roll. It consists of a total of four layers of carbon electrode (two layers each of positive and negative electrodes on either side of a positive and a negative current collector) and two separator sheets electrically isolating the electrodes. There are extensions in the current collectors which are welded to end caps that contain terminals for external electrical connection.

The total geometric volume of the carbon electrode in the jelly roll is the sum of the volumes of the individual electrodes.

$$v_{electrode} = v_{electrode,+} + v_{electrode,-}$$
(33)

The volumes of the positive and negative electrodes are given by:

$$v_{electrode,+} = L_{electrode,+} \times W_{electrode,+} \times D_{electrode,+}$$
(34)

$$v_{electrode,-} = L_{electrode,-} \times W_{electrode,-} \times D_{electrode,-}$$
(35)

where L, W and D denote the length, width, and thickness of the respective electrode layers.[†] Note that the thickness D includes the thickness of the two layers of electrodes on either side of the current collector. The widths of the positive and negative electrodes are typically the same. Although the lengths of the two electrodes are slightly different due to the spiral winding of the jelly roll, they can be considered the same in practical terms.[‡] Equations (34) and (35) can be written as

$$v_{electrode,+} = L_{electrode} \times W_{electrode} \times D_{electrode,+}$$
(36)

$$v_{electrode,-} = L_{electrode} \times W_{electrode} \times D_{electrode,-}$$
(37)

The total geometric volume of the electrode is then

$$v_{electrode} = L_{electrode} \times W_{electrode} \times \left(D_{electrode,+} + D_{electrode,-} \right)$$
(38)

The total open volume in the carbon electrodes is:

$$v_{electrode,open} = \left(v_{electrode,+} \times \mathcal{E}_{+}\right) + \left(v_{electrode,-} \times \mathcal{E}_{-}\right)$$
(39)

where ε_{+} and ε_{-} are the overall porosities of the positive and negative electrode. The overall porosity of an electrode includes the inter-particle porosity (i.e. the porosity between the activated carbon particles, binder, and conductive additive) and the intra-particle porosity of the activated

[†] In the jelly roll design, the length of the inner electrode is slightly smaller than that of the outer electrode. The cell design dictates which of these electrodes is positive and which one is negative.

[‡] The difference in lengths for a D-cell size (450-500F) is <4% and for large cell (~2800F) is <3%.

carbon. For a symmetric cell with identical positive and negative electrodes, the total geometric and open volumes in the electrodes are

$$v_{electrode} = 2 \times L_{electrode} \times W_{electrode} \times D_{electrode}$$
(40)

$$v_{electrode,open} = v_{electrode} \times \varepsilon_{electrode} = 2 \times L_{electrode} \times W_{electrode} \times D_{electrode} \times \varepsilon_{electrode}$$
(41)

where $\varepsilon_{\text{electrode}}$ is the overall electrode porosity.

There are two layers (inner and outer) of separator in the jelly roll. The lengths of the separators are usually the same and equal to the length of the outer electrode (i.e. $L_{separator,inner} = L_{separator,outer} = L_{electrode}$). The total geometric ($v_{separator}$) and open volumes ($v_{separator,open}$) of separator can be calculated as:

$$v_{separator,inner} = L_{separator,inner} \times W_{separator} \times D_{separator} = L_{electrode} \times W_{separator} \times D_{separator}$$
(42)

$$v_{separator,outer} = L_{separator,outer} \times W_{separator} \times D_{separator} = L_{electrode} \times W_{separator} \times D_{separator}$$
(43)

$$v_{separator} = v_{separator,inner} + v_{separator,outer} = 2 \times L_{electrode} \times W_{separator} \times D_{separator}$$
(44)

$$v_{separator,open} = v_{separator} \times \varepsilon_{separator} = 2 \times L_{electrode} \times W_{separator} \times D_{separator} \times \varepsilon_{separator}$$
(45)

It is useful to express the volume of the separator as a function of the volume of electrode used in the device, especially in a manufacturing line. From eqs. (38) and (44), for an asymmetric electrode design,

$$v_{separator} = v_{electrode} \times \frac{W_{separator}}{W_{electrode}} \times \frac{2 \times D_{separator}}{\left(D_{electrode,+} + D_{electrode,-}\right)}$$
(46)

Similarly, from eqs. (40) and (44), for a symmetric electrode design,

$$v_{separator,symm} = v_{electrode,symm} \times \frac{W_{separator}}{W_{electrode}} \times \frac{D_{separator}}{D_{electrode}}$$
(47)

The total open geometric volume available for the electrolyte to occupy in the jelly roll $(v_{jellyroll,open})$ is the sum of open volumes in the carbon electrode and the separator. This is also the

volume of electrolyte required to saturate the jelly roll and can be termed as the *electrolyte saturation volume* (v_{electrolyte,sat}) of the jelly roll.

$$v_{electrolyte,sat} = v_{jellyroll,open} = v_{electrode,open} + v_{separator,open}$$
(48)

From eqs. (41), (45), (47) and (48), for a symmetric electrode design,

$$v_{electrolyte,sat} = v_{electrode,symm} \left(\varepsilon_{electrode} + \left(\frac{W_{separator} \times D_{separator}}{W_{electrode} \times D_{electrode}} \right) \times \varepsilon_{separator} \right)$$
(49)

Table S3 shows the simulation of jelly roll saturation volume (mL) per cm³ of carbon electrode at various electrode and separator porosities, for an electrode thickness of 100 μ m on either side of the current collector and a separator thickness of 30.5 μ m (corresponding to that of a commercially available separator). Table S4 shows the simulation of saturation volume for a Dcell sized device. One can use such a table to quickly estimate the saturation volume for any sized device for a given separator and carbon electrode material. For example, for a D-cell device that contains 24 cm³ of carbon electrode with 70% porosity and a separator with 50% porosity, the minimum volume of electrolyte required to saturate the jelly roll is 18.8 mL. Consequently, the optimized electrolyte volume cannot be lower than this.

Table S3. Simulation of electrolyte saturation volume (mL) per cm³ of carbon electrode at various electrode and separator porosities ($\varepsilon_{separator}$ and $\varepsilon_{electrode}$). The saturation volumes for any sized device can be obtained by multiplying the corresponding values in this table by the total electrode volume in the jelly roll. This table was generated for a total electrode thickness of 200 µm (100 µm on either side of the current collector), a separator thickness of 30.5 µm and electrode-to-separator width ratio of 0.9 (i.e. $W_{electrode} = 0.9 \times W_{separator}$).

										C	arbo	n ele	ctroc	le								
	ε (%)	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100
	0	0.00	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50	0.55	0.60	0.65	0.70	0.75	0.80	0.85	0.90	0.95	1.00
	5	0.01	0.06	0.11	0.16	0.21	0.26	0.31	0.36	0.41	0.46	0.51	0.56	0.61	0.66	0.71	0.76	0.81	0.86	0.91	0.96	1.01
	10	0.02	0.07	0.12	0.17	0.22	0.27	0.32	0.37	0.42	0.47	0.52	0.57	0.62	0.67	0.72	0.77	0.82	0.87	0.92	0.97	1.02
	15	0.03	0.08	0.13	0.18	0.23	0.28	0.33	0.38	0.43	0.48	0.53	0.58	0.63	0.68	0.73	0.78	0.83	0.88	0.93	0.98	1.03
	20	0.03	0.08	0.13	0.18	0.23	0.28	0.33	0.38	0.43	0.48	0.53	0.58	0.63	0.68	0.73	0.78	0.83	0.88	0.93	0.98	1.03
	25	0.04	0.09	0.14	0.19	0.24	0.29	0.34	0.39	0.44	0.49	0.54	0.59	0.64	0.69	0.74	0.79	0.84	0.89	0.94	0.99	1.04
	30	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50	0.55	0.60	0.65	0.70	0.75	0.80	0.85	0.90	0.95	1.00	1.05
	35	0.06	0.11	0.16	0.21	0.26	0.31	0.36	0.41	0.46	0.51	0.56	0.61	0.66	0.71	0.76	0.81	0.86	0.91	0.96	1.01	1.06
2	40	0.07	0.12	0.17	0.22	0.27	0.32	0.37	0.42	0.47	0.52	0.57	0.62	0.67	0.72	0.77	0.82	0.87	0.92	0.97	1.02	1.07
ato	45	0.08	0.13	0.18	0.23	0.28	0.33	0.38	0.43	0.48	0.53	0.58	0.63	0.68	0.73	0.78	0.83	0.88	0.93	0.98	1.03	1.08
ara	50	0.08	0.13	0.18	0.23	0.28	0.33	0.38	0.43	0.48	0.53	0.58	0.63	0.68	0.73	0.78	0.83	0.88	0.93	0.98	1.03	1.08
Sep	55	0.09	0.14	0.19	0.24	0.29	0.34	0.39	0.44	0.49	0.54	0.59	0.64	0.69	0.74	0.79	0.84	0.89	0.94	0.99	1.04	1.09
	60	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50	0.55	0.60	0.65	0.70	0.75	0.80	0.85	0.90	0.95	1.00	1.05	1.10
	65	0.11	0.16	0.21	0.26	0.31	0.36	0.41	0.46	0.51	0.56	0.61	0.66	0.71	0.76	0.81	0.86	0.91	0.96	1.01	1.06	1.11
	70	0.12	0.17	0.22	0.27	0.32	0.37	0.42	0.47	0.52	0.57	0.62	0.67	0.72	0.77	0.82	0.87	0.92	0.97	1.02	1.07	1.12
	75	0.13	0.18	0.23	0.28	0.33	0.38	0.43	0.48	0.53	0.58	0.63	0.68	0.73	0.78	0.83	0.88	0.93	0.98	1.03	1.08	1.13
	80	0.13	0.18	0.23	0.28	0.33	0.38	0.43	0.48	0.53	0.58	0.63	0.68	0.73	0.78	0.83	0.88	0.93	0.98	1.03	1.08	1.13
	85	0.14	0.19	0.24	0.29	0.34	0.39	0.44	0.49	0.54	0.59	0.64	0.69	0.74	0.79	0.84	0.89	0.94	0.99	1.04	1.09	1.14
	90	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50	0.55	0.60	0.65	0.70	0.75	0.80	0.85	0.90	0.95	1.00	1.05	1.10	1.15
	95	0.16	0.21	0.26	0.31	0.36	0.41	0.46	0.51	0.56	0.61	0.66	0.71	0.76	0.81	0.86	0.91	0.96	1.01	1.06	1.11	1.16
	100	0.17	0.22	0.27	0.32	0.37	0.42	0.47	0.52	0.57	0.62	0.67	0.72	0.77	0.82	0.87	0.92	0.97	1.02	1.07	1.12	1.17

Table S4. Simulations of jelly roll saturation volume (mL) at various electrode and separator porosities for a D-cell sized device (Electrode volume, $v_{electrode} = 24 \text{ cm}^3$).

											Cart	oon e	lectr	ode								
	ε (%)	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100
	0	0.0	1.2	2.4	3.6	4.8	6.0	7.2	8.4	9.6	10.8	12.0	13.2	14.4	15.6	16.8	18.0	19.2	20.4	21.6	22.8	24.0
	5	0.2	1.4	2.6	3.8	5.0	6.2	7.4	8.6	9.8	11.0	12.2	13.4	14.6	15.8	17.0	18.2	19.4	20.6	21.8	23.0	24.2
	10	0.4	1.6	2.8	4.0	5.2	6.4	7.6	8.8	10.0	11.2	12.4	13.6	14.8	16.0	17.2	18.4	19.6	20.8	22.0	23.2	24.4
	15	0.6	1.8	3.0	4.2	5.4	6.6	7.8	9.0	10.2	11.4	12.6	13.8	15.0	16.2	17.4	18.6	19.8	21.0	22.2	23.4	24.6
	20	0.8	2.0	3.2	4.4	5.6	6.8	8.0	9.2	10.4	11.6	12.8	14.0	15.2	16.4	17.6	18.8	20.0	21.2	22.4	23.6	24.8
	25	1.0	2.2	3.4	4.6	5.8	7.0	8.2	9.4	10.6	11.8	13.0	14.2	15.4	16.6	17.8	19.0	20.2	21.4	22.6	23.8	25.0
	30	1.2	2.4	3.6	4.8	6.0	7.2	8.4	9.6	10.8	12.0	13.2	14.4	15.6	16.8	18.0	19.2	20.4	21.6	22.8	24.0	25.2
	35	1.4	2.6	3.8	5.0	6.2	7.4	8.6	9.8	11.0	12.2	13.4	14.6	15.8	17.0	18.2	19.4	20.6	21.8	23.0	24.2	25.4
	40	1.6	2.8	4.0	5.2	6.4	7.6	8.8	10.0	11.2	12.4	13.6	14.8	16.0	17.2	18.4	19.6	20.8	22.0	23.2	24.4	25.6
ator	45	1.8	3.0	4.2	5.4	6.6	7.8	9.0	10.2	11.4	12.6	13.8	15.0	16.2	17.4	18.6	19.8	21.0	22.2	23.4	24.6	25.8
ara	50	2.0	3.2	4.4	5.6	6.8	8.0	9.2	10.4	11.6	12.8	14.0	15.2	16.4	17.6	18.8	20.0	21.2	22.4	23.6	24.8	26.0
Sep	55	2.2	3.4	4.6	5.8	7.0	8.2	9.4	10.6	11.8	13.0	14.2	15.4	16.6	17.8	19.0	20.2	21.4	22.6	23.8	25.0	26.2
••	60	2.4	3.6	4.8	6.0	7.2	8.4	9.6	10.8	12.0	13.2	14.4	15.6	16.8	18.0	19.2	20.4	21.6	22.8	24.0	25.2	26.4
	65	2.6	3.8	5.0	6.2	7.4	8.6	9.8	11.0	12.2	13.4	14.6	15.8	17.0	18.2	19.4	20.6	21.8	23.0	24.2	25.4	26.6
	70	2.8	4.0	5.2	6.4	7.6	8.8	10.0	11.2	12.4	13.6	14.8	16.0	17.2	18.4	19.6	20.8	22.0	23.2	24.4	25.6	26.8
	75	3.0	4.2	5.4	6.6	7.8	9.0	10.2	11.4	12.6	13.8	15.0	16.2	17.4	18.6	19.8	21.0	22.2	23.4	24.6	25.8	27.0
	80	3.2	4.4	5.6	6.8	8.0	9.2	10.4	11.6	12.8	14.0	15.2	16.4	17.6	18.8	20.0	21.2	22.4	23.6	24.8	26.0	27.2
	85	3.4	4.6	5.8	7.0	8.2	9.4	10.6	11.8	13.0	14.2	15.4	16.6	17.8	19.0	20.2	21.4	22.6	23.8	25.0	26.2	27.4
	90	3.6	4.8	6.0	7.2	8.4	9.6	10.8	12.0	13.2	14.4	15.6	16.8	18.0	19.2	20.4	21.6	22.8	24.0	25.2	26.4	27.6
	95	3.8	5.0	6.2	7.4	8.6	9.8	11.0	12.2	13.4	14.6	15.8	17.0	18.2	19.4	20.6	21.8	23.0	24.2	25.4	26.6	27.8
	100	4.0	5.2	6.4	7.6	8.8	10.0	11.2	12.4	13.6	14.8	16.0	17.2	18.4	19.6	20.8	22.0	23.2	24.4	25.6	26.8	28.0

Note S6. Excess electrolyte volume

Excess electrolyte volume ($v_{electrolyte}^{excess}$) is the volume of electrolyte that is in excess of the electrolyte saturation volume.

$$v_{electrolyte}^{excess} = v_{electrolyte} - v_{electrolyte,sat}$$
(50)

where $v_{electrolyte}$ is the actual volume of electrolyte filled in the device. The calculations for excess electrolyte volume in this paper were based on $\varepsilon_{electrode} = 68\%$ for Type A carbon, $\varepsilon_{electrode} = 69\%$ for Type B carbon, and $\varepsilon_{separator} = 50\%$. The former values are based on measurements from several batches of carbon electrodes and the latter value was from the separator manufacturer's specification sheet.

Additional Tables and Figures

C _{sp,v}	V _{max}		c* (M) at various Г									
(F/cm^3)	(V)	0.8	0.9	1.0	1.1	1.2	1.3					
65	2.7	0.57	0.51	0.45	0.41	0.38	0.35					
65	3.0	0.63	0.56	0.51	0.46	0.42	0.39					
75	2.7	0.66	0.58	0.52	0.48	0.44	0.40					
75	3.0	0.73	0.65	0.58	0.53	0.49	0.45					
85	2.7	0.74	0.66	0.59	0.54	0.50	0.46					
85	3.0	0.83	0.73	0.66	0.60	0.55	0.51					

Table S5. Critical electrolyte concentration (c^*) at various volume ratios (Γ) for the different carbon electrode systems at maximum device voltages of 2.7 V and 3.0 V.

Table S6. Critical volume ratio (Γ^*) at various initial concentrations (c⁰) for the different carbon electrode systems at maximum device voltages of 2.7 V and 3.0 V.

C _{sp,v}	V _{max}		Γ^* at various c^0 (M)									
(F/cm^3)	(V)	1.0	1.1	1.2	1.3	1.4	1.5					
65	2.7	0.45	0.41	0.38	0.35	0.32	0.30					
65	3.0	0.51	0.46	0.42	0.39	0.36	0.34					
75	2.7	0.52	0.48	0.44	0.40	0.37	0.35					
75	3.0	0.58	0.53	0.49	0.45	0.42	0.39					
85	2.7	0.59	0.54	0.50	0.46	0.42	0.40					
85	3.0	0.66	0.60	0.55	0.51	0.47	0.44					

Table S7. Critical electrolyte volume ($v^*_{electrolyte}$) at various initial concentrations (c^0) for the different carbon electrode systems at maximum device voltages of 2.7 V and 3.0 V. The device capacitances correspond to the nominal capacitance of the commercial device ($C_{sp,v} = 65$ F/cm³, C = 350 F), Type A carbon electrode ($C_{sp,v} = 75$ F/cm³ C = 450 F) and Type B carbon electrode ($C_{sp,v} = 85$ F/cm³, C = 500 F) in a D-cell form factor.

C _{device}	V _{max}	$v^*_{electrolyte}$ (mL) at various c^0 (M)								
(F)	(V)	1.0	1.1	1.2	1.3	1.4	1.5			
350	2.7	9.8	8.9	8.2	7.5	7.0	6.5			
350	3.0	10.9	9.9	9.1	8.4	7.8	7.3			
450	2.7	12.6	11.4	10.5	9.7	9.0	8.4			
450	3.0	14.0	12.7	11.7	10.8	10.0	9.3			
500	2.7	14.0	12.7	11.7	10.8	10.0	9.3			
500	3.0	15.5	14.1	13.0	12.0	11.1	10.4			

Cell ID	c ⁰ (M)	Г	C (F)	$\mathrm{ESR}(\mathrm{m}\Omega)$	τ (s)	C _{sp,v} (F/cm ³)	ED _{max} (Wh/L)
B1	1.0	1.0	488	3.18	1.55	82.3	6.9
B2	1.0	1.2	496	2.86	1.42	83.7	7.0
B3	1.5	0.8	487	4.65	2.26	83.3	6.9
B4	1.5	1.0	501	2.40	1.20	83.6	7.1
B5	1.5	1.2	502	2.37	1.19	83.8	7.1
B6	1.5	1.3	503	2.28	1.15	85.9	7.1
D	-	-	355	3.30	1.17	-	5.0

Table S8. Summary of capacitance and ESR data measured from 20 A constant current cycling for the Type B electrode system (nominal $C_{sp,v} = 85$ F/cm³). The values for the commercial device (cell "D") are shown for comparison.

Table S9. % Improvement (weight basis) in the salt (TEATFB) consumption per D-cell compared to a baseline concentration of 1.5 M TEATFB / ACN and volume ratio of 1.3. The total volume of carbon electrode is taken as 24 cm³, typical for a D-cell. These improvements directly translate into significant cost savings due to the high cost of the electrolyte salt.[§]

		Γ										
0/	0	0.8	0.9	1.0	1.1	1.2	1.3					
	1.0	59	54	49	44	38	33					
	1.1	55	49	44	38	32	27					
(M)	1.2	51	45	38	32	26	20					
с ₀ (1.2	47	40	33	27	20	13					
-	1.4	43	35	28	21	14	7					
	1.5	38	31	23	15	8	0					

[§] For example, the price of 25 g TEATFB is \$76 (TCI Chemicals, https://www.tcichemicals.com/US/en/p/T0983, accessed 11/8/2021). The price at bulk volumes would be lower but still a significant amount.

A note on figures in supplemental information

Here, we present additional simulations for the commercial carbon ($C_{sp,v} = 65$ F/cm³) and Type B carbon ($C_{sp,v} = 85$ F/cm³) electrode systems. Furthermore, simulations are also presented for all the carbon electrode systems for a maximum voltage of 3.0 V (although not common, there are now commercial supercapacitors available at this rated voltage). Finally, results from D-cell sized supercapacitors built with Type B carbon electrodes at various initial concentrations and volume ratios are presented. It must be noted that although the Type B electrode system shows superior power and energy density performance, its aging and self-discharge behaviors were poorer than the Type A electrode system. Thus, it is important to optimize the device performance as a whole and not just the initial performance as shown in the Ragone plots.¹¹



Figure S1. Comparison of electrolyte utilization factor at $V_{max} = 2.7$ V and $V_{max}/2 = 1.35$ V as a function of c^0 and Γ for (a) typical commercial carbon ($C_{sp,v} = 65$ F/cm³) and (b) Type B electrode system ($C_{sp,v} = 85$ F/cm³).



Figure S2. Comparison of electrolyte utilization factor at $V_{max} = 3.0$ V and $V_{max}/2 = 1.5$ V as a function of c^0 and Γ for (a) $C_{sp,v} = 65$ F/cm³ and (b) $C_{sp,v} = 75$ F/cm³ and (c) $C_{sp,v} = 85$ F/cm³.



Figure S3. (a) Critical electrolyte concentration (c^*) vs. volume ratio (Γ) plots for the three electrode systems. (b) Critical volume ratio (Γ^*) vs. initial electrolyte concentration (c^0) plots for the three electrode systems. (c) Critical electrolyte volume ($v^*_{electrolyte}$) vs. initial electrolyte concentration (c^0) plots for D-cell sized supercapacitors with three different electrode systems studied in this paper. All plots were simulated at a voltage of 3.0 V. Nominal capacitances for D-cell sized supercapacitor are: i) commercial = 350 F, ii) Type A = 450 F and Type B = 500 F. All calculations are for a 1:1 electrolyte system (i.e. $z_+ = z_- = 1$).



Figure S4. Comparison of c^{charged} at maximum voltage ($V_{max} = 2.7 \text{ V}$) and half the maximum voltage ($V_{max}/2 = 1.35 \text{ V}$) for (a) $C_{sp,v} = 65 \text{ F/cm}^3$ and (b) $C_{sp,v} = 85 \text{ F/cm}^3$.



Figure S5. Comparison of c^{charged} at maximum voltage ($V_{max} = 3.0 \text{ V}$) and half the maximum voltage ($V_{max}/2 = 1.5 \text{ V}$) for **(a)** $C_{sp,v} = 65 \text{ F/cm}^3$ and **(b)** $C_{sp,v} = 75 \text{ F/cm}^3$ and **(c)** $C_{sp,v} = 85 \text{ F/cm}^3$.



Figure S6. Comparison of $\sigma^{charged}$ at maximum voltage (V_{max} = 2.7 V) and half the maximum voltage (V_{max}/2 = 1.35 V) for (a) C_{sp,v} = 65 F/cm³ and (b) C_{sp,v} = 85 F/cm³.



Figure S7. Comparison of $\sigma^{charged}$ at maximum voltage ($V_{max} = 3.0 \text{ V}$) and half the maximum voltage ($V_{max}/2 = 1.5 \text{ V}$) for **(a)** $C_{sp,v} = 65 \text{ F/cm}^3$ and **(b)** $C_{sp,v} = 75 \text{ F/cm}^3$ and **(c)** $C_{sp,v} = 85 \text{ F/cm}^3$.



Figure S8. Performance of D-cell size supercapacitors containing TEATFB / ACN electrolyte at different concentrations and volume ratios for the Type B electrode system ($C_{sp,v} = 85 \text{ F/cm}^3$). (a) ESR as a function of excess electrolyte volume and conductivity at charged state. Inset shows the data as a bubble plot. (b) Volumetric Ragone plots of the D-cells. The cell IDs correspond to those shown in Supplemental Table S8. Commercial D-cell device (C = 350 F) is shown in red for comparison. Power and energy densities were calculated based on the device volume. The inset shows the simulations of the conductivity at charged state (2.7 V) vs. electrolyte volume at various initial electrolyte concentrations for a 500 F device (the typical capacitance of the D-cell device containing Type B electrode system). The actual cells tested are indicated in the plots by diamond symbols along with cell IDs next to them. (c) and (d) Bubble plots of power and energy densities as a function of the excess electrolyte volume and the conductivity at charged state (2.7 V) corresponding to a time constant of 1 second.



Figure S9. Larger versions of the $\sigma^{charged}$ vs. $v_{electrolyte}$ graphs. (a) Inset from Figure 3b in the main manuscript (Type A electrode system, $C_{sp,v} = 75$ F/cm³). (b) Inset from Supplemental Figure S8 (Type B electrode system, $C_{sp,v} = 85$ F/cm³).

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