



Tailored porous electrode resistance for controlling electrolyte depletion and improving charging response in electrochemical systems

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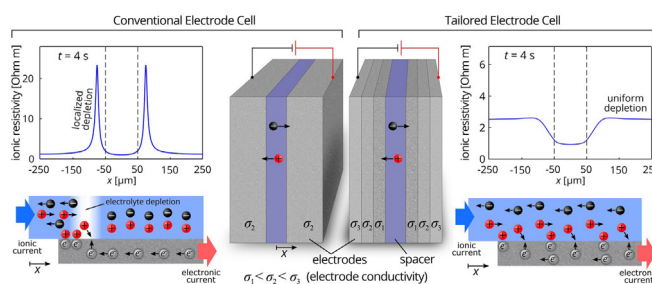
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HIGHLIGHTS

- Reduced electrode conductivity to avoid ion depletion and achieve uniform charging.
- A transport model capturing the effect of electrode conductivity distributions.
- Reduction in ion depletion results in 2-fold increase in average charging rate.

GRAPHICAL ABSTRACT



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ABSTRACT

The rapid charging and/or discharging of electrochemical cells can lead to localized depletion of electrolyte concentration. This depletion can significantly impact the system's time dependent resistance. For systems with porous electrodes, electrolyte depletion can limit the rate of charging and increase energy dissipation. Here we propose a theory to control and avoid electrolyte depletion by tailoring the value and spatial distribution of resistance in a porous electrode. We explore the somewhat counterintuitive idea that increasing local spatial resistances of the solid electrode itself leads to improved charging rate and minimal change in energy loss. We analytically derive a simple expression for an electrode matrix resistance profile that leads to highly uniform electrolyte depletion. We use numerical simulations to explore this theory and simulate spatiotemporal dynamics of electrolyte concentration in the case of a supercapacitor with various tailored electrode matrix resistance profiles which avoid localized depletion. This increases charging rate up to ~ 2 -fold with minimal effect on overall dissipated energy in the system.

1. Introduction

Electrochemical systems are commonly used in situations which strongly benefit from the rapid storage of energy [1], including time sensitive charging situations for electric vehicles [2], storage of short lived energy surges as in regenerative braking [3], and capacitive deionization (CDI) applications where increasing throughput is

essential [4]. System resistances, particularly series resistances, can have a strong impact on both charge/discharge time and dissipated energy. Constant voltage charging of a simple capacitor in series with a resistance provides a useful example. For fixed resistance, the charge stored by the capacitor asymptotically approaches a maximum value following an exponential dependence with a time constant equal to the product of series resistance and capacitance ($\tau = RC$) [5].

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Consequently, electrochemical system design has traditionally sought to reduce all sources of resistance [6], including solution resistance, electrode matrix resistance, and in some cases, contact resistance between the electrodes and current collectors. Solution resistance generally dominates compared to resistance of electrode or current collector materials [6,7].

Supercapacitors are representative of electrochemical systems designed for fast charging and high power densities and employ strategies to minimize series resistance. The thickness of spacer layers between the electrodes is minimized to reduce solution resistance for ion transport. Additionally, except for applications with low electrode utilization, electrode thickness is generally minimized to reduce the ion transport resistance associated with migration through the depth of the porous electrode. Contact resistance between electrode and current collector is also minimized by a variety of collector surface preparations and electrode deposition techniques [6]. The standard design philosophy has been to maximize the conductivity of both current collectors and electrode materials.

Local solution conductivity variations can also severely impact overall performance. As an electrochemical system is charged or discharged, ions are removed from or added to solution resulting in solution conductivities which evolve in time and space. Localized depletion of the electrolyte may significantly increase the net series resistance of the cell by introducing a choke point which limits charging rate. For example, electrolyte depletion can be important in a number of battery chemistries, such as Li-ion, operating at high currents [8–10] and in supercapacitors [11]. Likewise, the ability to deplete the working solution forms the basis of CDI [4]. Significant depletion of electrolyte has a substantial effect on the charging response of the system [12].

Depletion depends on electrolyte concentration and the charge storage capacity of the electrode. The ultimate limit for electrolyte concentration is set by its solubility in the solvent, but other constraints often further limit electrolyte concentrations including cost and decreasing conductivity with further solute addition. Many electrochemical systems use solutions based on organic solvents in order to allow larger operating voltages with negligible electrolysis [13]. Organic carbonates are popular solvent choices [14]. Lithium hexafluorophosphate (LiPF₆) salt is the most commonly used electrolyte in Li-ion batteries [15], while tetraethylammonium (TEA, (C₂H₅)₄N⁺) tetrafluoroborate (TFB, BF₄⁻) salt is commonly used for supercapacitors [16]. Electrolyte concentrations are commonly limited to ~ 1 mol L⁻¹ [16,17].

Due to their high charge storage capacity, battery electrodes are usually capable of significant or complete local depletion of the electrolyte solution. This may be due to consumption of species in an electrochemical reaction (e.g. SO₄²⁻ in lead-acid cell discharge) [18] and/or electromigration of passive electrolyte species that do not participate in reactions (e.g. PF₆⁻ in “rocking chair” cells) [8]. Commercial intercalation electrode materials for Li-ion batteries can show volumetric capacities that are many times the electrolyte concentration, exceeding 26 mol L⁻¹ and 16 mol L⁻¹ for cathodes and anodes, respectively (based on the total electrode volume) [19]. High volumetric capacities exacerbate electrolyte depletion. Newer materials under development show capacities that are dramatically higher still. Local electrolyte distribution has been measured directly during operation using magnetic resonance imaging in supercapacitors [20] and lithium batteries [21].

Substantial depletion can also occur with current supercapacitor electrode materials, and the potential for depletion is compounded by recent advances in electrode materials, which have dramatically increased electrode capacitance along with energy storage capability. Fang and Binder obtained specific capacitance of 160 F g⁻¹ in carbon aerogels treated to improve their hydrophobic character [22]. Kim et al. showed specific capacitance of 170 F g⁻¹ for aligned carbon nanotubes in acetonitrile with 1 mol L⁻¹ TEA-TFB [23]. Chmiola et al. measured

volumetric capacitance of 180 F cm⁻³ for thin (~ 2 μm) films of carbide derived carbons in organic electrolytes [24]. Yan et al. showed specific capacitance of 1020 F g⁻¹ in 1 mol L⁻¹ LiClO₄/CH₃CN [25]. For a symmetric cation/anion adsorbing capacitor, assuming unity charge efficiency, the maximum total-volume-averaged (not local) change in concentration of ions in the pore volume is given by the following (refer to Section S.1 of the Supplementary Information (SI) for details).

$$\Delta c = \frac{CV_{max}}{2F(2p_e + p_s L_s/L_e)}$$

where, C is volumetric capacitance (in units of Farads per electrode volume $A_e L_e$). Total cell capacitance can be written as $C_{cell} = CA_e L_e/2$. V_{max} is the maximum cell voltage (split evenly in each electrode), F is Faraday's constant, p_e is porosity of the electrodes, p_s is the porosity of the spacer, and L_e and L_s are respectively thickness of electrodes and spacer. In eq (1), Δc corresponds to charge/discharge cycle with 0 to V_{max} voltage window and constant (voltage-independent) capacitance. As an example, for specific capacitance of 250 F g⁻¹, apparent density of 0.4 g cm⁻³, porosity of 80%, V_{max} of 3 V, and L_e of 200 μm and L_s of 100 μm, the maximum concentration change (Δc) is 0.78 mol L⁻¹ (i.e. 78% depletion of a standard 1 mol L⁻¹ electrolyte). Newer capacitive materials would allow removal of electrolyte many times the solubility limit. We note that the extremely large capacity of the electrodes for batteries, which provide volumetric storage of species rather than only the surface action of capacitive systems, further exacerbates localized depletion effects. Beyond the effect on charge/discharge rate, depletion has potentially important consequences for battery safety. Depletion has been implicated in the transition to dendritic lithium growth and consequent shorting in cells with lithium metal anodes [26].

Design of battery and supercapacitor electrodes to overcome mass transport limitations by optimizing porosity and tortuosity [27–30] and electrode conductivity [31–35] has been an active field of study. For example, a graded and spatially varying electrode conductivity was used by Masliy and Poddubny [32–35] to achieve more uniform electric current distribution for redox electrodes under a strict steady state condition. This strategy was recently used by Zhang et al. [31] in a four-layer, graded, Li-ion battery electrode to improve Li diffusivity and battery capacity. In the current paper, we adopt the idea of a tailored electrode but, unlike these previous studies, we use the spatial variation of electrode matrix conductivity to control and avoid local depletion of electrolytes. As we shall show, the tailoring approach also significantly increases charging rate of the system. We begin with an introduction to our approach based on a transmission line circuit model describing the essential coupling of distributed electrolyte and electrode conductivities. We present a numerical model based on detailed porous electrode transport theory and use this model to study spatiotemporal dynamics of electrolyte conductivity in the spacer and electrode pores. We then derive an analytical form of electrode conductivity for uniform salt adsorption and show that a spatially variable and decreased electrode conductivity profile avoids local depletion and increases charging rate by ~ 2-fold. Lastly, we show the effect of electrode conductivity on energy dissipation and the negligible effect of our tailored electrodes on overall resistive loss.

One potentially important phenomena that we do not consider here is conduction along the surface of the electrode matrix resulting from the high ionic concentration in the double layer. This effect has been shown to allow enhanced charging kinetics in porous electrodes [36]. Such conduction can help ameliorate the effect of electrolyte depletion in the bulk solution by providing an alternative ionic conduction path. However, the surface conduction path must be continuous throughout the electrode to significantly improve charging kinetics, which may limit its effect in many electrodes such as those formed by compacted powders with poor contact between particles.

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