# IV. Transport Phenomena

# Lecture 37: Pseudocapacitors and batteries

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## 1. Pseudocapacitance

In this lecture, we will discuss pseudocapacitors and batteries, which store energy in two ways: (i) By capacitive charging of the double layers of the electrodes, energy is stored electrostatically in proportion to the area density of double layers, and (ii) via the products of Faradaic reactions, energy is stored electrochemically.

First let us define the pseudocapacitance. Assume we have an electron transfer reaction
$O + ne^- \leftrightarrow R$
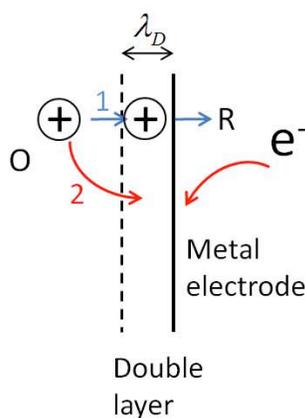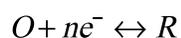


Fig. 1 Two types of capacitance at the interface between electrolyte and metal phase with a double layer lying in between.

There are two types of charge storage that can occur at the interface: pseudocapacitance and double layer capacitance. For example, if the electrode is a carbon nanotube with some functional groups on it or nanoparticles that allow interecalation of Li ions, then electron transfer reaction (Faradaic reaction) occurs at the surface of the electrode, and this type of capacitance is called 'pseudocapacitance'. If no Faradaic reaction is allowed, charges can only be physically absorbed in to the double layer without any electron transfers. In this latter case we only have purely electrostatic double-layer capacitance. When we view the electrode/electrolyte interface as a black box, we only see that ions and electrons enter and are stored at a given voltage, and it is difficult to distinguish whether charge is stored capacitively or Faradaically. The time scales and nonlinear response of each process is very different, however, so it is possible to separate these processes from experimental data using suitable mathematical models.

Recall the Nernst equation:

$$\Delta\phi = \phi_e - \phi = \Delta\phi^0 - \frac{kT}{ne}\ln\left(\frac{a_R}{a_O}\right), \ where \ a_R(c_R) = a_O \cdot e^{\frac{(\Delta\phi^0 - \Delta\phi)ne}{kT}}$$

For example, if R is the solid reactant, then for every reaction $O + ne^- \leftrightarrow R$ at the cathode, charge of $-ne$ is stored, which can be recovered by reversing the reaction. Let $c_R$ be the concentration of species R. The Faradaic reaction corresponds to a differential pseudocapacitance (per volume) is:

$$C_F = \frac{dq_F^{eq}}{d\Delta\phi} = -nel_S\frac{dc_R^{eq}}{d\Delta\phi}$$

## 1.1   Dilute solid solution
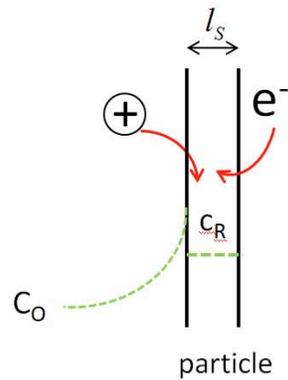


Fig. 2 Concentration distributions inside particle and in the electrolyte close to the particle. Particle has a typical length scale $l_S$.

If we assume the solid solution is dilute, $a_R = c_R$, (O is ion in electrolyte at constant activity R is dilute solid solution), and reactions are fast ($R_F = 0$), we have $\Delta\phi = \Delta\phi_{eq}$ and $c_R$ is almost uniform inside the particle with a typical length scale $l_S$. There will be no transport of reduced state R on the CNT surface (not true in Li battery case). Then there is an effective 'pseudocapacitance' $C_F$

$$C_F = \frac{dq_F}{d\Delta\phi} = -nel_s\frac{dc_R^{eq}}{d\Delta\phi}$$

Following dilute solid solution approximation, we have

$$C_F = \frac{(ne)^2}{kT}a_O l_S e^{(\Delta\phi^0 - \Delta\phi)ne/kT}$$

We can plot $c_R^{eq}$ and $C_F$ as a function of voltage drop across the double layer $\Delta\phi$ (Fig.3).
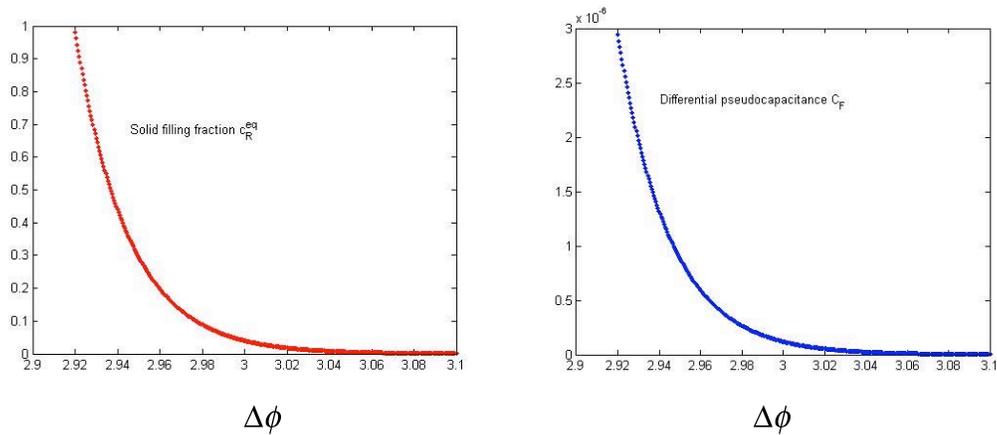
Fig. 3 $c_R^{eq}$ and $C_F$ as a function of voltage drop across the double layer $\Delta\phi$ when $\Delta\phi^0 = 3$

In some cases, continuous redox reactions are possible (e.g., converting one solution species into another), but in energy storage devices at least one reactant is a solid (surface group, intercalated ion, etc) which stores the net reaction energy between cathode and anode reactions. The solid reactant is always finite! So we know that at some point, the space to store R will run out, and the model based on dilute solid solution approximation is obviously too simple.

## 1.2    Solid solution model / Lattice gas model

Next, we let R to be non-dilute solid solution, and take into account the excluded volume effect (finite set) of the reaction sites by using solid solution (lattice gas) model. We know that activity of the reduced state can be expressed as follows

$$a_R = \frac{c_R}{c_R^{max} - c_R}$$

This will dramatically change the pseudocapacitance features. When all sites are occupied, we are done, and there is no more pseudocapacitance. When $a_O = 1$,

$$\Delta\phi = \Delta\phi^0 - \frac{kT}{ne}\ln\left(\frac{c}{1-c}\right) = \Delta\phi^0 - \frac{kT}{ne}2\tanh^{-1}(2c-1)$$

$$where\ filling\ fraction\ c = c_R\Big/c_R^{max}$$

This form of expression allows us to solve filling fraction $c$ as a function of $\Delta\phi$:

$$c = \frac{1}{2}\left[1 + \tanh\left(\frac{(\Delta\phi^0 - \Delta\phi)ne}{2kT}\right)\right]$$

Then we can take derivative. Recall $q_F = -necc_R^{max}l_S$, the differential pseudocapacitance becomes:

$$C_F = \frac{dq_F}{d\Delta\phi} = -nec_R^{\max}l_S\frac{dc}{d\Delta\phi} = \frac{(ne)^2 c_R^{\max}l_S}{4kT}\sec h^2\left(\frac{(\Delta\phi^0 - \Delta\phi)ne}{2kT}\right)$$
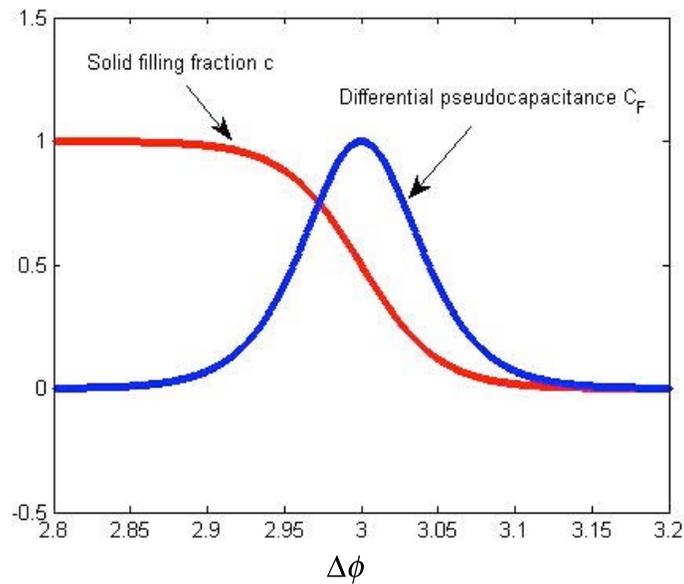


Fig. 4 Solid filling fraction c and differential pseudocapacitance curves when $\Delta\phi^{eq} = 3.0V$
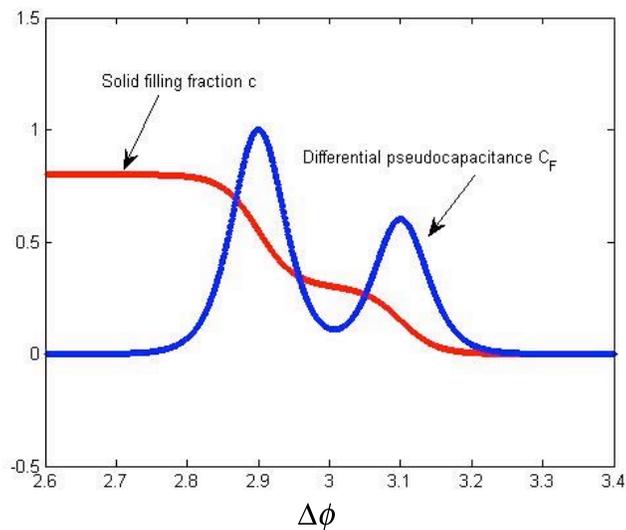


Fig. 5 Solid filling fraction c and diffferential pseudocapacitance curves when two Faradaic reactions occur in the same system with $\Delta\phi_1^{eq} = 2.9V$ and $\Delta\phi_2^{eq} = 3.1V$

When multiple Faradaic reactions occur in the same system, the pseudocapacitance curve will have multiple peaks corresponding to different equilibrium voltage $\Delta\phi^{eq}$. Fig.5 shows the case where two Faradaic reactions occur with $\Delta\phi_1^{eq} = 2.9V$ and $\Delta\phi_2^{eq} = 3.1V$.

## 2. Double layer model with Faradaic Reactions

From HW5 Problem3 we know that Faradaic reaction rate can be expressed as a function of overpotential, charge in the double layer, charge in solid phase, and the reduced species concentration in bulk electrolyte.

$$R_i = R_i(\eta, q, c_S, c_i)$$
$$\eta = \Delta\phi - \Delta\phi^{eq} \ (where \Delta\phi \ is \ total \ DL \ voltage \ drop)$$
$$c_S = concentration \ of \ reaction \ product \ in \ solid \ (= \ c_R)$$
$$c_i = concentration \ of \ oxided \ state \ in \ electrolyte$$
$$q = surface \ charge = -q_D \ (- \ DL \ charge \ density)$$

There is an expression like this for each active species:  $\hat{n} \cdot F_i = R_i = l_S \dfrac{\partial c_S}{\partial t}$

In this case, the equivalent circuit is shown in Fig. 6, ($C_D$ is diffuse layer capacitance, $C_S$ is stern layer capacitance, $C_F$ is Faradaic reaction capacitance, $R_F$ is Faradaic reaction resistance) and generally these elements are nonlinear.
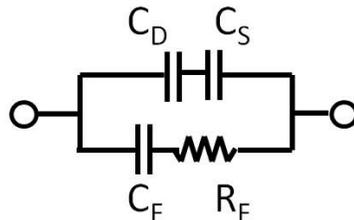


Fig.6 Equivalent circuit for GCS double layer model with Faradaic Reactions.

From GCS model, we can plot the total double layer capacitance $C_{DL} = \dfrac{1}{\dfrac{1}{C_D} + \dfrac{1}{C_S}}$, and we can

also plot pseudocapacitance $C_F$ in the same figure. Note that when we combine double layer capacitance and pseudocapacitance, two curves may be shifted because the equilibrium voltage can be different.
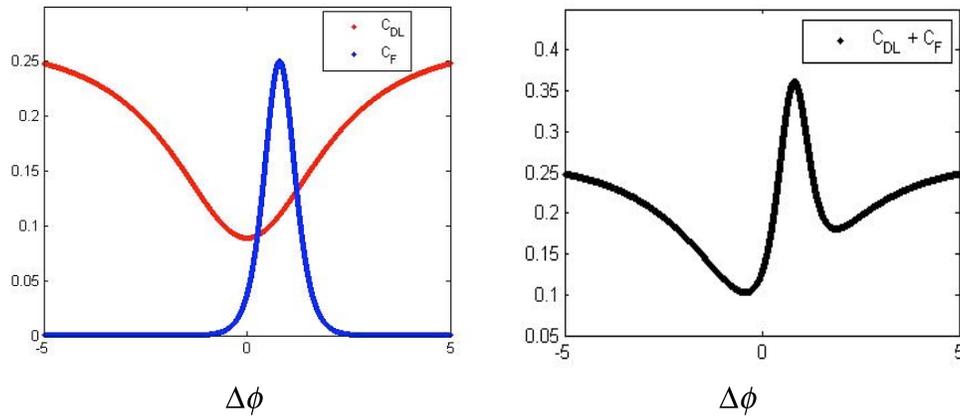
Fig.7 Left: Shapes of double layer capacitance from GCS model and pseudocapacitance from Faradaic Reactions. Right: Possible shape of total capacitance ($C_{DL}+C_F$) when both types of charge storage mechanism exist. $\Delta\phi^{eq} = 0.5$ is used in these plots.

From lecture 36, we know that CV scans will reflect total capacitance (Fig. 8) at low scan rates, such that various transients (RC charging, diffusion, etc.) can be neglected.
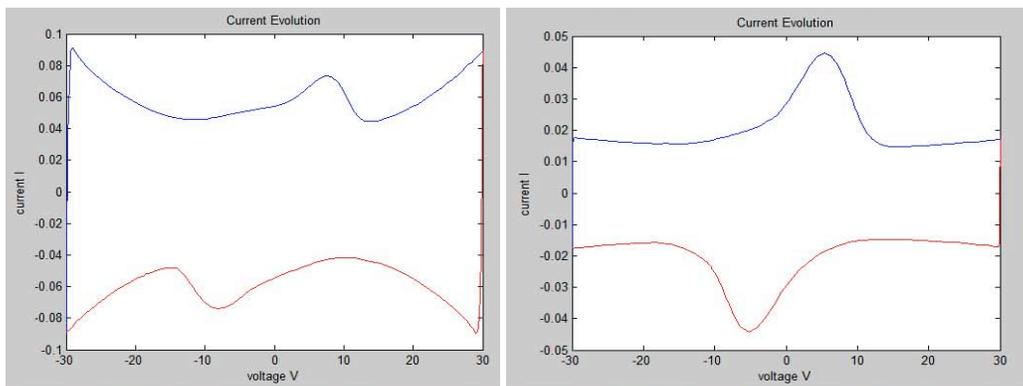


Fig. 8 Cyclic voltammetry curves that reflect the total capacitance (as well as some transient effects) from porous electrode numerical simulations using the full numerical model below (by Y. Fu and MZB). Left: when GCS model plays an important role, and the Faradic peaks exist in the middle ( $\Delta\phi^{eq} = 0$ is used in these plots). Right: when double layer effect is weak, and reaction resistance is very small, Faradic peaks become more clear, although there is a shift between the forward and backward peaks due to transient effects.

Note the reaction peaks are shifted because of the transient process due to $\tau_F = R_F C_F$ time scale, as well as diffusion in the electrolyte (not captured by a transmission line model).

Fig. 9 and 10 can help better understand effects from Faradaic reaction resistance. The concentration of reduced state inside or at the surface of the solid phase $c_S$ in terms of voltage drop $\Delta\phi$ are shown in Fig.9. When current is almost zero (infinitely slow charge or discharge),

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$\Delta\phi = \Delta\phi^{eq}$. When current increases, then $\Delta\phi = \Delta\phi^{eq} - \eta(I, c, c_S)$ where equilibrium voltage drop $\Delta\phi^{eq}$ comes from Nernst equation, and overpotential $\eta(I, c, c_S)$ comes from Butler-Volmer reaction kinetics. This overpotential $\eta(I, c, c_S)$ increases as the current increases, and thus makes the $c_S$ curve going down and the corresponding pseudocapacitance $C_F$ peak are shifted to left and become broader (Fig. 10).
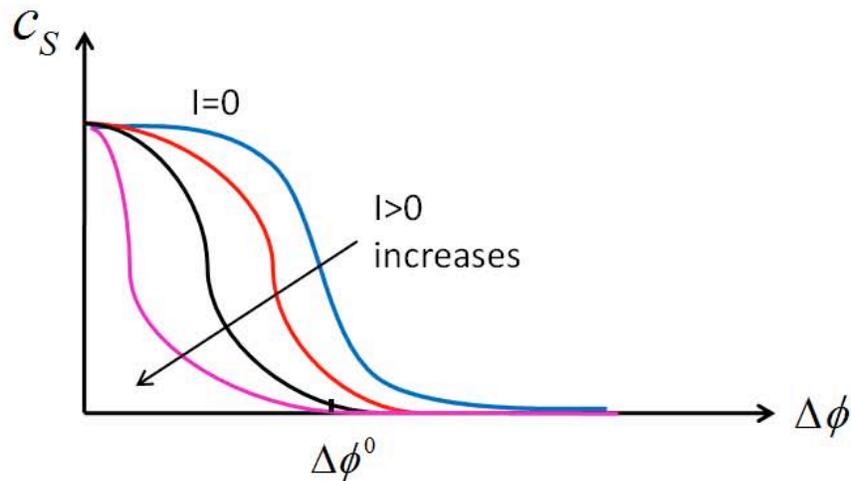


Fig. 9 Reduced species concentration $c_S$ versus voltage drop $\Delta\phi$
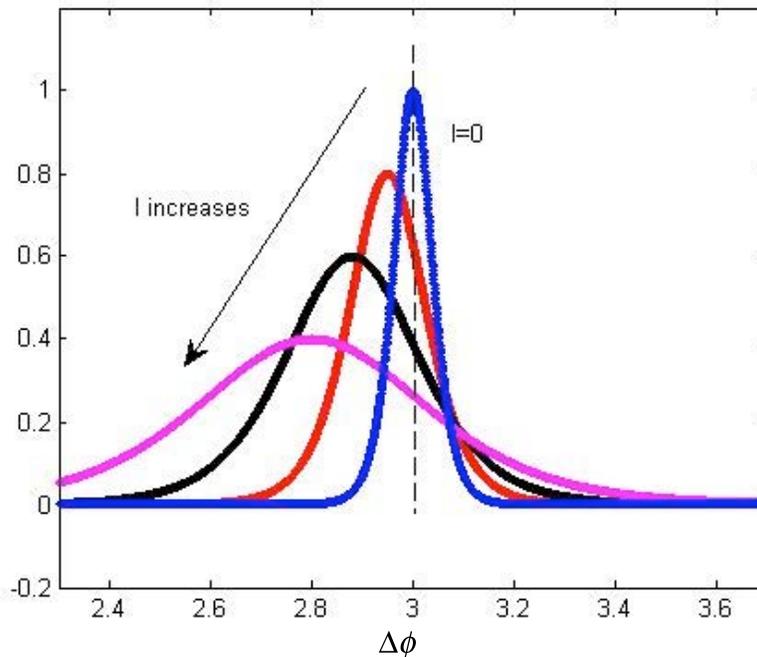


Fig. 10 Pseudocapacitance ($C_F$) peaks shift when current increases. ($\Delta\phi^{eq} = 3$ is used in this plot)

However, it is important to note CV scans include transient effects which can significantly distort the pseudocapacitance peaks. In particular, the broadening of the pseudocapacitance peak with increasing current in Fig 10 leads to a broad increase the relaxation time $\tau_F = R_F C_F$ over a large portion of the scan, thereby slowing down the charging process away from the peak. This leads to shifting and tilting of the upper/forward peak to the right (higher voltage) and the lower/backward peak to the left (lower voltage), as seen in Fig. 8. Diffusion limitation in the electrolyte also contributes to these transients in the CV scan.

## 3. Porous Pseudocapacitor Electrodes

Remember there is a time scale $\tau_F = R_F C_F >> \tau_D = R_D C_D$, which might delay Faradaic reactions and shift the Faradaic peaks in the cyclic voltammetry curves. At the same time, diffusion time scale $\tau_D = R_D C_D$ may also raise transients due to diffusion limitation. This diffusion limitation can become important in porous electrodes.

Examples for porous pseudocapacitor electrodes include:
1) Carbon aerogel or carbon nanotubes (CNT) with functionalized surfaces or with reactive sites for redox reactions.
2) Battery with active nanoparticles (Due to the small size of the particles, diffusion inside solid can be treated as fast, and the overall process is always limited by reactions and electrolyte diffusion).

In the following parts, we will first set up a full nonlinear model with possibility of electrolyte depletion, and then discuss linear equivalent circuit models for small perturbations in electrolyte concentration. Some numerical solutions are shown in Figs 8 and 12.

## 3.1 Full nonlinear model (with salt depletion)

Following conservation of species, we will have the following equations for the porous electrode pseudocapacitor:

$$a_F R_i + a_P \frac{\partial \Gamma_i}{\partial t} + \epsilon_P \frac{\partial c_i}{\partial t} = \epsilon_P \overline{D} \nabla \cdot (c_i \nabla \overline{\mu}_i)$$

$$where \ \epsilon_P = \ porosity$$

$$a_F = \frac{active\ area}{volume}$$

$$a_P = \frac{DL\ area}{volume}$$

$$c_i = \ oxidized\ species\ in\ electroly$$

The first tem $a_F R_i$ is 'ion adsorption by Faradaic reactions', the second term $a_P \dfrac{\partial \Gamma_i}{\partial t}$ describes

'double layer ion adsorption', and the other two terms account for 'bulk electrolyte transport in pores'.

In pseudocapacitance approximation, all the species reacted go in to the solid phase (either stay at the surface or diffuse into the bulk of the solid phase). We also know that charge stored by reaction equals unit charge times the reduced species concentration.

$$\begin{cases} a_F R_i = \in_S \dfrac{\partial c_S}{\partial t} \\ e c_S = q_F \end{cases}$$

$$where \in_S = active\ solid\ volume\ fraction$$

$$c_S = reduced\ species\ concentration\ in\ solid$$

In this case, the full nonlinear model equation can be rewritten as:

$$a_F \frac{\partial q_F}{\partial t} + a_P \frac{\partial q_S}{\partial t} + \in_P \frac{\partial c_i}{\partial t} = \in_P \overline{D} \nabla \cdot (c_i \nabla \overline{\mu}_i)$$

## 3.2 Transmission Line ( $c_i \approx const\ in\ electrolyte$ )

Linear transmission line model is valid if parameter $\beta = \dfrac{c_S^{max} \in_S}{c_0 \in_P} \ll 1$. This $\beta$ parameter

describes the ratio of maximum ion storage in solid over that in electrolyte. When it is far less than 1, it means reactions will not significantly deplete salt in the electrolyte, and corresponding equivalent transmission line is shown in Fig.11.

**Metal or Carbon phase in the electrode**
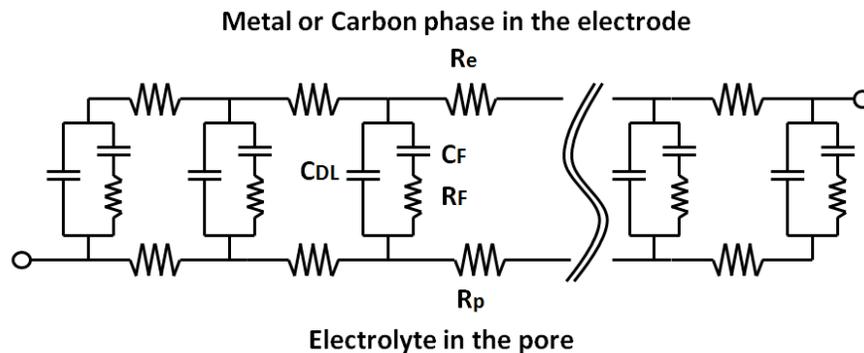


Fig. 11 Equivalent circuit model of one electrode of a pseudocapacitor

A possible CV scan curve is plotted in Fig. 12. Now the RC transient (with diffusion time scale $\tau_D$) makes the starting of the scan curved, and therefore the double layer capacitance effect may become less obvious. Then reaction peaks will also be shifted due to the delay from RC transients as well as medium reaction time scale $\tau_F$.
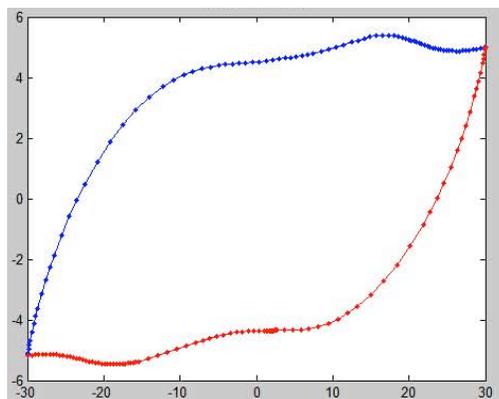


Fig. 12 Possible CV scan curve for a porous pseudocapacitance electrode (by Yeqing Fu).

We can also find some experimental Cyclic voltammogram data from literatures. Fig.13 is two plots reprinted from the paper of High-power lithium batteries from functionalized carbon-nanotube electrodes (SeungWoo Lee, Yang ShaoHorn, Paula Hammond et al., *Nature Nanotechnology*, 5, p531, 2010). We can see the reaction peak is broad and weak in these CV curves. At the beginning of both forward and reverse scans, transients can be observed with a curved starting portion of the current evolution. And the double layer effects are also shown at the ends of both forward and reverse scans (curves taking off).
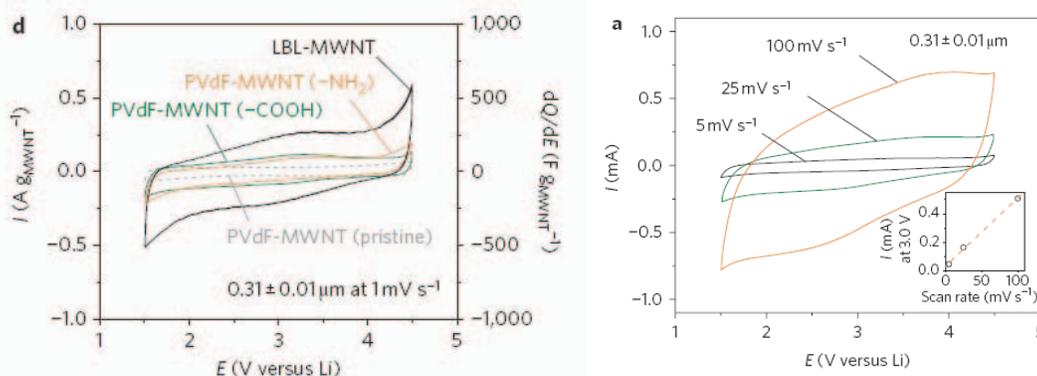


Fig. 13 Experimental CV curves from functionalized multiwall carbon nanotube porous electrode.
Left:  Cyclic voltammogram data for an LBL-MWNT electrode and composite electrodes of pristine MWNT, MWNT-COOH and MWNT-NH₂.  Right: Cyclic voltammogram data for a 0.3mm LBL-MWNT electrode over a range of scan rates. The current at 3 V versus scan rate is shown in the inset.

## 4. Batteries

When $\beta$ parameter mentioned above is much bigger than 1, then salt can be depleted and generally we must consider electrolyte diffusion. For Li-ion batteries, we must often account for slow solid diffusion of the intercalated Li, therefore, $c_S$ is spatially dependent. It is typically assumed for simplicity that intercalated lithium undergoes isotropic linear diffusion $\frac{\partial c_S}{\partial t} = D_S \nabla^2 c_S$ in a representative (spherical) particles.

Typical battery discharge curves for a solid solution electrode system are plotted in Fig.14. When the current increases, over potential become larger, shifting the voltage curves down mainly due to two effects (Faradaic overpotential $\eta_F$ and concentration overpotential $\eta_C$ due to diffusion limitation).

The Faradaic overpotential $\eta_F$ dominates at the beginning of the discharging curves, and concentration overpotential $\eta_C$ becomes dominant at the latter stages of the discharging. This diffusion limitation can either comes from solid particles or the electrolyte, and it mainly limits the usable capacity of the secondary batteries.
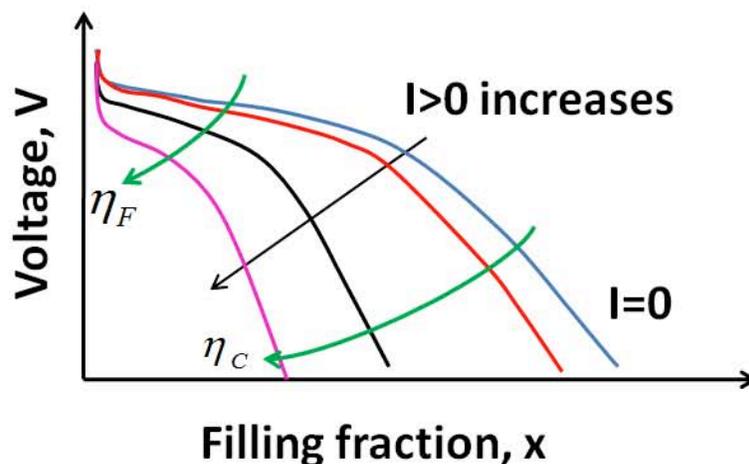


Fig.14 Typical Li-ion battery discharge curves for a solid solution electrode, showing that Faradaic (or surface, or activation) overpotential dominates at early times and low cathode filling, while concentration overpotential (due to diffusion limitation in either the solid or electrolyte phases) usually becomes rate limiting and dominates the polarization at later times and high filling.

**References**

1. B. E. Conway, *Electrochemical Supercapacitors* (Plenum, 1999). (pseudocapacitors)
2. J. Newman and K. Thomas-Alyea, Electrochemical Systems (Wiley, 2004, 2nd ed). (batteries, porous electrode theory)

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