Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Smart Membrane Separator - Physical Properties

The equivalent resitance of a pore filled with electrolyte is given by

$$R = \frac{t}{\kappa A}[\Omega]$$

where κ is the equivalent conductance, $R$is the resistance, t is the length of the pore and A is the area of the pore.

The PPy(DBS) membrane used in Figure 2 has an charge density of 0.3 $\mathrm{C/cm^2}$ that corresponds to a thickness of

$$t = 3[\mu\mathrm{m}]$$

The specific conductance of LiCl is

$$\kappa = \Lambda \times \mathrm{molarity}[\frac{\mathrm{S}}{\mathrm{cm}}]$$

where $\Lambda = 0.0115[\frac{\mathrm{S.m^2}}{\mathrm{mol}}]$ and $\mathrm{molarity}$ = 1 M = 1 $\mathrm{mol/dm^3}$= $1 \times 10^3 \mathrm{mol/m^3}$ LiCl. Therefore,

```
clc;clear all;close all;warning('off','all');
Lambda = 0.0115;
molarity = [1e1 5e1 1e2 2e2 5e2 1e3];
```

Geometry of the pores are -

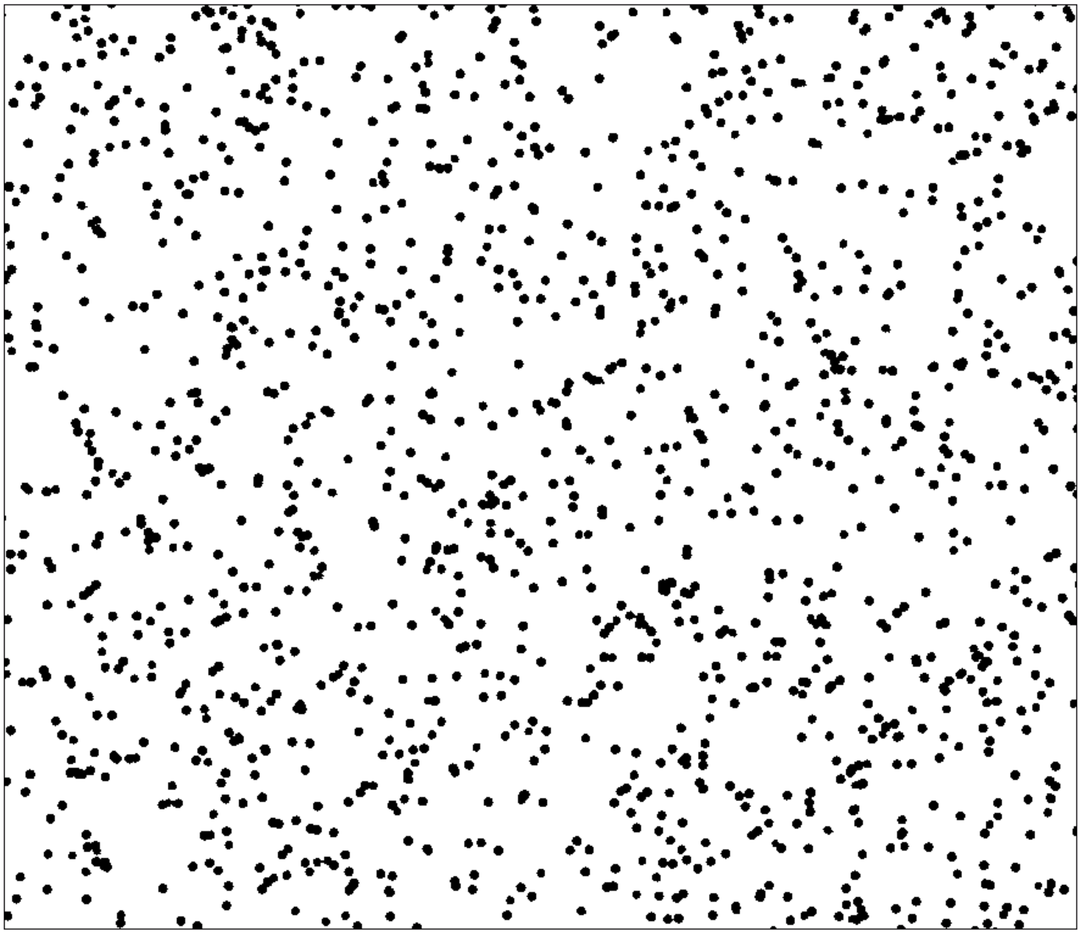
```
r_PPyDBS = 3.1e-3;
t_ox = 3e-6;
dia_pore = 600e-9;
```

Electrical properties from experimental data -

```
R_ox = [49e3 6e3 5e3 3.5e3 18e3 25e3];
R_red = [408e2 35e2 23e2 14e2 750 530];
```

The pososity (χ_p) is determined by SEM image analysis

```
[BWImage,chi_p] = Image_creator();
figure(1)
imshow(BWImage)
```



```
chi_p
```

```
chi_p = 0.0934
```

The area of PPy(DBS) deposited on PCTE substrate is

$$A_{\mathrm{PPy(DBS)}} = \pi \times r_{\mathrm{PPy(DBS)}}^2 [\mathrm{m}^2]$$

where $r_{PPy(DBS)} = 25.4 \times 10^{-3}/8 \approx 3.1 \times 10^{-3}\mathrm{m}$, and the porosity is 9.34%. The area of PPy(DBS) over the pores is

$$A_{\mathrm{PPy(DBS)overpores}} = A_{\mathrm{PPy(DBS)}} \times \chi_p [\mathrm{m}^2]$$

```
A_PPyDBS = pi*r_PPyDBS^2;
A_eff_PPyDBS = A_PPyDBS*chi_p
```

```
A_eff_PPyDBS = 2.8208e-06
```

The number of pores with PPy(DBS) is given by

$$\text{No. of pores} = \frac{A_{\text{PPy(DBS)overpores}}}{A_{\text{pore}}}$$

```
A_singlepore = pi*dia_pore^2/4
```

```
A_singlepore = 2.8274e-13
```

```
no_pores = A_eff_PPyDBS/A_singlepore
```

```
no_pores = 9.9767e+06
```

Estimation of Equivalent Resistances and Specific Conductance of PPy(DBS) in Oxidized and Reduced States

The equivalent resistances of the membrane is calculated from

$$R_{\text{total}} = R_{\text{pore}} + R_{\text{ac}}[\Omega]$$

where

$$R_{\text{pore}} = \frac{t_p}{A_{\text{pore}}\kappa}[\Omega] \text{ and } R_{\text{ac}} = \frac{1}{2\kappa d_{\text{pore}}}[\Omega]$$

with t_p= pore length; A_{pore}= pore area; κ = specific conductance of the electrolyte in the pore and d_{pore} = pore diameter

```
t_p = 6e-6;
R_pore = t_p./(A_singlepore*Lambda*molarity)
```

```
R_pore = 1x6 double

   1.0e+08 *
    1.8453    0.3691    0.1845    0.0923    0.0369    0.0185
```

```
R_ac = 1./(2*Lambda*molarity*dia_pore)
```

```
R_ac = 1x6 double

   1.0e+06 *
    7.2464    1.4493    0.7246    0.3623    0.1449    0.0725
```

```
R_poretotal = R_ac + R_pore
```

```
R_poretotal = 1x6 double

   1.0e+08 *
    1.9177    0.3835    0.1918    0.0959    0.0384    0.0192
```

The resistance of the entire membrane is modeled as equal resistances in parallel. Hence, the overall resistance of the electrolyte in the pores (in the absence of PPy(DBS) on the pore),

$$R_{\text{PCTE}} = \frac{R_{\text{total}}}{\text{No. of pores}}[\Omega]$$

```
R_PCTE = R_poretotal/no_pores
```

```
R_PCTE = 1x6 double

   19.2222    3.8444    1.9222    0.9611    0.3844    0.1922
```

Similarly, resistance of the PPy(DBS) in each pore in the oxidized and reduced state is calculated as -

```
R_ox_perpore = R_ox*no_pores
```

```
R_ox_perpore = 1x6 double

   1.0e+11 *
    4.8886    0.5986    0.4988    0.3492    1.7958    2.4942
```

```
R_red_perpore = R_red*no_pores
```

```
R_red_perpore = 1x6 double

   1.0e+11 *
    4.0705    0.3492    0.2295    0.1397    0.0748    0.0529
```

```
R_m_ox_perpore = R_ox_perpore-R_poretotal
```

```
R_m_ox_perpore = 1x6 double

   1.0e+11 *
    4.8867    0.5982    0.4986    0.3491    1.7958    2.4942
```

```
R_m_red_perpore = R_red_perpore-R_poretotal
```

```
R_m_red_perpore = 1x6 double

   1.0e+11 *
    4.0686    0.3488    0.2293    0.1396    0.0748    0.0529
```

Specific conductance of the PPy(DBS) in oxidized and reduced state is calculated from

$$\sigma_{ox} = \frac{t_{ox}}{R_{ox} \times A_{\mathrm{pore}}} \left[S/m\right]$$

$$\sigma_{red} = \frac{t_{red}}{R_{red} \times A_{\mathrm{pore}}} \left[S/m\right]$$

For this calculation, the thickness of the membrane in the reduced state is calculated from using $t_{red} = t_{ox}(1 + \varepsilon_{ox\rightarrow red})[\mathrm{m}]$, where $\varepsilon_{ox\rightarrow red}$ is obtained from mechanoelectrochemistry of PPy(DBS) [Northcutt and Sundaresan, 2015]

```
epsilon_redox = 0.35;
t_red = t_ox*(1+epsilon_redox)
```

```
t_red = 4.0500e-06
```

```
sigma_ox = t_ox./(R_m_ox_perpore*A_singlepore);
sigma_red = t_red./(R_m_red_perpore*A_singlepore);
sigma_ox_mScm = sigma_ox*1e3*1e-2
```

```
sigma_ox_mScm = 1x6 double
```

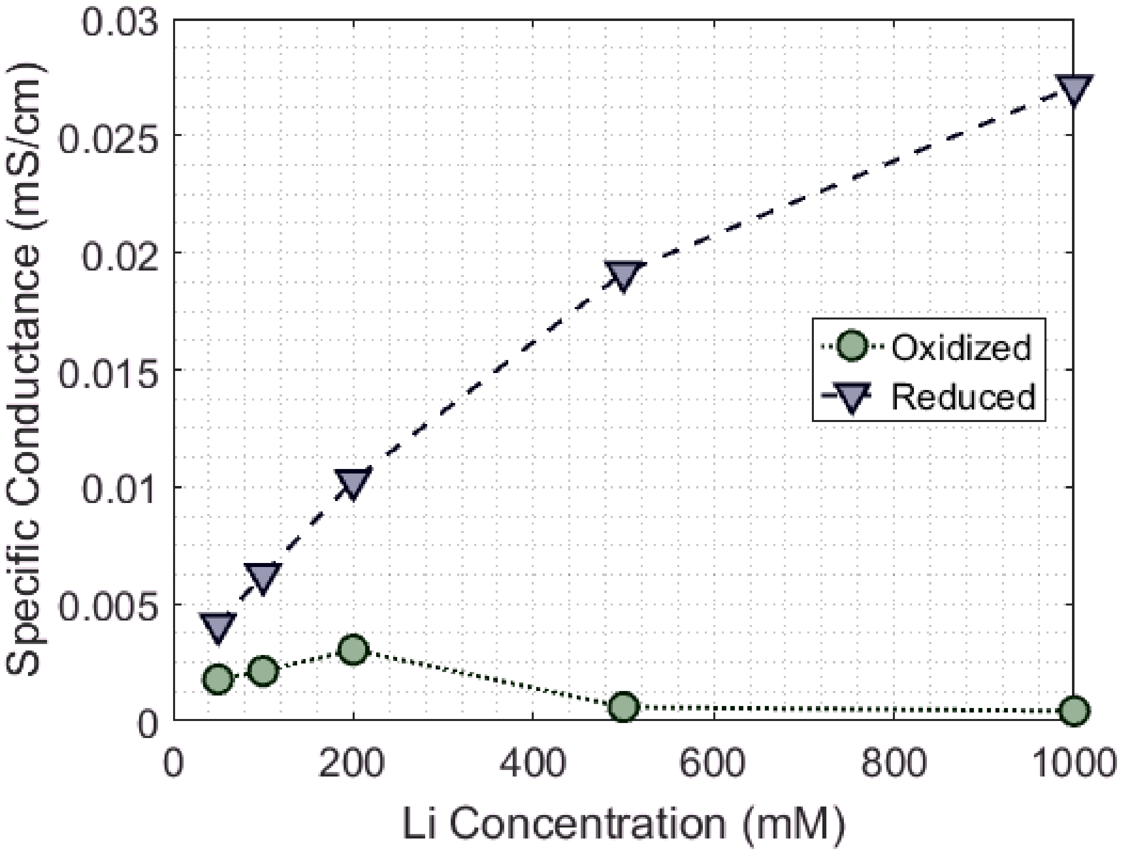
```
    0.0002    0.0018    0.0021    0.0030    0.0006    0.0004
```

```
sigma_red_mScm = sigma_red*1e3*1e-2
```

```
sigma_red_mScm = 1x6 double

    0.0004    0.0041    0.0062    0.0103    0.0192    0.0271
```

```
figure(2)
plot(molarity(2:6),sigma_ox_mScm(2:6),'o:','Color',[0 0.1 0],'MarkerEdgeColor'...
    ,[0 0.1 0],'MarkerFaceColor',[0.6 0.7 0.6],'Markersize',10,'LineWidth',1.5)
hold on;
plot(molarity(2:6),sigma_red_mScm(2:6),'v--','Color',[0 0 0.1],'MarkerEdgeColor'...
    ,[0 0 0.1],'MarkerFaceColor',[0.6 0.6 0.7],'Markersize',10,'LineWidth',1.5)
set(gca,'Fontname','Helvetica','Fontsize',14)
legend('Oxidized','Reduced','Location','East')
xlabel('Li Concentration (mM)')
ylabel('Specific Conductance (mS/cm)')
box on;grid minor;
```



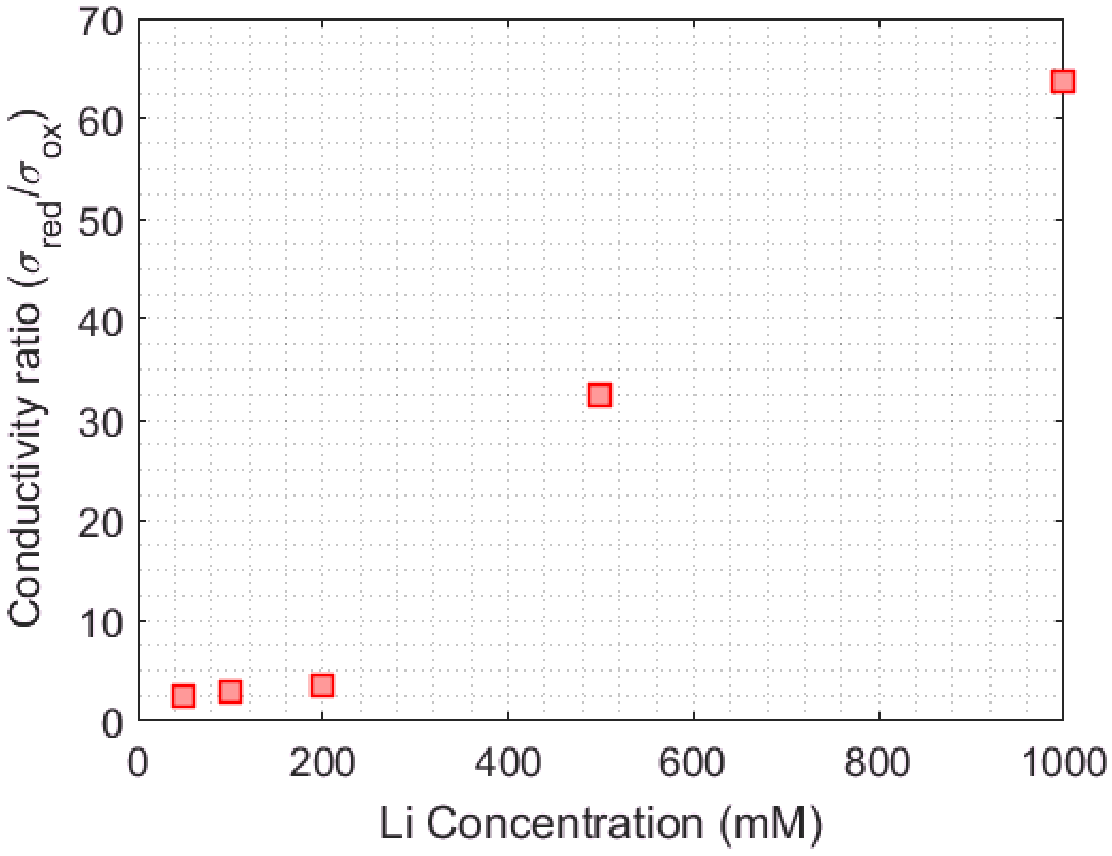
The change in specific conductance between oxidized and reduced state is expressed by $\Gamma = \frac{\sigma_{red}}{\sigma_{ox}}$

```
Gamma = sigma_red./sigma_ox
```

```
Gamma = 1x6 double

    1.6215    2.3153    2.9361    3.3764   32.4159   63.7019
```

```
figure(3);
plot(molarity(2:6),Gamma(2:6),'s','Color',[0 0.1 0],'MarkerEdgeColor'...
    ,[1 0 0],'MarkerFaceColor',[1 0.6 0.6],'Markersize',10,'LineWidth',1.5)
set(gca,'Fontname','Helvetica','Fontsize',14)
xlabel('Li Concentration (mM)')
ylabel('Conductivity ratio (\sigma_{red}/\sigma_{ox})');
box on;grid minor;
```



DBS chains as ionic hopping sites for transmembrane Li ion turnover

With the charge density of 0.3 C/cm^2 (3000 C/m^2) and the area of PPy(DBS), the total number of redox sites, which correlates to the number of DBS, is obtained from mechanoelectrochemistry of PPy(DBS) [Northcutt and Sundaresan, 2015]

$$\text{No. of DBS} = \frac{3000 \times A_{\text{PPy(DBS)}} \times N_A}{(\eta_p - \eta_c) \times F}$$

Where N_A is the Avogradro consant, η_p and η_c are the number of electrons produced and consumed, respectively, during polymerization, amounting to 7.2 net electrons, and F is the Faraday consant.

```
dep_charge = 0.3e4*A_PPyDBS
```

```
dep_charge = 0.0906
```

```
no_redox_sites = dep_charge/(7.2*96485)*6e23
```

```
no_redox_sites = 7.8226e+16
```

Using the porosity and number of pores, as well as the pore geometry, the volume of space for each redox site within the pores V_{DBS} can be calculated as

$$V_{\mathrm{DBS}} = \frac{t_{ox} \times A_{\mathrm{pore}} \times \mathrm{No.\ of\ pores}}{\mathrm{No.\ of\ DBS} \times \chi_p} \left[\mathrm{m}^3\right]$$

```
no_redox_sites_in_pores = no_redox_sites*chi_p
```

```
no_redox_sites_in_pores = 7.3090e+15
```

```
no_redox_sites_per_pore = no_redox_sites_in_pores/no_pores
```

```
no_redox_sites_per_pore = 7.3261e+08
```

```
volume_PPyDBS_in_pore = t_ox*A_singlepore
```

```
volume_PPyDBS_in_pore = 8.4823e-19
```

```
space_per_DBS = volume_PPyDBS_in_pore/no_redox_sites_per_pore
```

```
space_per_DBS = 1.1578e-27
```

Assuming the volume takes the shape of a cube, the length of the sides can be determined

$$s_{\mathrm{DBS}} = V_{\mathrm{DBS}}^{1/3} [\mathrm{m}]$$

```
s_per_DBS = (space_per_DBS)^(1/3)
```

```
s_per_DBS = 1.0501e-09
```

Assuming the cubes stack from one side of the PPy(DBS) to the other to form a chain, the number of DBS per chain and the number of chains in the pores are as follows

$$\mathrm{DBS\ per\ chain} = \frac{t_{ox}}{s_{\mathrm{DBS}}}$$

$$\mathrm{No.\ of\ chains} = \frac{\mathrm{No.\ of\ DBS} \times \chi_p}{\mathrm{DBS\ per\ chain}}$$

```
no_DBS_per_chain = t_ox/(s_per_DBS)
```

```
no_DBS_per_chain = 2.8570e+03
```

```
no_chains_per_pore = no_redox_sites_per_pore/no_DBS_per_chain
```

```
no_chains_per_pore = 2.5643e+05
```

```
no_chains = no_chains_per_pore*no_pores
```

```
no_chains = 2.5583e+12
```

Transmembrane current due to an applied 100 mV potential from experimental data -

```
I_ox = [2e-6 17e-6 20e-6 28e-6 5.6e-6 4e-6];    %A
I_red = [2.5e-6 28e-6 44e-6 72e-6 133e-6 188e-6];
```

Each electron corresponds to one Li^+ transversing the PPy(DBS). Therefore the Li^+ turnover for each DBS chain in oxidized and reduced state is calculated as

$$v^{Li^+}_{chain,Y} = \frac{I_Y \times N_A}{\mathrm{No.\ of\ chains} \times F}\left[\mathrm{s}^{-1}\right]$$

Where Y is either ox or red.

```
Li_flowrate_ox = I_ox/96485*6.022e23
```

```
Li_flowrate_ox = 1x6 double

   1.0e+14 *
    0.1248    1.0610    1.2483    1.7476    0.3495    0.2497
```

```
Li_flowrate_red = I_red/96485*6.022e23
```

```
Li_flowrate_red = 1x6 double

   1.0e+15 *
    0.0156    0.1748    0.2746    0.4494    0.8301    1.1734
```

```
Li_per_chain_ox = Li_flowrate_ox/no_chains
```

```
Li_per_chain_ox = 1x6 double

    4.8793   41.4742   48.7932   68.3105   13.6621    9.7586
```

```
Li_per_chain_red = Li_flowrate_red/no_chains
```

```
Li_per_chain_red = 1x6 double

    6.0991   68.3105  107.3450  175.6555  324.4747  458.6560
```

The asymptotic nature of the Li^+ turnover curve vs Li^+ concenctration is noted, similar to that found in nature for an enzyme reaction rate and substrate concentration, often modeled by Michaelis-Menten kinetics. Therefore a modified Michaelis-Menten equation is used as a model fit for the data

$$V^{Li^+}_{chain,Y} = \frac{V^{Li^+}_{max} \times \mathrm{molarity}}{K_M + \mathrm{molarity}}\left[\mathrm{s}^{-1}\right]$$

Where $V^{Li^+}_{max}$ is the maximum rate of Li^+ turnover and K_M is the concentration at which the Li^+ turnover is half the maximum rate.

```
ft = fittype('(a*x)/(b+x)');
[v,gof_v,p_v] = fit(molarity.',Li_per_chain_red.',ft,'TolFun',10e-9,'TolX',10e-9);

v_Li_max = v.a
```

```
v_Li_max = 738.0053
```

```
k_m = v.b
```

```
k_m = 619.4939
```

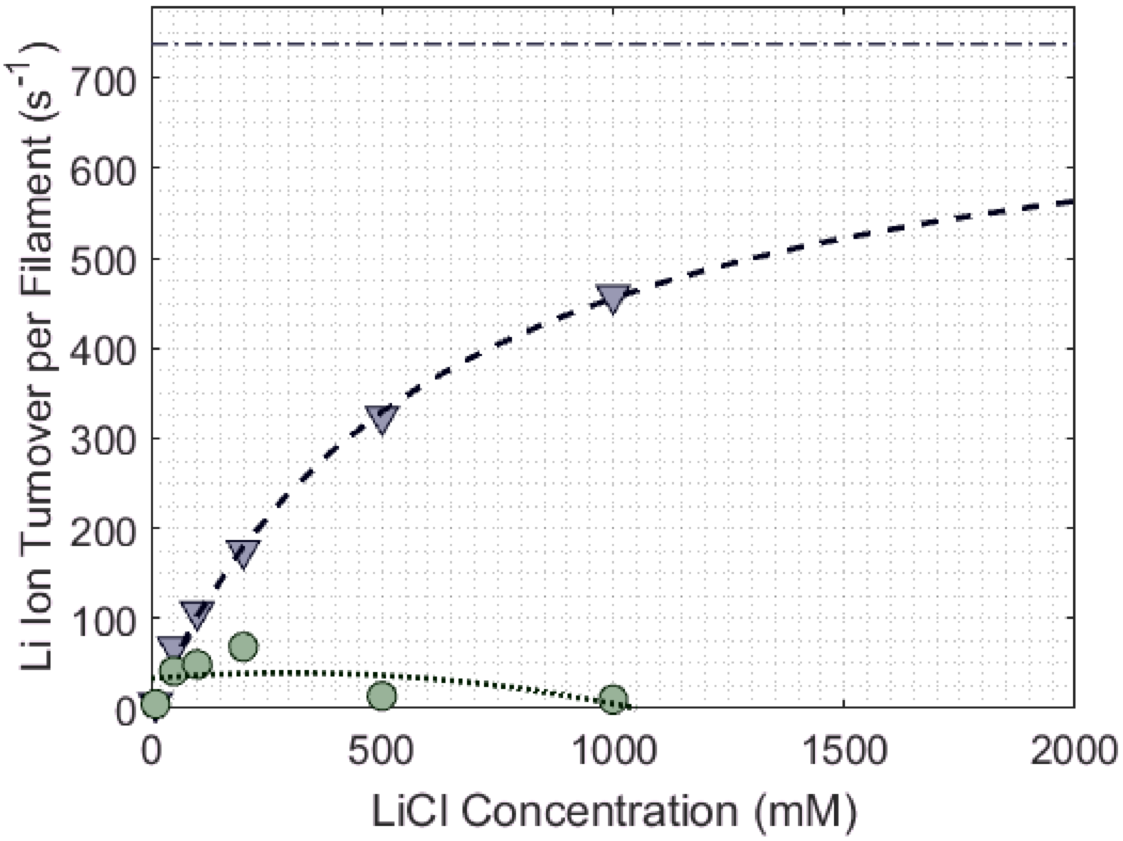
```
molarity_m = 0:100:2000;
v_Li = v_Li_max*molarity_m./(k_m+molarity_m);

p_ox = polyfit(molarity,Li_per_chain_ox,2);

figure(4); hold on;
plot(molarity,Li_per_chain_red,'v','MarkerEdgeColor',[0 0 0.1]...
    ,'MarkerFaceColor',[0.6 0.6 0.7],'Markersize',10);
plot(molarity_m,v_Li,'--','Color',[0 0 0.1],'Linewidth',2)
plot(molarity_m,v_Li_max*ones(length(molarity_m)),'-.',...
    'Color',[0.2 0.2 0.3],'Linewidth',1)

plot(molarity,Li_per_chain_ox,'o','MarkerEdgeColor',[0 0.1 0]...
    ,'MarkerFaceColor',[0.6 0.7 0.6],'Markersize',10);
plot(molarity_m,polyval(p_ox,molarity_m),':'...
    ,'Color',[0 0.1 0],'Linewidth',2);

set(gca,'Fontname','Helvetica','Fontsize',14,'XLim',[0 2000],'YLim',[0 780]);
xlabel('LiCl Concentration (mM)')
ylabel('Li Ion Turnover per Filament (s^{-1})')
box on;grid minor;
```



The performance of the PPy(DBS) is characterized by the amplification factor β, which is defined as the ratio of the Li^+ turnover in the reduced and oxidized states

$$\beta = \frac{V^{Li^+}_{chain,red}}{V^{Li^+}_{chain,ox}}$$

```
Beta = Li_per_chain_red./Li_per_chain_ox
```

```
Beta = 1x6 double

    1.2500    1.6471    2.2000    2.5714   23.7500   47.0000
```

Power calculations for control of transmembrane ion transport

The peak power required to reduce the PPy(DBS), as well as the continuous transmembrane power upon reduction, specific to the area over which the power transmission is occurring, can be calculated as

$$P_{m,max} = \frac{I_{m,max} \times V_{m,red}}{A_{\mathrm{PPy(DBS)}}}$$

$$P_{AC} = \frac{I_{red} \times V_{AC}}{A_{\mathrm{PPy(DBS)overpores}}}$$

These values area explored for a 100mM NaCl aqueous solution and PPy(DBS) areal densities of 0.6-.15 $\mathrm{C/cm^2}$, where

```
v_m = -1.1;
I_m_max = [-22e-4 -20e-4 -27e-4 -26e-4];    %A
v_ac = 0.9;
I_red_na = [5.39e-4 4.07e-4 4.41e-4 4.49e-4];
```

Such that

```
p_m_max = v_m*I_m_max*1000/(10000*A_PPyDBS)         %mA/cm^2
```

```
p_m_max = 1x4 double

    7.2870    6.6246    8.9431    8.6119
```

```
p_ac = v_ac*I_red_na*1000/(10000*A_eff_PPyDBS)
```

```
p_ac = 1x4 double

   17.1970   12.9855   14.0703   14.3255
```

```
arealdensity = [0.6 1.0 1.2 1.5];
f5 = figure(5);
% set(f5,'defaultAxesColorOrder',[0.2 0.2 0.4;0.2 0.4 0.2]);
% yyaxis left
plot(arealdensity,p_ac,'^--','Color',[0.2 0.4 0.2],'LineWidth',2,...
'MarkerEdgeColor',[0.2 0.4 0.2],'MarkerFaceColor',[0.5 0.7 0.5],'Markersize',10)
hold on
```

```
plot(arealdensity,p_m_max,'v--','Color',[0.2 0.2 0.4],'LineWidth',2,...
    'MarkerEdgeColor',[0.2 0.2 0.4],'MarkerFaceColor',[0.5 0.5 0.7],'Markersize',10)
% ylabel('Peak Membrane Power (mW/cm^2)')
% yyaxis right
ylabel('Power (mW/cm^2)')
xlabel('A_E (C/cm^2)')
legend('Steady-State Transmembrane Power','Peak Membrane Reduction Power')
set(gca,'Fontname','Helvetica','Fontsize',14)
box on;grid minor;
```