The optimal electrode thickness and porosity

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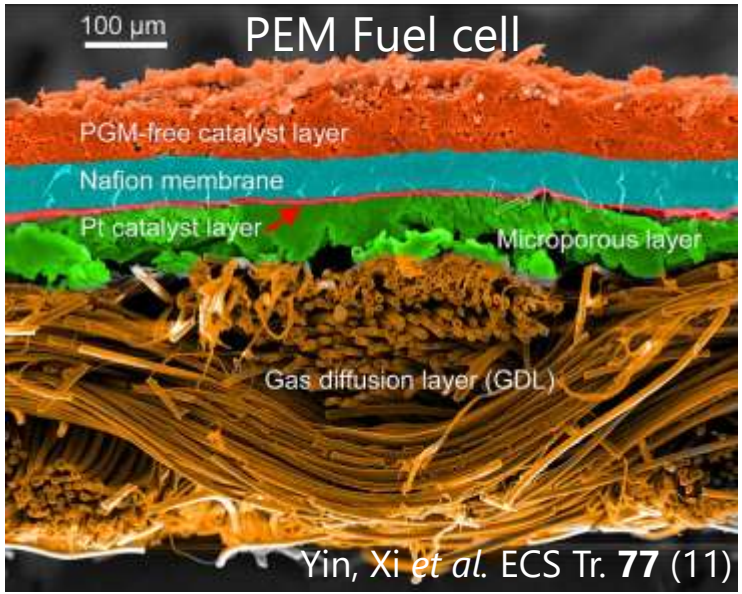
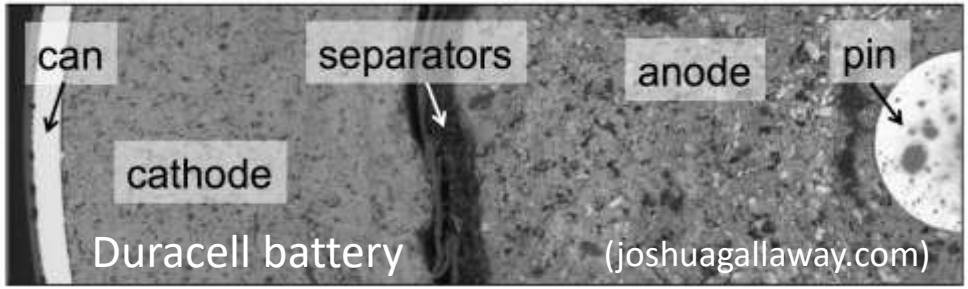
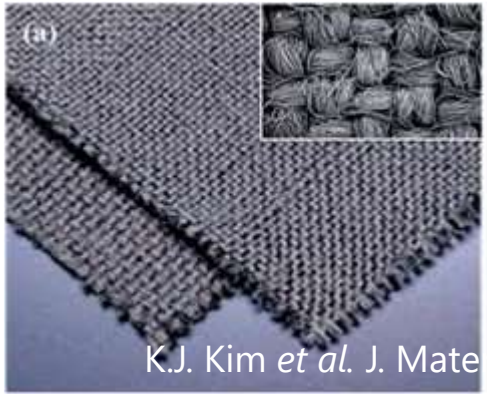
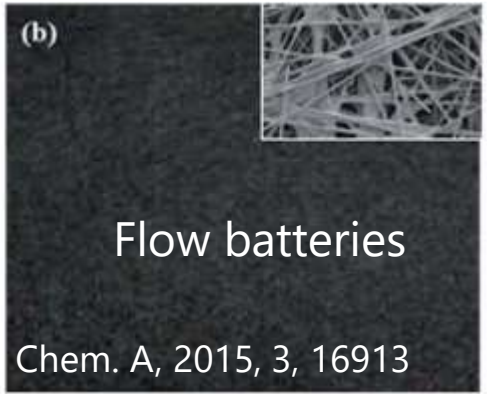
Porous electrodes

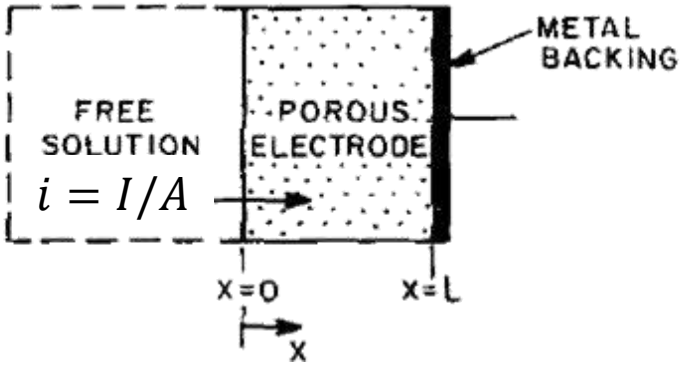


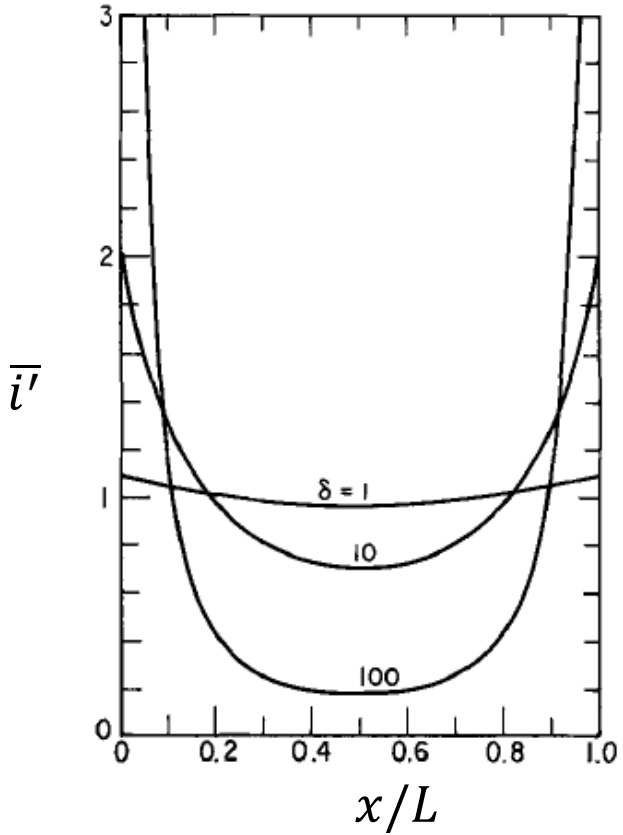






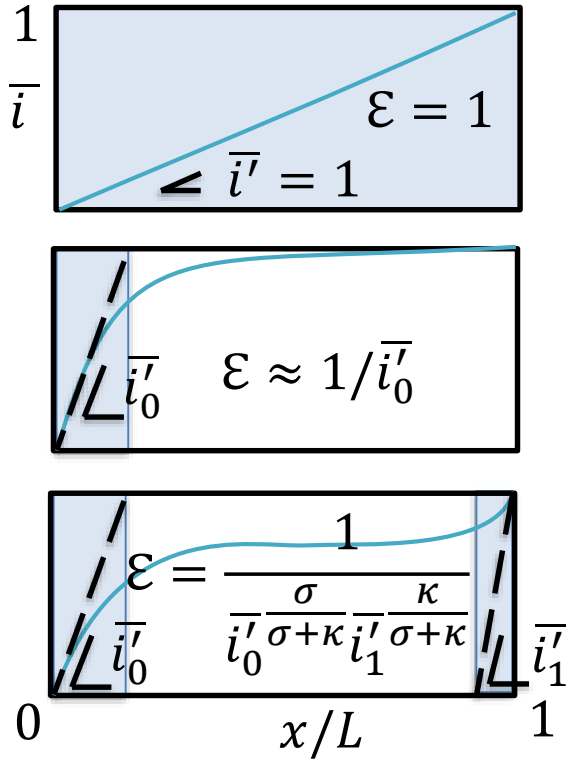
Newman & Tobias 1962





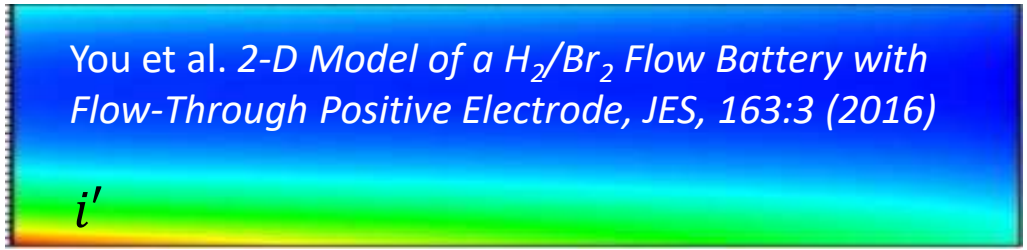
- Conductivities σ, κ
- Tafel slope $b = RT/\alpha F$

Electrode *Effectiveness Factor* Ɛ



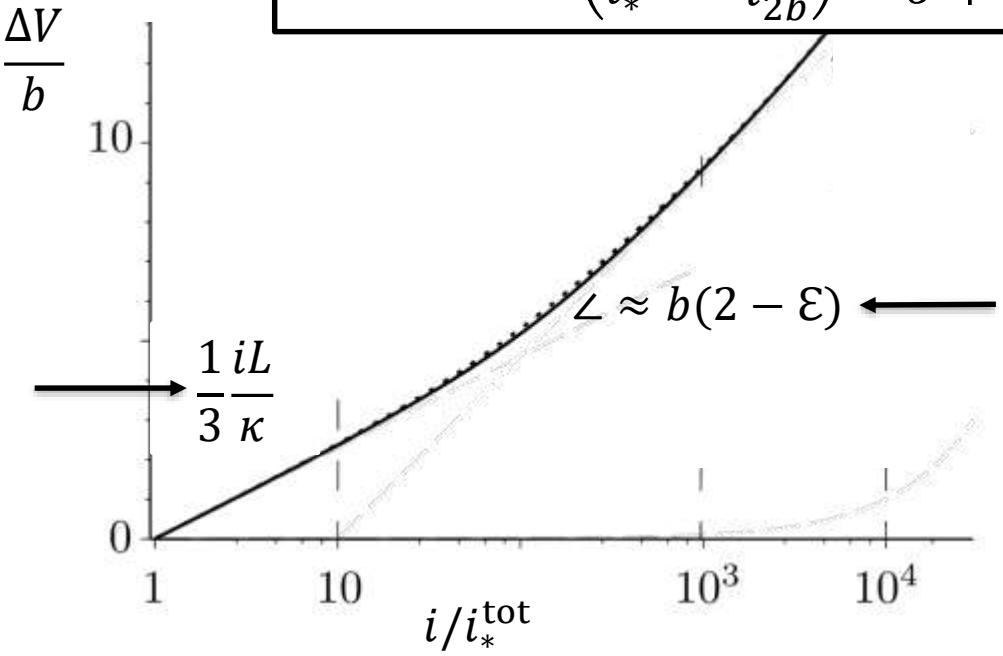
$$\Delta V = b \ln\left(\frac{i}{\mathcal{E} i_*^{\mathrm{tot}}}\right) + \frac{iL}{\sigma + \kappa} \qquad i_*^{\mathrm{tot}} = aLi_*$$

Paulin *et al.* ‘77, Scott ‘82, Costamagna *et al.*, ‘98
Catalyst utilization, e.g. Gasteiger *et al.*



Explicit $i - \Delta V$ relation

$$\Delta V \approx b \ln\left(\frac{i}{i_*^{\mathrm{tot}}} + \frac{i^2}{i_{2b}^2}\right) + \frac{iL}{\sigma + \kappa}$$

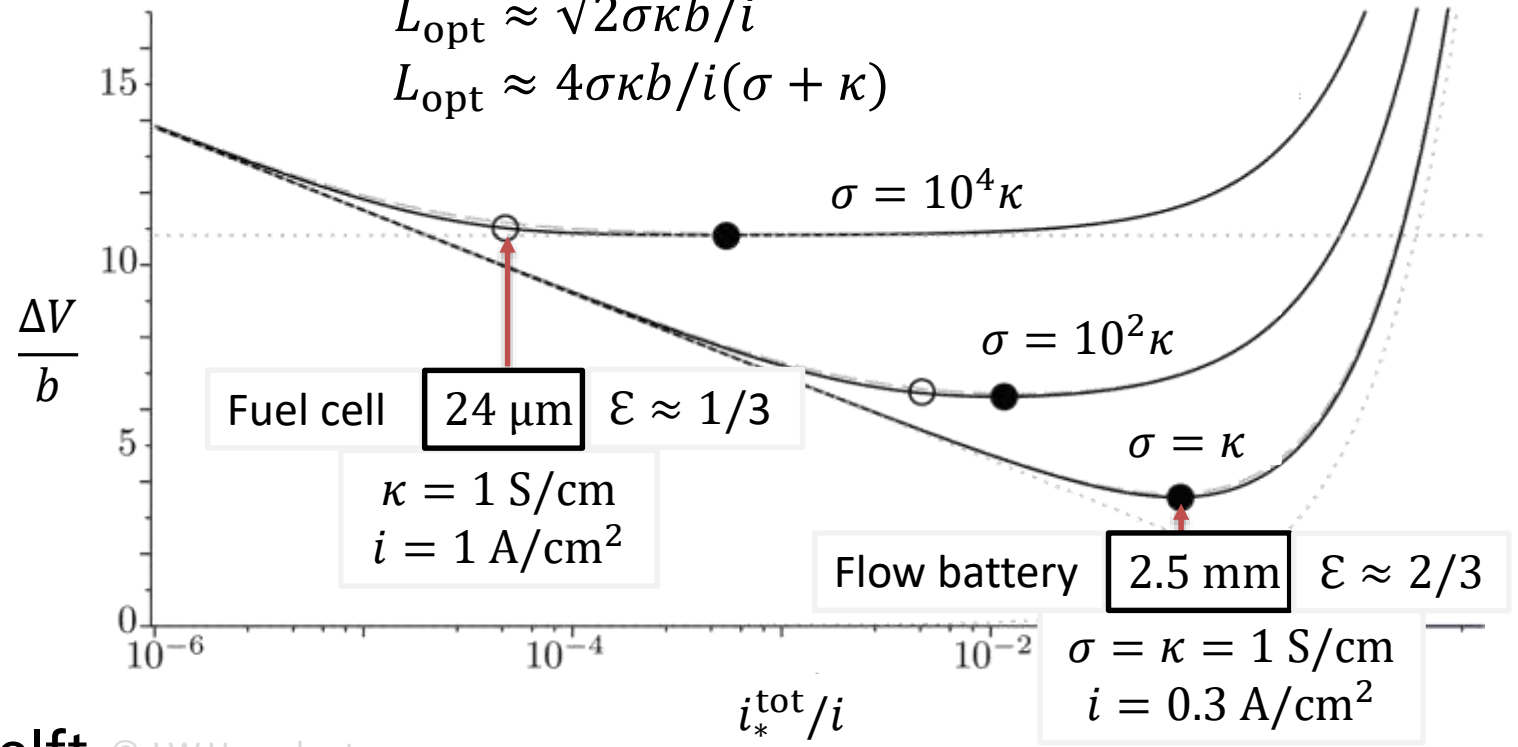


De Levie, Lasia, Neyerlin,…

Tafel slope doubling Austin, Eikerling, Kulikovsky, Soderberg,..

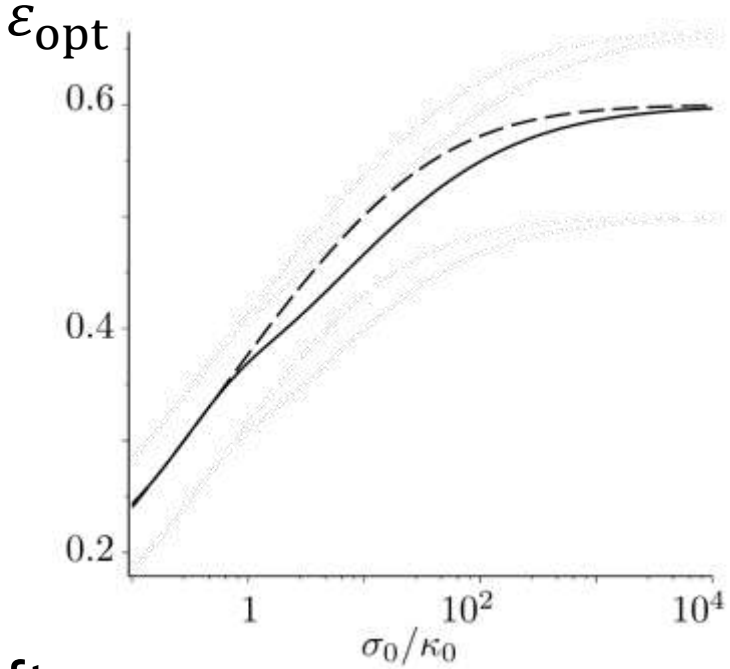
Optimal electrode thickness

$$L_{\text{opt}} \approx \sqrt{2\sigma\kappa}b/i$$
$$L_{\text{opt}} \approx 4\sigma\kappa b/i(\sigma+\kappa)$$

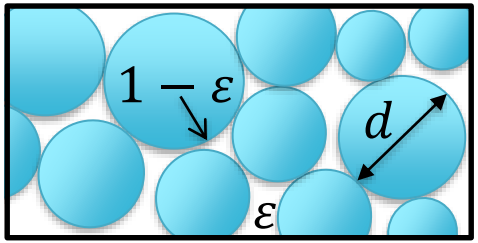


Optimal porosity

$$\kappa = \kappa_0 \varepsilon^n, \sigma = \sigma_0 (1-\varepsilon)^n$$

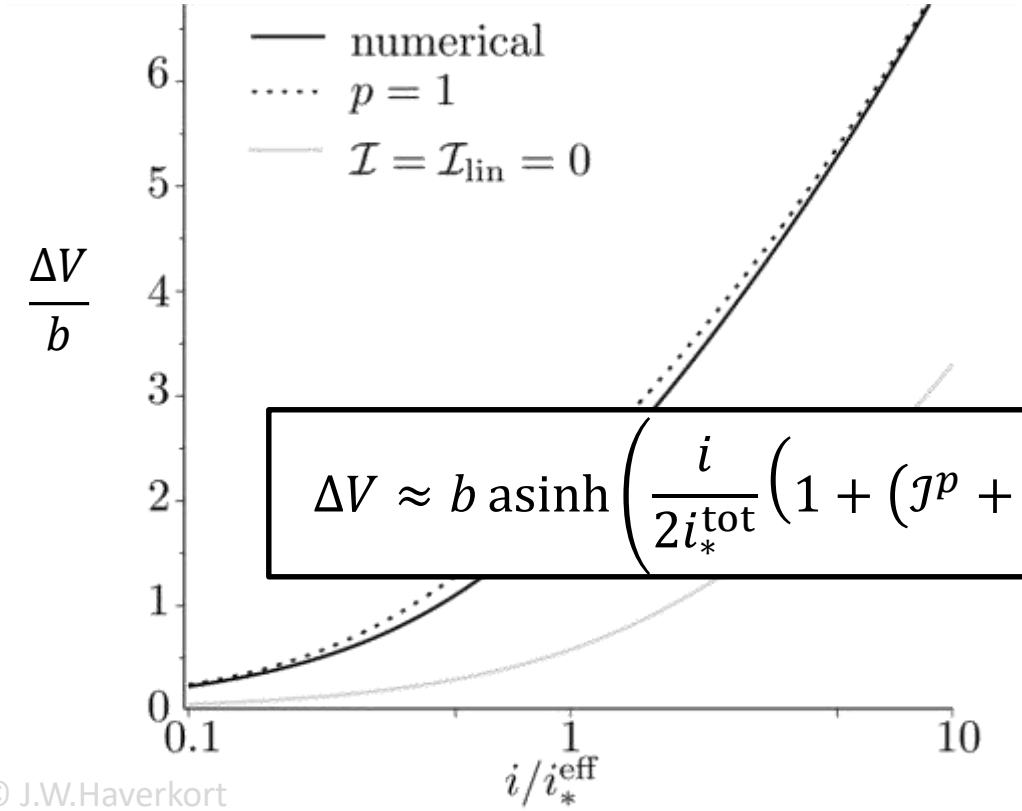


$$\frac{n}{1+n} \xrightarrow{n=1.5} 0.6$$



$$a = \frac{6(1-\varepsilon)}{d}$$

Butler-Volmer kinetics (α=1/2)



Ineffectiveness factor
$\mathcal{I} = \mathcal{E}^{-1} - 1$

$$\Delta V \approx b \operatorname{asinh}\left(\frac{i}{2i_*^{\text{tot}}}\left(1 + \left(\mathcal{I}^p + \mathcal{I}_{\text{lin}}^p\right)^{\frac{1}{p}}\right)\right) + \frac{iL}{\sigma + \kappa}$$

Conclusions

- Thickness $L_{\mathrm{opt}} \approx \frac{4b\sigma\kappa}{i(\sigma+\kappa)}$ so that $\frac{1}{3} \leq \varepsilon \leq \frac{2}{3}$
- Tafel slope $b(2-\varepsilon)$
- Accurate *explicit* polarisation equation

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