# Permselectivity and Transport of Membranes for Redox Flow Batteries

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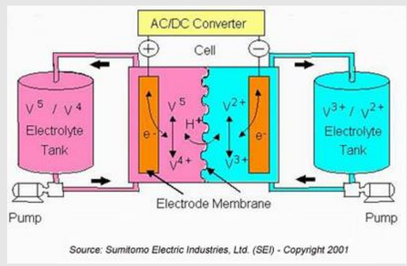
## Introduction

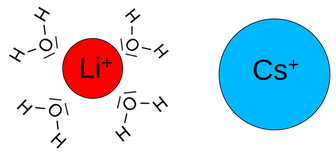
A redox flow battery is an electrochemical energy storage device utilising the different oxidation states of ions in solution. Membranes for redox flow batteries must efficiently separate these electrochemically active ions present in anolyte and catholyte while conducting some other ion for maintaining electroneutrality during battery charging or discharging. A good separation prevents a loss of capacity and therefore provides high coulombic efficiency.

In order to understand the ion exchange, we are studying model systems consisting of membranes and permeating ions of diverse, extreme properties. As redox flow batteries are using highly concentrated electrolyte solutions for capacity reasons, our investigations focus on preferences in ion uptake (permselectivity) at high salt concentrations. It happens to be at such conditions, where the permselectivity drops dramatically and the swelling of the membrane becomes an important selectivity limiting parameter.



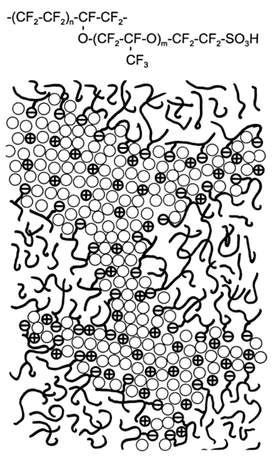

Vanadium redox flow battery (schematic)

## Two extreme ions: Li vs Cs



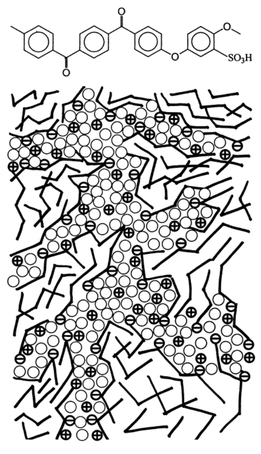

| Ion | $Li^+$ | $Cs^+$ |
|---|---|---|
| hydration enthalpy [kJ/mol] | -520 | -264 |
| Ionic radius [pm] | 76 | 167 |
| Hydrated radius [pm] | 340 | 228 |
| Hydration shell | Strong, 4 water molecules | weak |
| Lewis acid strength | higher | lower |
| Interaction with sulfonate group | lower | higher |

## Two extreme membranes: PFSA vs SPEEK [1]




- wide channels
- more separated
- less branched
- small $-SO_3^-/-SO_3^-$ separation
- $pK_a$ ~ -6

- narrow channels
- less separated
- highly branched
- large $-SO_3^-/-SO_3^-$ separation
- $pK_a$ ~ -1
- backbone with ether and carbonyl groups




⊖ : $-SO_3^-$

⊕ : counterion

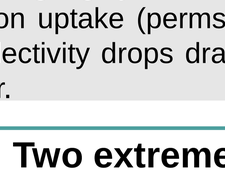
○ : $H_2O$

In this study we use:

- PFSA: Nafion N117
- SPEEK: Fumapem FKE55

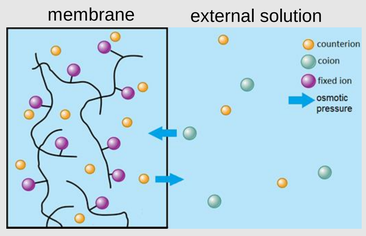
## overall electrolyte uptake: cation / anion selectivity

**(counter- / coion)**



**Modeling the cation / anion selectivity:**

**The Donnan equilibrium**




thermodynamical equilibrium [2]:

$$a^{m}_{\text{coion}} \cdot a^{\text{m}}_{\text{counterion}} = a^{\text{e}}_{\text{coion}} \cdot a^{\text{e}}_{\text{counterion}}$$

common assumptions [3]:

- activity coefficients within the membrane are the same as in external solution
- electroneutrality

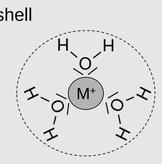
$$b_{\text{counterion}} = \frac{1}{2} \cdot \left( \sqrt{b^2_{\text{fixed}} + 4 \cdot b^2_{\text{extern}}} + b^2_{\text{fixed}} \right)$$

**First improvement:**
incorporation of a hydration shell

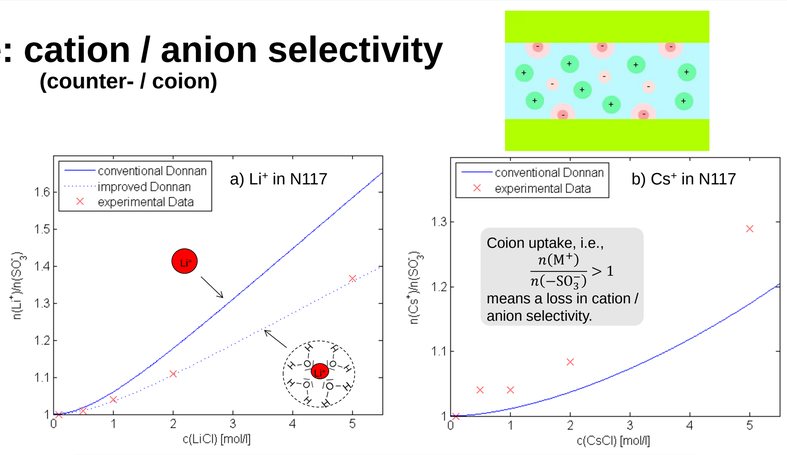
Hydrated species $M^+ \cdot xH_2O$

less bulk water

higher $b_{\text{fixed}}$



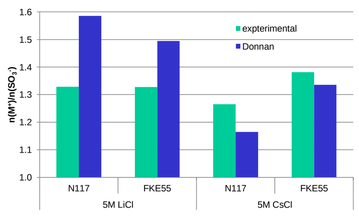

theoretical coion exclusion increases




Coion uptake, i.e., $\frac{n(M^+)}{n(-SO_3^-)} > 1$ means a loss in cation / anion selectivity.

no severe „breakthrough“ → with concentration continuous permeation

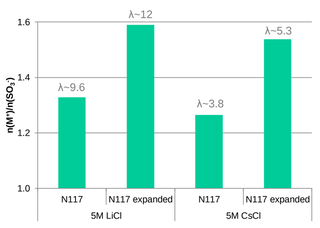
- $Li^+$ uptake is overestimated by conventional Donnan prediction
- $Cs^+$ uptake is underestimated by conventional Donnan prediction
- $Li^+$ uptake in Nafion can be predicted, assuming an hydration shell of 4 water molecules




smaller deviations for SPEEK:

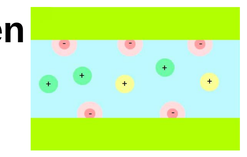
- $Li^+$ may have smaller hydration shell
- less $Cs^+$ interactions with sulfonated groups

Influence of water uptake:
N117 vs preboiled (1h) N117



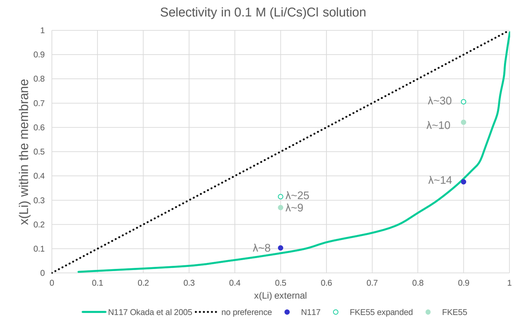

**water uptake** is crucial for cation / anion selectivity

## selectivity between counterions



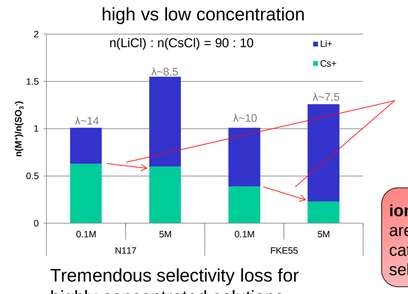
$Cs^+$ is favorised against $Li^+$:

- less membrane swelling → less stress on the polymer
- stabilizing interactions with the sulfonate groups




- higher selectivity for PFSA than for SPEEK
- water increase is reducing selectivity slightly

high vs low concentration




Decrease in the absolute $Cs^+$ uptake!

**ionic interactions** are crucial for cation / cation selectivity

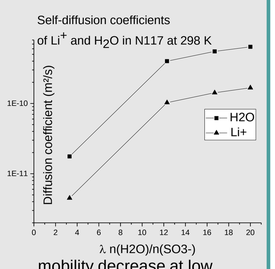
Tremendous selectivity loss for highly concentrated solutions

## Conclusions

- No perfect exclusion of coions (even at low concentrations)
- Membrane swelling limits the counterion / coion selectivity at high electrolyte concentrations
- Selectivity between counterions depends on:
  ionic interactions (low concentrations)
  ionic interactions + water uptake (high concentrations)

## Outlook

- Selectivities in anion exchange membranes
- permselectivity / conductivity trade-off
- Controlling of the key parameter „water uptake“ by polymer blending
- Modelling effective selectivities (actual ion flux) with diffusion data




mobility decrease at low water content

## Literature

[1] K. D. Kreuer, *Journal of Membrane Science*, 2001, 185, 1, 29-39.
[2] T. Okada et al, *Electrochimica Acta*, 2005, 50, 16.
[3] F. G. Donnan, *Zeitschrift für Elektrochemie und angewandte physikalische Chemie*, 1911, 17.
[4] K. D. Kreuer, *Chemistry of Materials*, 2014, 26, 1, 361-380.

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