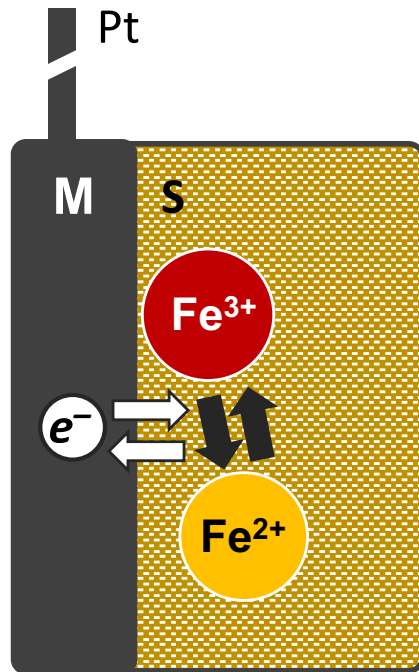


# **(1) Thermodynamics (reversibility, equilibrium)**

# Equilibrium

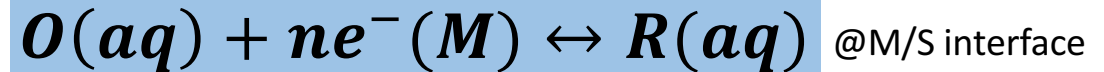
When an electrode dips into sol'n, a potential is established.

@equilibrium



'tiny # of  $e^-$ '

(free  $e^-$ , no usage of PS\*)



- (1) A net electrical charge on each of phase
- (2) A charge separation  $\rightarrow$  potential difference b/w the **M/S**
- (3) *Chemical process establishes electrode potential (potential determining equilibrium)*

$$\Delta G^\ominus = -nFE^\ominus = -RT \ln K$$

$$\overline{\mu}_A = \mu_A + z_A F \phi$$

$$\phi_M - \phi_S = \phi^\ominus + \frac{RT}{nF} \ln \left\{ \frac{[O]}{[R]} \right\}$$

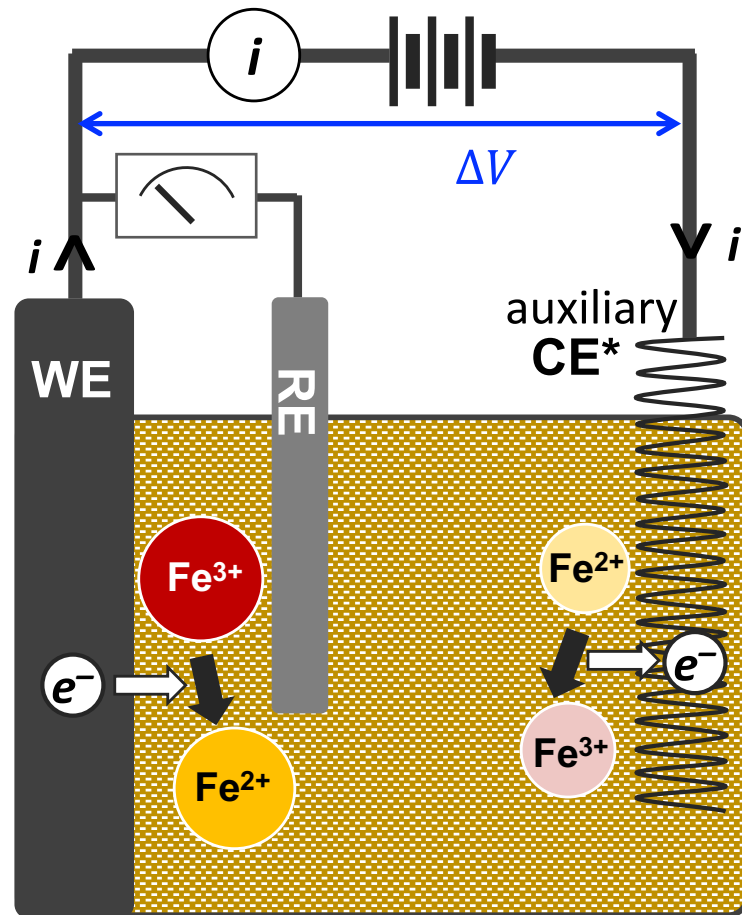
$$E = E^\ominus + \frac{RT}{nF} \ln \frac{C_O^*}{C_R^*} = E^\ominus + \frac{RT}{nF} \ln \frac{a_O^{v_O}}{a_R^{v_R}}$$

$$E^\ominus = \frac{1}{nF} (v_O \mu_O^\ominus + \mu_{e^-} - v_R \mu_R^\ominus)$$

$a$ : activity

$v$ : stoichiometric coefficient

## Three electrode system (half cell)

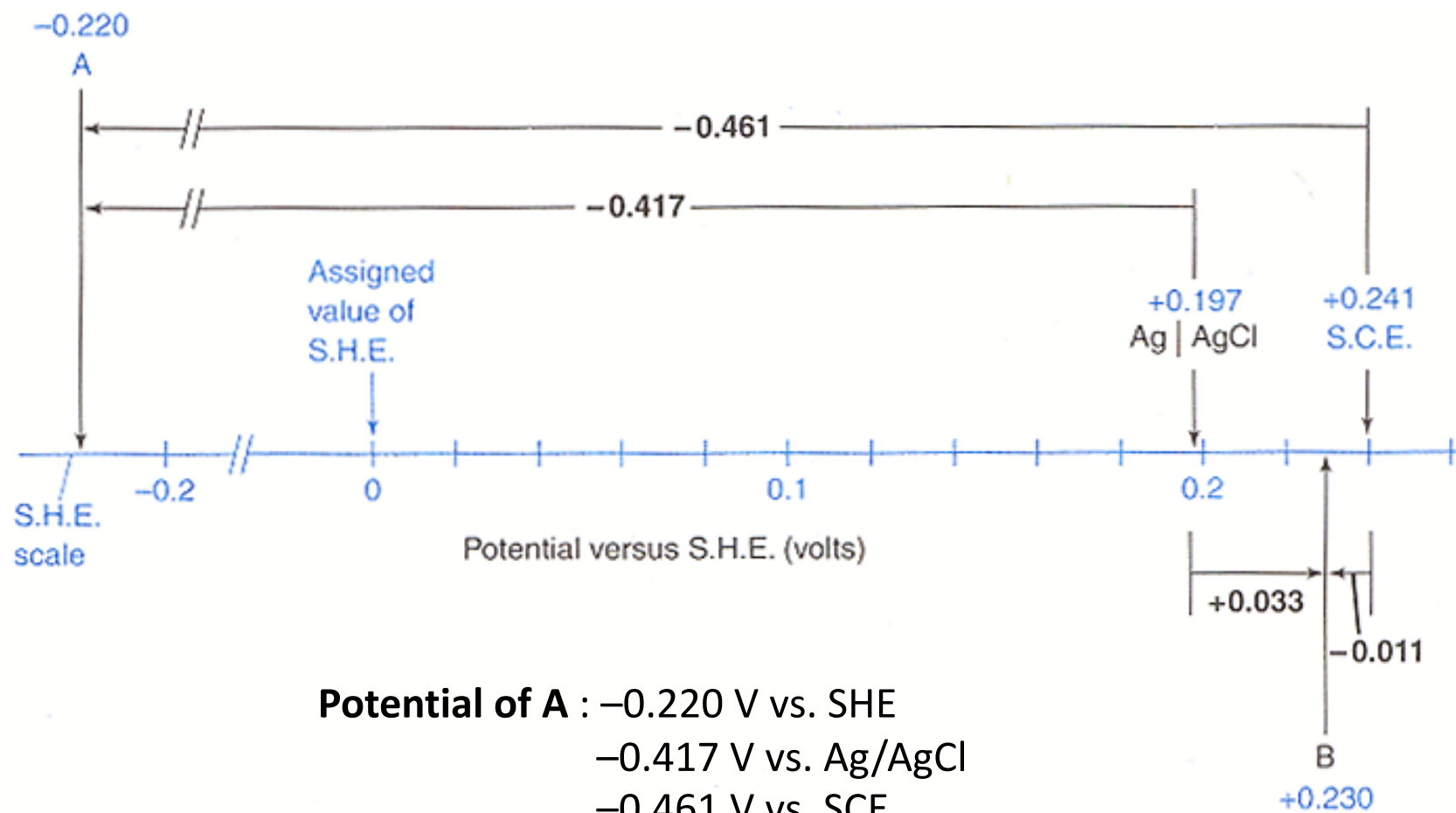


Interest: only WE

### Successful RE → equilibrium

- The chemical composition of the **M** and the **S** must be held fixed.
- A small electric current should be passed through the RE (no electrolysis, no perturbation of the conc. of the species)
- Potential term ( $\phi_{RE} - \phi_S$ ) attains its thermodynamic equilibrium value rapidly. In other words the potential determining equilibrium should display fast electrode kinetics.

## 7-5. Converting potential vs REs



**Potential of A :** -0.220 V vs. SHE  
 -0.417 V vs. Ag/AgCl  
 -0.461 V vs. SCE

**Potential of B :** +0.230 V vs. SHE  
 +0.033 V vs. Ag/AgCl  
 -0.011 V vs. SCE

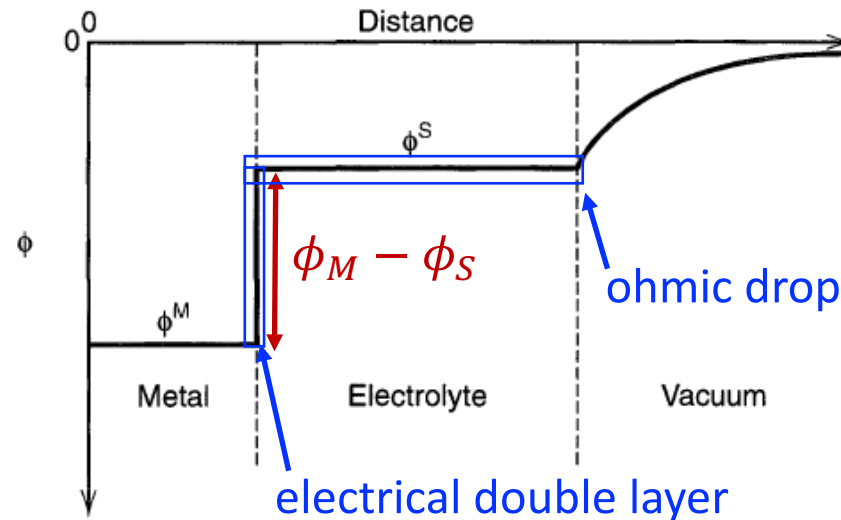
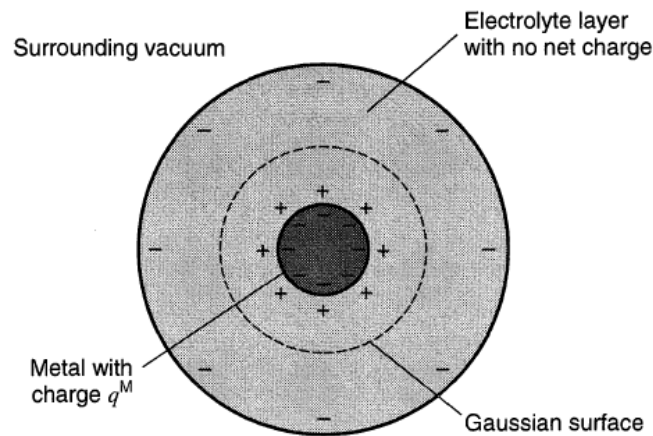
# Liquid junction potential : difference of cation & anion velocity

- **Phase potential:**  $\phi_M - \phi_S$  
$$\phi_M - \phi_S = \phi^\ominus + \frac{RT}{nF} \ln \left\{ \frac{[O]}{[R]} \right\}$$

Since the rxn involves the transfer of the  $e^-$  b/w the two distinct phases, (**M**) and (**S**, aq), as this  $e^-$  transfer rxn moves towards equilibrium, a *net charge separation* must develop b/w the **M** and **S**.

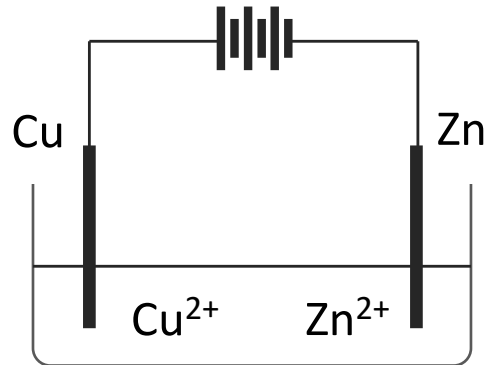
This charge separation creates a *potential difference* at the **M/S** interface.

On the contrary, the difference in potential b/w any two points in the interior of the phase must be *zero* (inner potential).

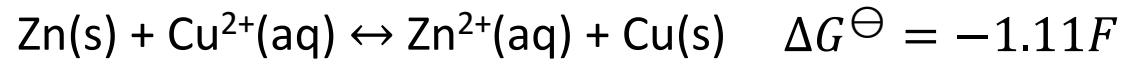


## 10. Salt bridge

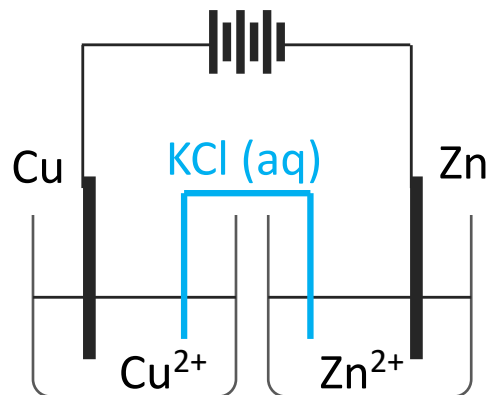
Liquid junction potential : difference of cation & anion velocity



**In the single container (mixing all)**



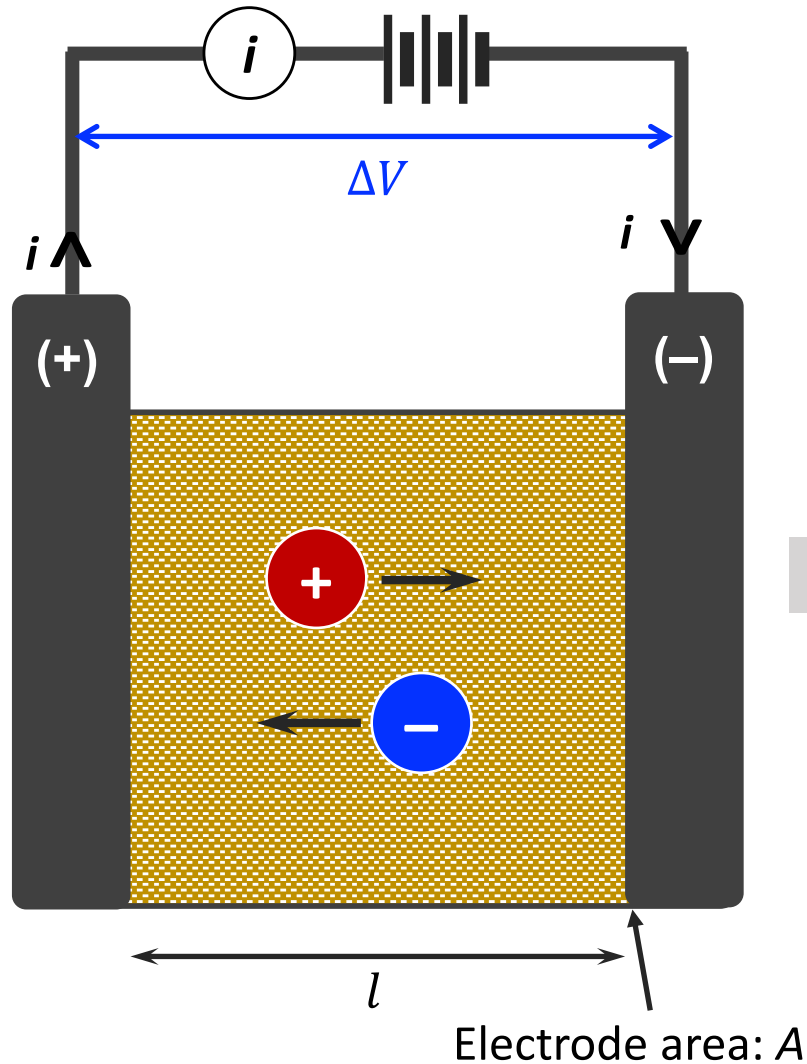
➔ The zinc electrode would very rapidly become copper plated.



**w/ salt bridge**

- ➔ Avoiding the copper plating on the zinc electrode
- ➔ Considering 'liquid junction potential' due to high conc. of KCl in the salt bridge

# 11. Liquid junction potential : difference of cation & anion velocity



## • Migration of ion in S

The movement of the cation and anion constitutes **the flow of  $i$  in the bulk of the sol'n.**

$$\kappa = \frac{1}{\rho} = \frac{l}{RA} = \frac{(I/A)}{(V/l)} \leftarrow \begin{array}{l} \text{current density} \\ \text{voltage gradient} \end{array}$$

$$\left\{ \begin{array}{l} \kappa : \text{conductivity } (\Omega^{-1}\text{m}^{-1}) \\ \rho : \text{resistivity } (\Omega \text{ m}) \\ R : \text{resistance } (\Omega) \end{array} \right.$$

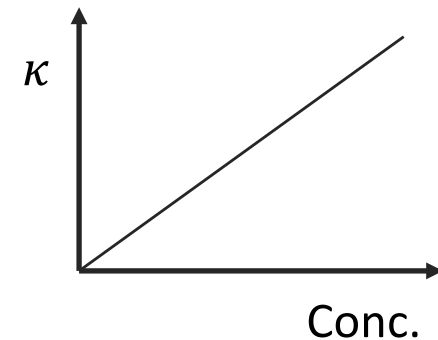
**$\therefore$  Conductivity  $\propto$  Current density ( $j$ , **velocity** of ions)**

## • Molar conductivity, $\Lambda$ ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ )

$$\Lambda = \frac{\kappa}{c}$$

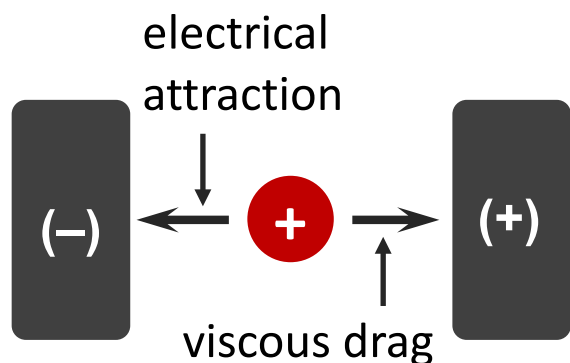
$$\Lambda_{\text{salt}} = a\Lambda_{+} + b\Lambda_{-}$$

( $a, b$ : mole)



The cations and anions move independently of each other.

## • Single ion molar conductivities



Viscous force (Stokes' Law)

A frictional force due to the movement of the ion past and over '*solvent*' molecules which serve to impede the progress of the ion

Electrical force = viscous force

$$ze \left( \frac{V}{l} \right) = 6\pi a v \eta \quad \begin{cases} a: \text{radius} \\ v: \text{velocity} \\ \eta: \text{viscosity} \end{cases}$$

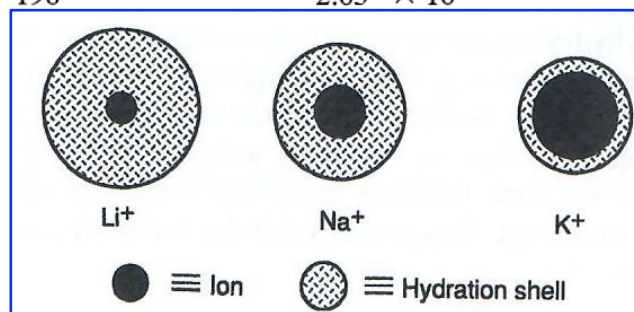
$$\Lambda \propto \frac{v}{(V/l)} \propto \frac{ze(V/l)}{6\pi a \eta (V/l)} \propto \frac{ze}{6\pi a \eta}$$

➔  $\Lambda$  should be large for

- Small ions
- Highly charged ions
- Solvents of low viscosity

TABLE 2.3.2 Ionic Properties at Infinite Dilution in Aqueous Solutions at 25°C

Ion	$\lambda_0$ , cm <sup>2</sup> Ω <sup>-1</sup> equiv <sup>-1a</sup>	$u$ , cm <sup>2</sup> sec <sup>-1</sup> V <sup>-1b</sup>
H <sup>+</sup>	349.82	$3.625 \times 10^{-3}$
K <sup>+</sup>	73.52	$7.619 \times 10^{-4}$
Na <sup>+</sup>	50.11	$5.193 \times 10^{-4}$
Li <sup>+</sup>	38.69	$4.010 \times 10^{-4}$
NH <sub>4</sub> <sup>+</sup>	73.4	$7.61 \times 10^{-4}$
$\frac{1}{2}\text{Ca}^{2+}$	59.50	$6.166 \times 10^{-4}$
OH <sup>-</sup>	198	$2.05 \times 10^{-3}$
Cl <sup>-</sup>		
Br <sup>-</sup>		
I <sup>-</sup>		
NO <sub>3</sub> <sup>-</sup>		
OAc <sup>-</sup>		
ClO <sub>4</sub> <sup>-</sup>		
$\frac{1}{2}\text{SO}_4^{2-}$		
HCO <sub>3</sub> <sup>-</sup>	44.48	$4.610 \times 10^{-4}$
$\frac{1}{3}\text{Fe}(\text{CN})_6^{3-}$	101.0	$1.047 \times 10^{-3}$
$\frac{1}{4}\text{Fe}(\text{CN})_6^{4-}$	110.5	$1.145 \times 10^{-3}$

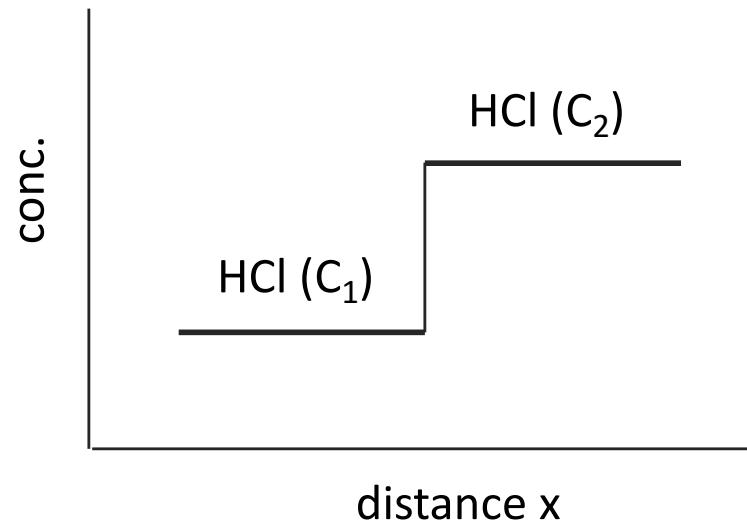


<sup>a</sup>From D. A. MacInnes, "The Principles of Electrochemistry," Dover, New York, 1961, p. 342

<sup>b</sup>Calculated from  $\lambda_0$ .



- Liquid junction potential (at different conc. and transference #)



- Diffusion

Conc. gradient: from high conc. to low conc.

Flux = ***D*** x conc. gradient (mol cm<sup>-2</sup> s<sup>-1</sup>)

*D*: the diffusion coefficient of the moving species

Nernst-Einstein eq.

$$D_i = \Lambda_i \frac{k_B T}{z^2 e^2}$$

- Liquid junction potential (at different conc. and transference #)

**TABLE 2.3.2 Ionic Properties at Infinite Dilution in Aqueous Solutions at 25°C**

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OH <sup>-</sup>	198	$2.05 \times 10^{-3}$
Cl <sup>-</sup>	76.34	$7.912 \times 10^{-4}$
Br <sup>-</sup>	78.4	$8.13 \times 10^{-4}$
I <sup>-</sup>	76.85	$7.96 \times 10^{-4}$
NO <sub>3</sub> <sup>-</sup>	71.44	$7.404 \times 10^{-4}$
OAc <sup>-</sup>	40.9	$4.24 \times 10^{-4}$
ClO <sub>4</sub> <sup>-</sup>	68.0	$7.05 \times 10^{-4}$
$\frac{1}{2}$ SO <sub>4</sub> <sup>2-</sup>	79.8	$8.27 \times 10^{-4}$
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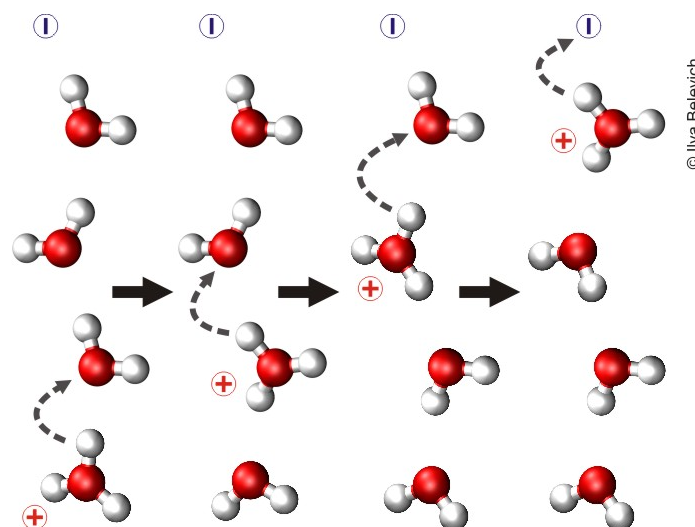
<sup>a</sup>From D. A. MacInnes, "The Principles of Electrochemistry," Dover, New York, 1961, p. 342

<sup>b</sup>Calculated from  $\lambda_0$ .

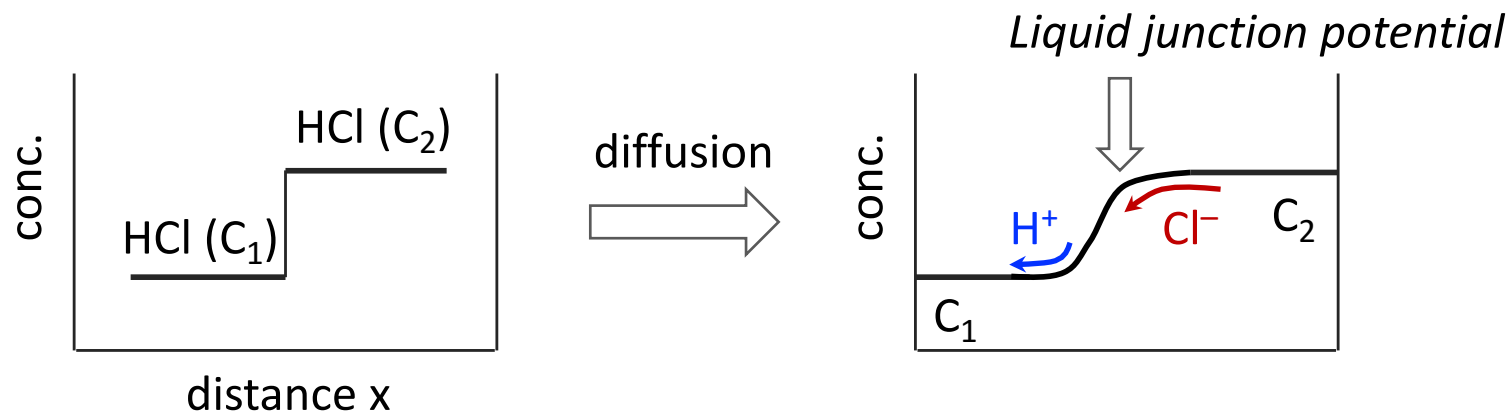
- H<sup>+</sup> and OH<sup>-</sup>: large conductivity

➔ Whereas other ions are pulled to the electrode by coulombic attraction and move by pushing aside solvent molecules, the H<sup>+</sup> and OH<sup>-</sup> ions can take advantage of the water via hydrogen-bond (much less frictional resistance)

➔ Grotthuss mechanism



- Liquid junction potential (at different conc. and transference #)



$$\left. \begin{aligned} j_{H^+} &= D_{H^+} \frac{\partial [H^+]}{\partial x} \\ j_{Cl^-} &= D_{Cl^-} \frac{\partial [Cl^-]}{\partial x} \end{aligned} \right\} \begin{aligned} (1) \text{ Initially } j_{H^+} \text{ is higher (diffusion of } H^+ \text{ is faster) than } j_{Cl^-} \\ \Rightarrow \text{ Charge difference and potential difference will be set up across the interface b/w the two sol'ns.} \end{aligned}$$

(2) Then the rate of the  $Cl^-$  transport will be accelerated (since *migration* will now contribute to the rate of transport) and the  $H^+$  transport rate will be retarded

(3) Ultimately a *steady state* will be reached: a potential difference will exist at the boundary of the two sol'ns  $\Rightarrow$  a liquid junction potential.

$$E_{LJP} = (t_+ - t_-) \frac{RT}{F} \ln \left( \frac{C_2}{C_1} \right) \quad \begin{aligned} &\bullet \text{ related to transference number (ionic conductivity)} \\ &\bullet \text{ concentration ratio} \end{aligned}$$

**TABLE 2.3.2 Ionic Properties at Infinite Dilution in Aqueous Solutions at 25°C**

Ion	$\lambda_0, \text{cm}^2 \Omega^{-1} \text{equiv}^{-1a}$	$u, \text{cm}^2 \text{sec}^{-1} \text{V}^{-1b}$
H <sup>+</sup>	349.82	$3.625 \times 10^{-3}$
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<sup>a</sup>From D. A. MacInnes, "The Principles of Electrochemistry," Dover, New York, 1961, p. 342

<sup>b</sup>Calculated from  $\lambda_0$ .

$$E_{LJP} = (t_+ - t_-) \frac{RT}{F} \ln \left( \frac{C_2}{C_1} \right)$$

### • Transference number ( $t_+$ , $t_-$ )

The fraction of the current carried by the cation and the anion

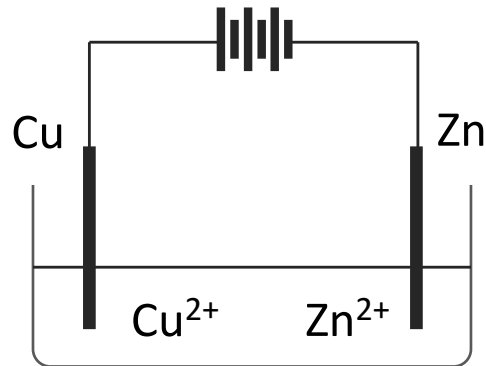
$$t_+ = \frac{\Lambda_+}{\Lambda_+ + \Lambda_-} \quad t_- = \frac{\Lambda_-}{\Lambda_+ + \Lambda_-}$$

ex 1) LiCl:  $t_+ : 0.34$ ,  $t_- = 0.66$

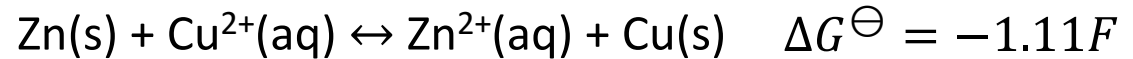
➔ 66% of the current is carried by the Cl<sup>-</sup>

ex 2) KCl :  $t_+ : 0.49$ ,  $t_- = 0.51$

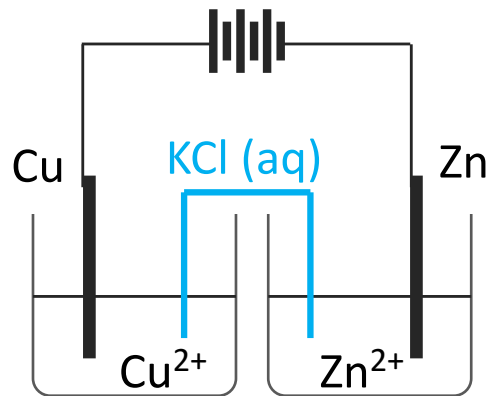
## 10. Salt bridges



**In the single container (mixing all)**



➔ The zinc electrode would very rapidly become copper plated.



**w/ salt bridge**

➔ e.g. measurement of standard electrode potential

➔ negligible liquid junction potential

ex) saturated aqueous KCl (5 M) w/ the half cell containing 0.01 M Cu<sup>2+</sup>

(1) K<sup>+</sup> and Cl<sup>-</sup> diffusing out of the salt bridge  
(but tiny amount of Cu<sup>2+</sup> in the opposite direction)

$$(2) t_{K^+} \approx t_{Cl^-} \approx 0.5 \quad E_{LJP} = (t_+ - t_-) \frac{RT}{F} \ln \left( \frac{c_2}{c_1} \right) = 0$$

**TABLE 2.3.2 Ionic Properties at Infinite Dilution in Aqueous Solutions at 25°C**

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<sup>a</sup>From D. A. MacInnes, "The Principles of Electrochemistry," Dover, New York, 1961, p. 342

<sup>b</sup>Calculated from  $\lambda_0$ .

- Representative salt bridges (similar :  $t_+$ ,  $t_-$ )
  - (1) an aqueous solution of KCl
  - (2) a solution of ammonium nitrate electrolyte
  - (3) porous frit

$$E_{LJP} = (t_+ - t_-) \frac{RT}{F} \ln \left( \frac{C_2}{C_1} \right)$$

# 12. Good example for usage of Nernst equation

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*J. Am. Chem. Soc.* **2013**, *135*, 4450-4456.

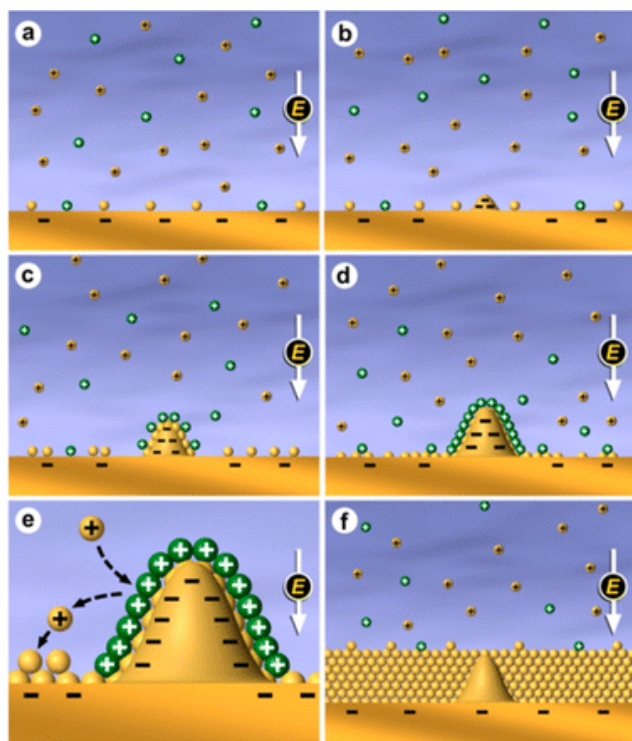
## Dendrite-Free Lithium Deposition via Self-Healing Electrostatic Shield Mechanism

Fei Ding,<sup>†,||</sup> Wu Xu,<sup>\*,†</sup> Gordon L. Graff,<sup>†</sup> Jian Zhang,<sup>†</sup> Maria L. Sushko,<sup>‡</sup> Xilin Chen,<sup>†</sup> Yuyan Shao,<sup>‡</sup> Mark H. Engelhard,<sup>§</sup> Zimin Nie,<sup>†</sup> Jie Xiao,<sup>†</sup> Xingjiang Liu,<sup>||</sup> Peter V. Sushko,<sup>†,⊥</sup> Jun Liu,<sup>‡</sup> and Ji-Guang Zhang<sup>\*,†</sup>

<sup>†</sup>Energy and Environment Directorate, <sup>‡</sup>Fundamental and Computational Sciences Directorate, and <sup>§</sup>Environmental and Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington 99354, United States

<sup>||</sup>National Key Laboratory of Power Sources, Tianjin Institute of Power Sources, Tianjin 300381, People's Republic of China

<sup>⊥</sup>University College London, London WC1E 6BT, United Kingdom



The SHES mechanism depends on an additive cation ( $M^+$ ) that exhibits an effective reduction potential  $E_{\text{red}}$  less than that of  $\text{Li}^+$ . According to the Nernst equation:

$$E_{\text{Red}} = E_{\text{Red}}^{\phi} - \frac{RT}{zF} \ln \frac{\alpha_{\text{Red}}}{\alpha_{\text{Ox}}} \quad (1)$$

where  $R$  is the universal gas constant ( $8.314472 \text{ J K}^{-1} \text{ mol}^{-1}$ ),  $T$  is the absolute temperature (assume  $T = 298.15 \text{ K}$  in this work), and  $\alpha$  is the chemical activity for the relevant species ( $\alpha_{\text{Red}}$  is for the reductant and  $\alpha_{\text{Ox}}$  for the oxidant).  $\alpha_x = \gamma_x c_x$ , where  $\gamma_x$  and  $c_x$  are the activity coefficient and the concentration of species  $x$ .  $F$  is the Faraday constant ( $9.64853399 \times 10^4 \text{ C mol}^{-1}$ ), and  $z$  is the number of moles of electrons transferred. Although  $\text{Li}^+$  has the lowest standard reduction potential ( $E_{\text{Red}}^{\phi}(\text{Li}^+)$ ) among all of the metals when measured at standard conditions [ $1 \text{ mol L}^{-1} (\text{M})$ ], another cation ( $M^+$ ) may have an effective reduction potential lower than that of  $\text{Li}^+$  if  $M^+$  has a chemical activity  $\alpha_x$  lower than that of  $\text{Li}^+$ . In the case of low concentration,  $\alpha_x$  can be simplified to equal the concentration  $c_x$ ; then eq 1 can be simplified as:

$$E_{\text{Red}} = E_{\text{Red}}^{\phi} - \frac{0.05916 \text{ V}}{z} \log_{10} \frac{1}{\alpha_{\text{Ox}}} \quad (2)$$

The effective reduction potentials (vs SHE) of selected metal cations at various concentrations were calculated according to eq 2 and listed in Table 1 (assuming the activity coefficients  $\gamma_x$

**Table 1. Effective Reduction Potentials of Two Selected Alkali Cations at Different Concentrations**

cations	$E^{\circ}$ (V) <sup>a</sup>	effective reduction potential (V)			
	1 M	0.001 M	0.01 M	0.05 M	0.1 M
Li <sup>+</sup>	−3.040				
Cs <sup>+</sup>	−3.026	−3.203	−3.144	−3.103	−3.085
Rb <sup>+</sup>	−2.980	−3.157	−3.098	−3.057	−3.039

<sup>a</sup>Note:  $E^{\circ}$  is the standard reduction potential (vs SHE) of the cation at 1 M concentration.

= 1). When the concentration of cations of cesium ( $\text{Cs}^+$ ) or rubidium ( $\text{Rb}^+$ ) is less than 0.05 M in the electrolyte, their effective reduction potentials (see the shaded cells in Table 1) are lower than that of  $\text{Li}^+$  at 1.0 M concentration ( $-3.040 \text{ V}$ ). As a result, in a mixed electrolyte where the additive ( $\text{Cs}^+$  or  $\text{Rb}^+$ ) concentration is much lower than the  $\text{Li}^+$  concentration, these additives should not be deposited at the Li deposition potential and do not form thin layers of Li alloys at the electrode surface. In contrast, the inorganic additives (including



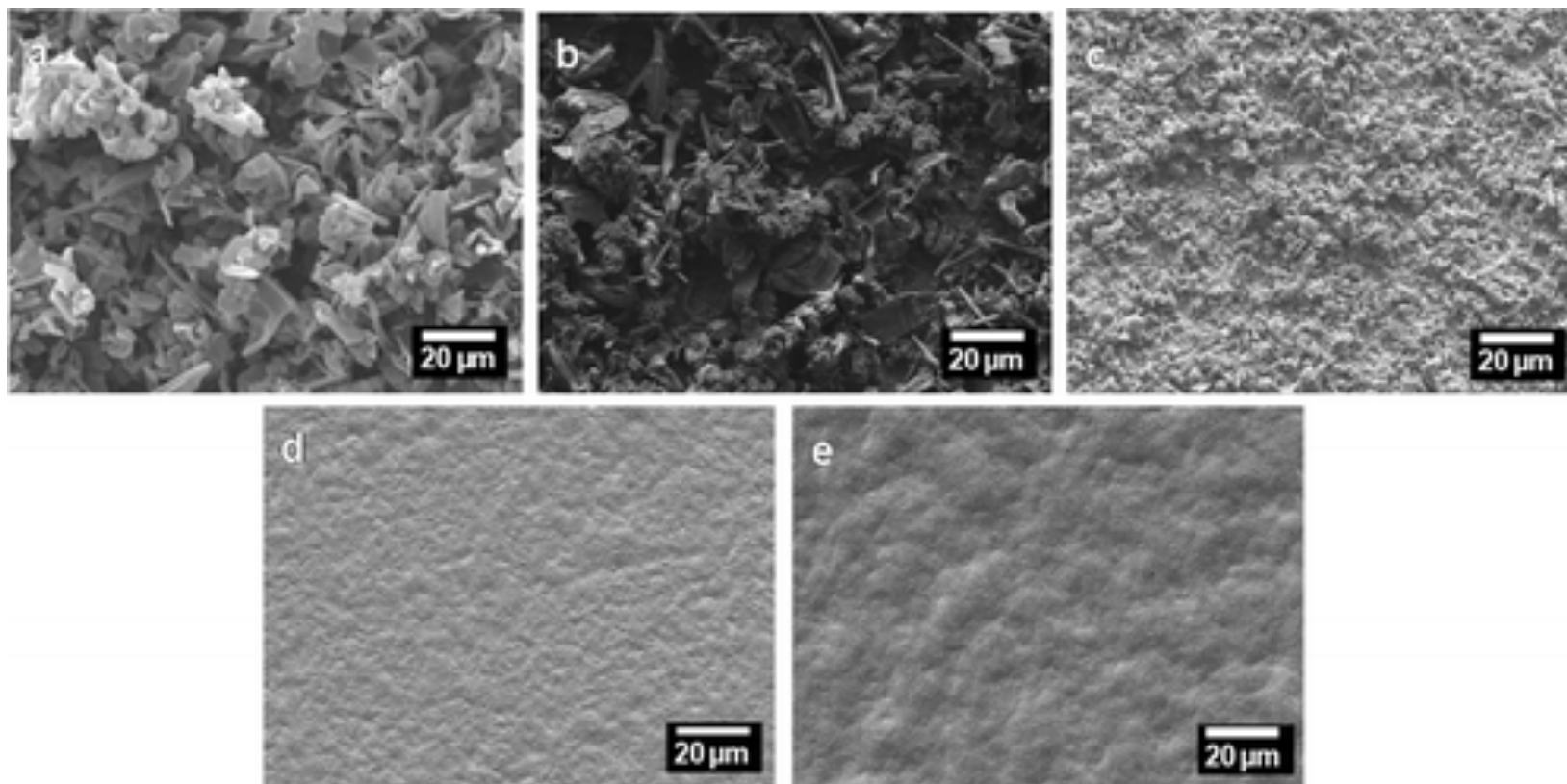


Figure 2. SEM images of the morphologies of Li films deposited in electrolyte of 1 M  $\text{LiPF}_6/\text{PC}$  with  $\text{CsPF}_6$  concentrations of (a) 0 M, (b) 0.001 M, (c) 0.005 M, (d) 0.01 M, and (e) 0.05 M, at a current density of  $0.1 \text{ mA cm}^{-2}$ .