taogao-echem.net
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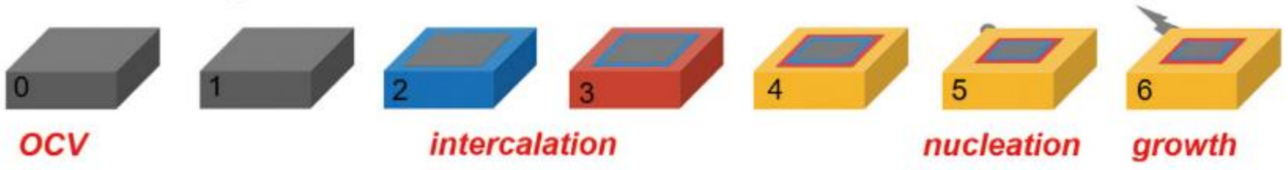

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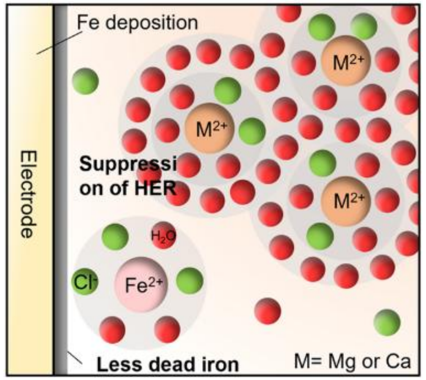
ACS Spring Meeting 2025, March 25th

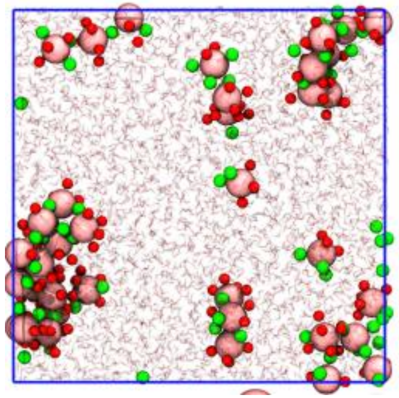
Iron redox chemistry in concentrated aqueous electrolytes: applications, mechanisms and theory

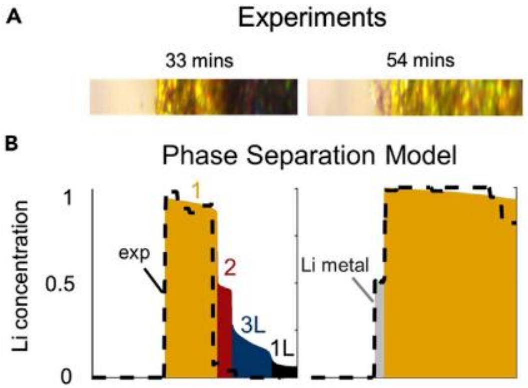
Tao Gao*, Jing Liu, Thomas Webb, Juliana Castillo, Nicolas Andreas, Alan Larrea Caro, Dengpan Dong, Dmstry Bedrov

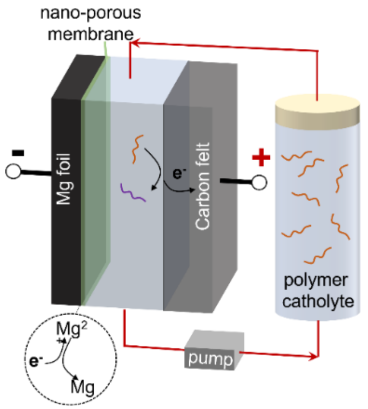
Department of Chemical Engineering

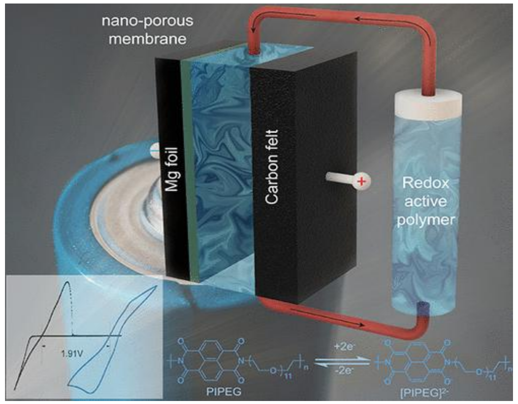
The University of Utah





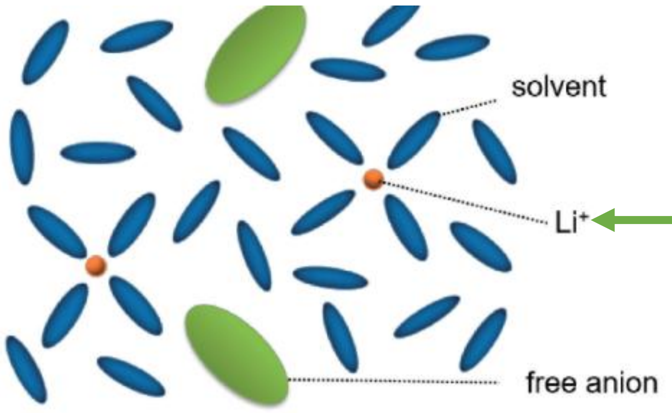


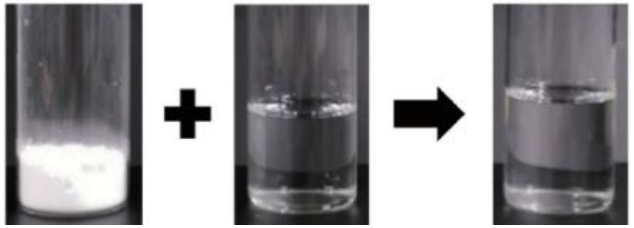




Concentrated electrolytes: a less explored regime

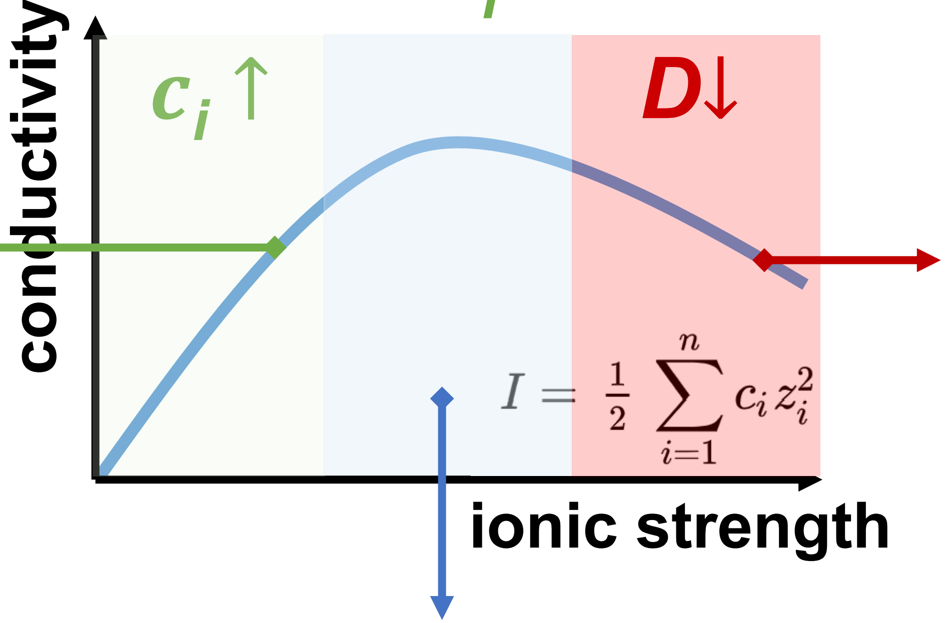
Dilute electrolyte





- Solvent outnumbers ions
- Weak ion-ion interactions
- Ions fully separated by solvent

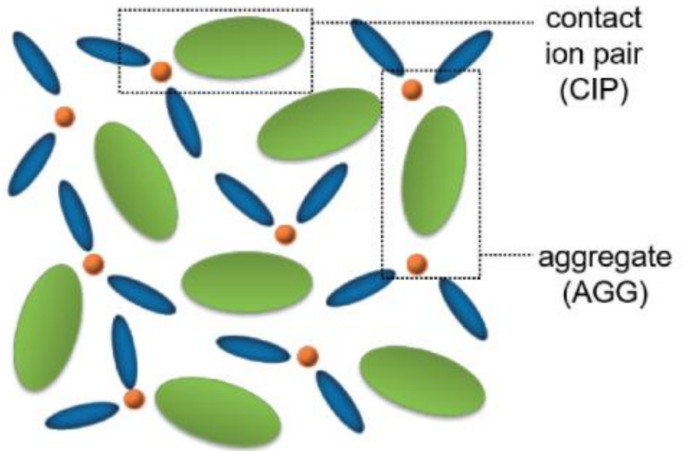
$\kappa \sim c_i D$

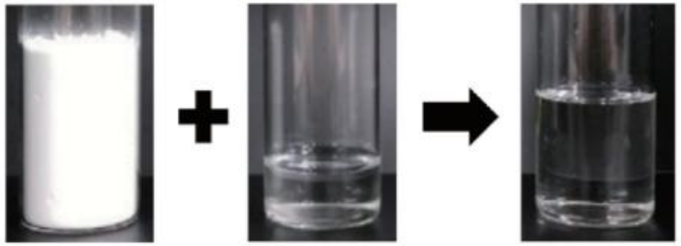


Regular electrolyte

- Maximal conductivity
- Default choice for most applications
- For example,
  - 1-2M $LiPF_6$ in EC-DMC

Concentrated electrolyte



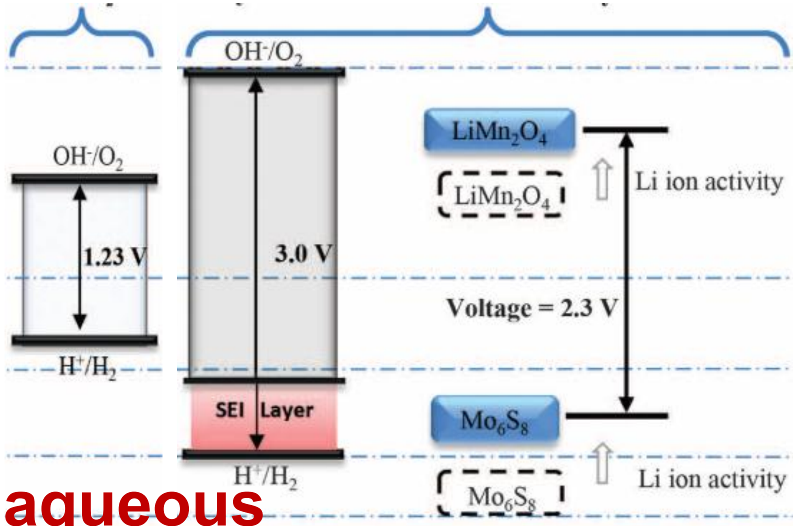


- Not enough solvents to screen charge
  - Solvent-in-salt: solvent < ions
  - Molten salt: solvent→0
- Strong ion-ion interactions
- Ion pair, aggregate, clusters and network

Y. Yamada, *Bull. Chem. Soc. Jpn.* 2020, *93*, 109.

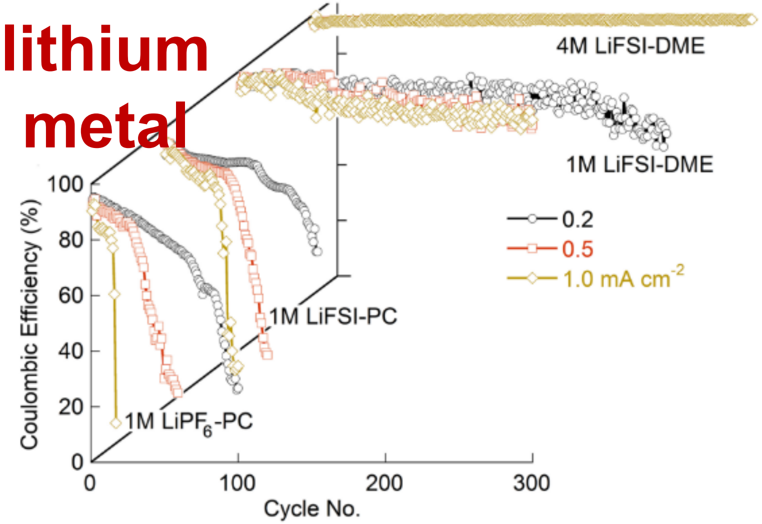
Concentrated electrolytes: application gaps

Lithium and alkali battery

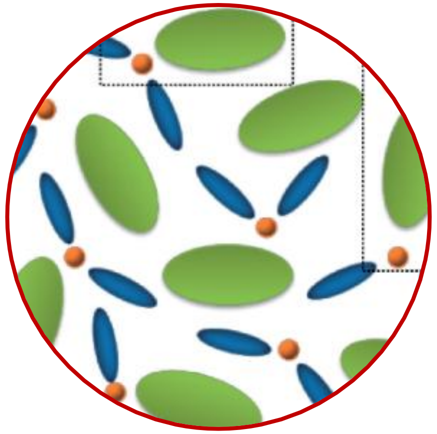


aqueous

lithium metal

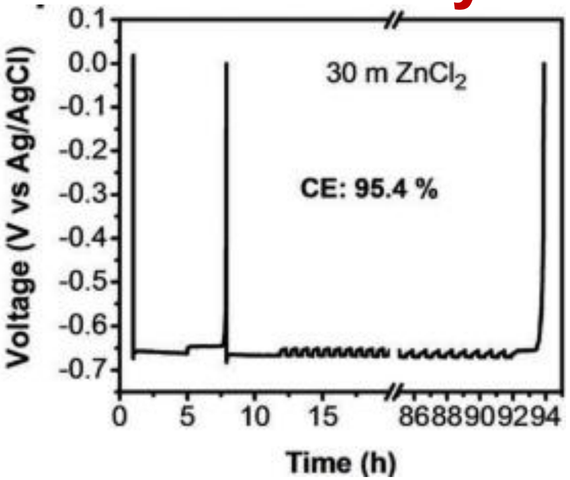


Concentrated electrolyte

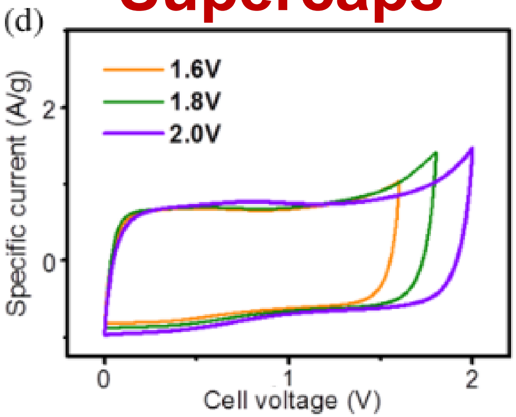


Other applications

Zn battery



Supercaps



- **Concentrated electrolytes enables unprecedented performance**
- **They may offer new opportunities for other applications**

C. Wang, K. Xu, *Science (80-.).* **2015**, *350*, 938.
O. Borodin, C. Wang, K. Xu, Joule 2020, 4, 69.
X. Ji, *Chem. Commun.* **2018**, *54*, 14097.
O. Borodin, J. G. Zhang, *Nat. Commun.* **2015**, *6*, DOI 10.1038/ncomms7362.
F. Pan, *Funct. Mater. Lett.* **2017**, *10*, 1.

Concentrated electrolytes: fundamental gaps

- **How do the strong ion-ion interaction affect electrolyte structure and properties?**
- **How do we model and predict such effects?**

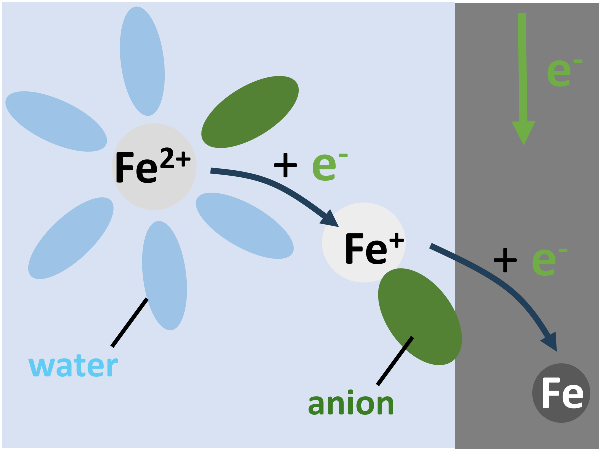
	Dilute electrolyte	Concentrated electrolyte
Thermodynamics	**Classical model (Nernst Equation)** $E = E^\circ - \frac{RT}{nF} \ln Q$ $a_i = \gamma_i c_i$	?
Transport	**Vehicle mechanism** $\kappa = F^2 \sum_i z_i^2 \frac{c_i}{RT} D_i$ **Nernst-Einstein relation** Debye–Hückel–Onsager theory, Fuoss–Onsager, Pitzer equation	**Hopping/structural mechanism** Kinetic Monte Carlo, Continuous-Time Random Walk, Molecular Dynamics
…	…	…

Outline

Applications

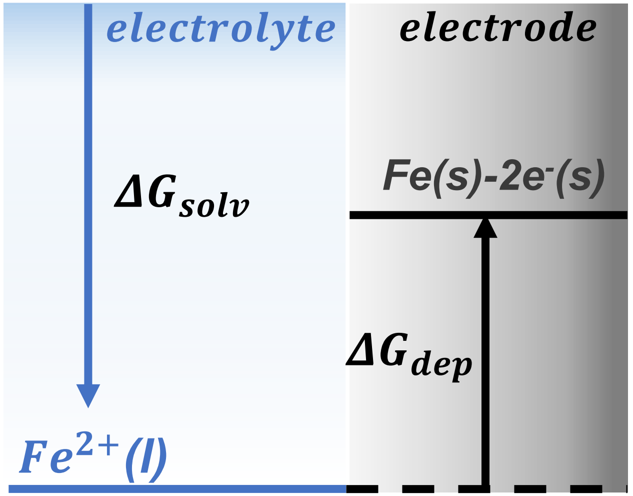
How do concentrated electrolytes solve the problems in applications?

Mechanistic Picture



Why the unprecedented performance?

Theory

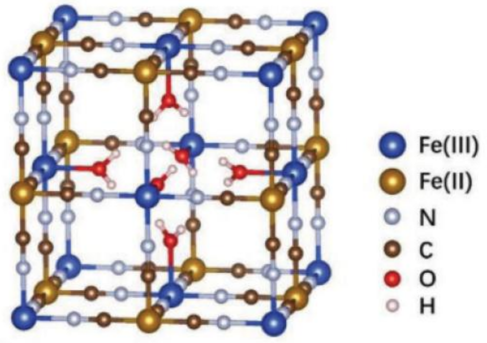


How do we model and predict the electrochemical behavior?

Fe metal battery: low-cost energy storage

Intercalation

$Fe^{2+} + 2e^{-} + H = FeH$

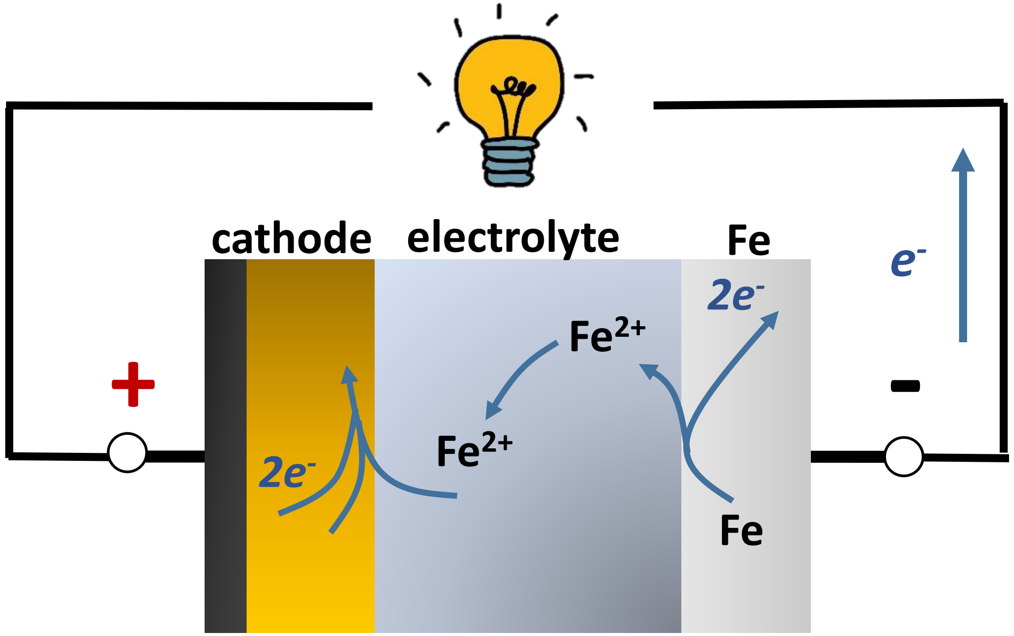


Conversion

$2Fe^{3+} + 2e^{-} = 2Fe^{2+}$

$Br_2 + 2e^{-} = 2Br^{-}$

Fe metal battery



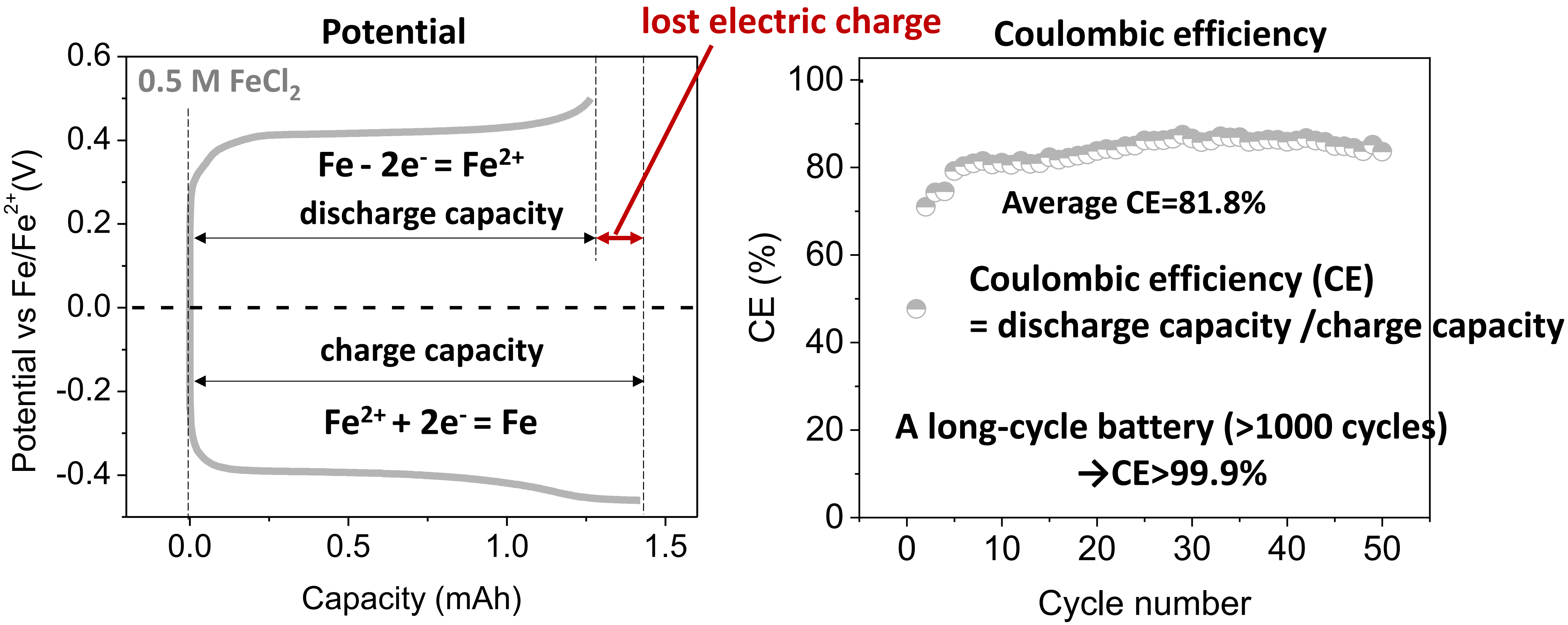
In acidic environment

$Fe \leftarrow Fe^{2+} + 2e^{-}$
(discharge)

$Fe^{2+} + 2e^{-} \rightarrow Fe$
(charge)

X. Ji et al, *Adv. Funct. Mater.* 2019, *29*, 1.,
P. Liu, et al. *J. Power Sources* 2021.,
R. F. Savinell, *J. Electrochem. Soc.* 2019, *166*, A1725.

Challenge of Fe metal battery



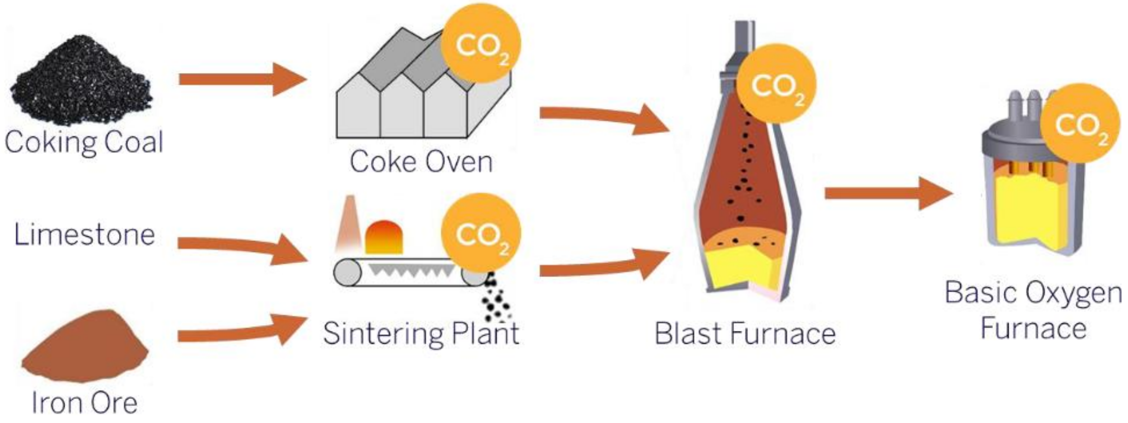
Cu|Fe cell, 1 mA/cm2, 1 hour, 0.5V

Very low coulombic efficiency of the Fe metal anode in regular electrolytes

J. Liu, D. Bedrov*, **T. Gao***, et. al., ***ACS Cent. Sci.* 2022**

Fe electrowinning: sustainable ironmaking

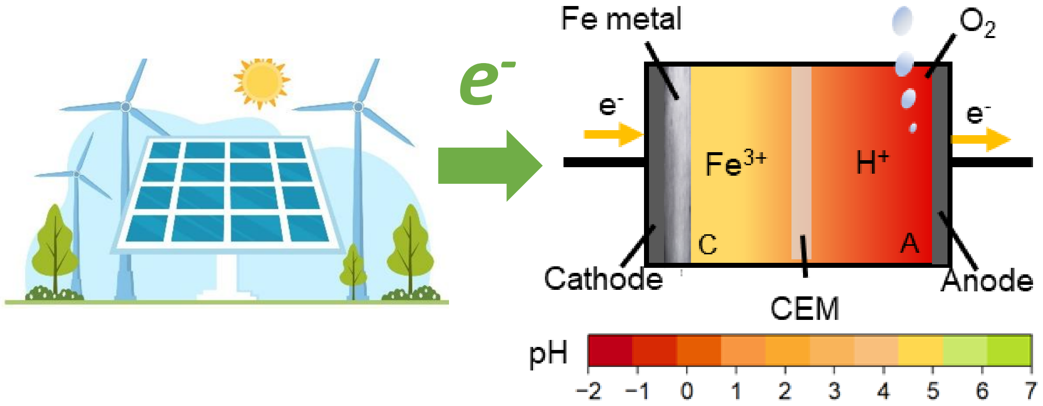
Traditional route



Iron Ore + Carbon (Coal) = Iron + Carbon Dioxide

$$Fe_2O_3 + C = Fe + CO_2$$

Electrowinning



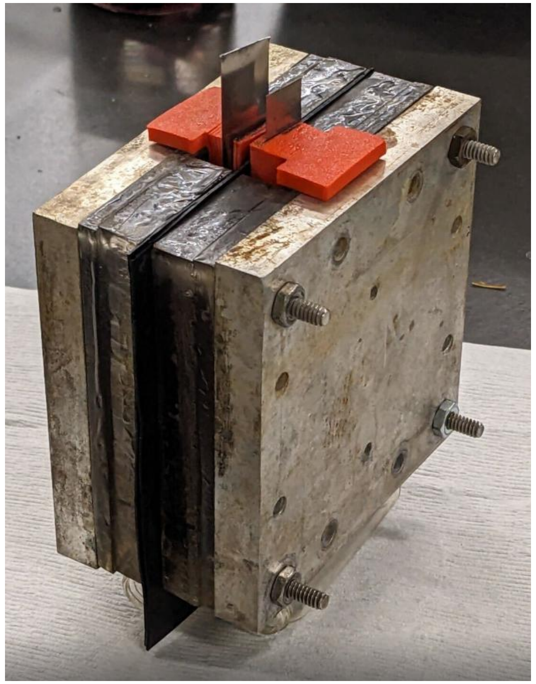
- Iron and steel industry accounts for 8% of industry CO_2 emission
- Blast furnace route produces 71% of global crude iron

$Fe^{2+} + 2e^- \longrightarrow Fe$

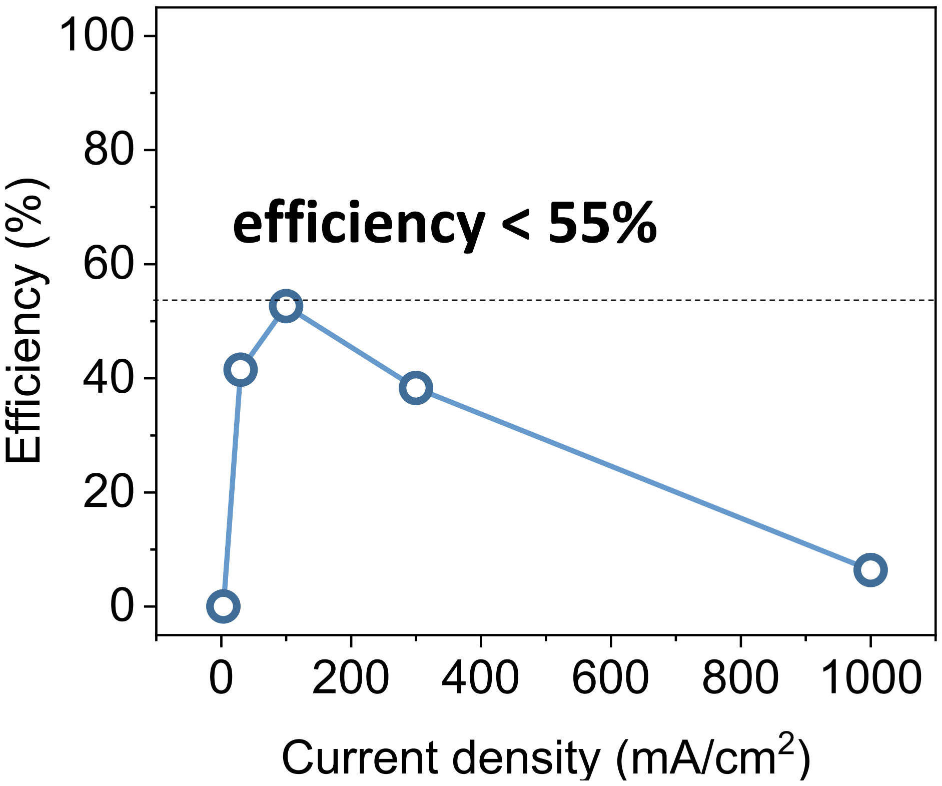
Electro-deposition

Rauwerdink, A. Steel Production through Electrolysis: Impacts for Electricity Consumption. **2019**.

Challenge of Fe electrowinning



Faradaic Efficiency of Fe electrowinning



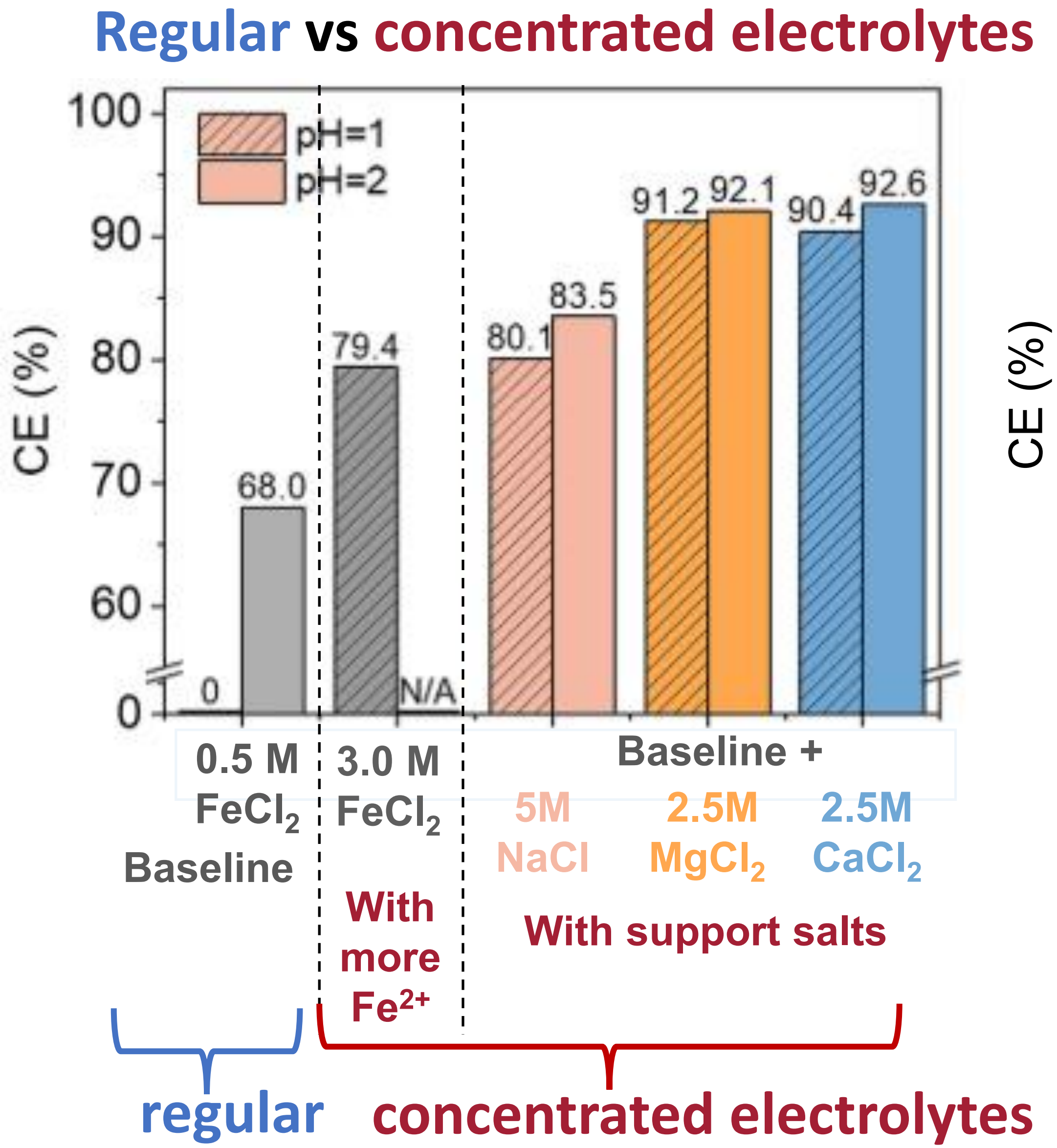
Iron deposit

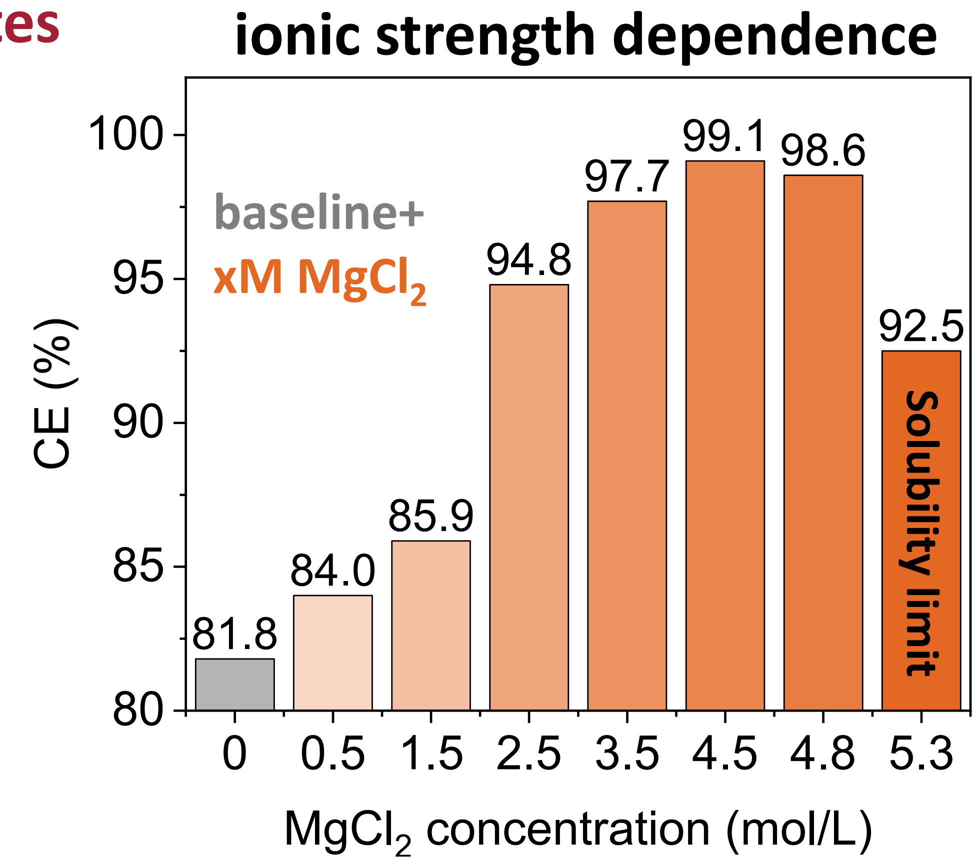
Thin and loose

Very low faradaic efficiency (< 55%) at practical currents (>50 mA/cm^2)

J. Liu, **T. Gao***, *ChemRxiv* **2024**, DOI 10.26434/chemrxiv-2024-stwdn.

Fe electro-deposition: regular vs concentrated electrolytes



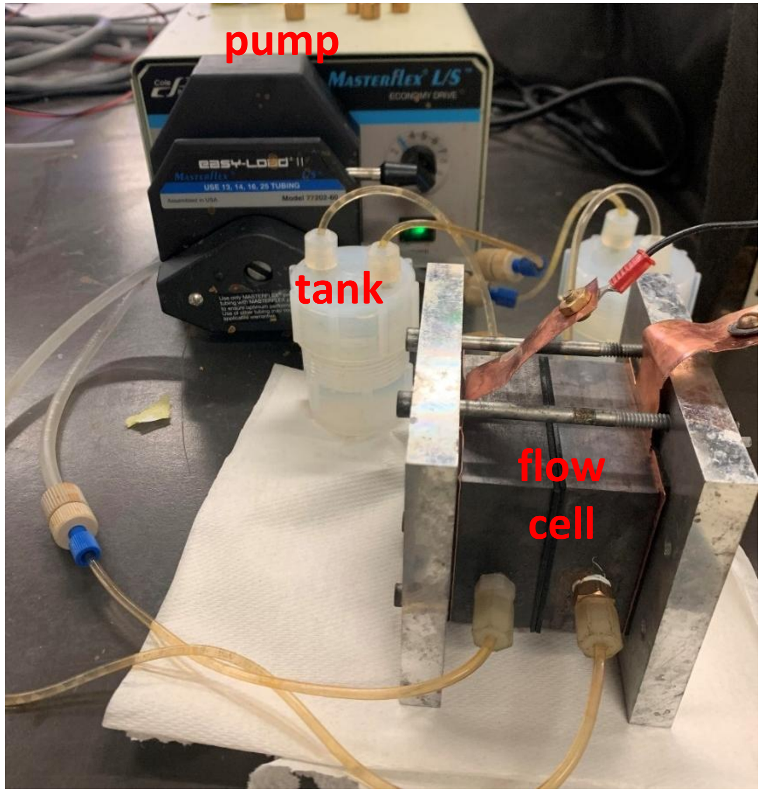


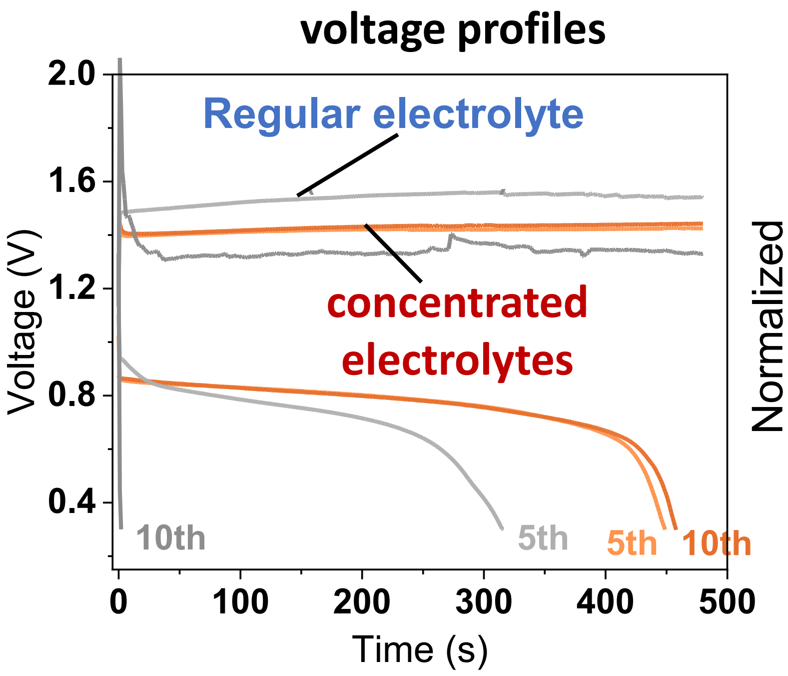
- Concentrated electrolytes show significantly improved coulombic efficiency than regular electrolytes

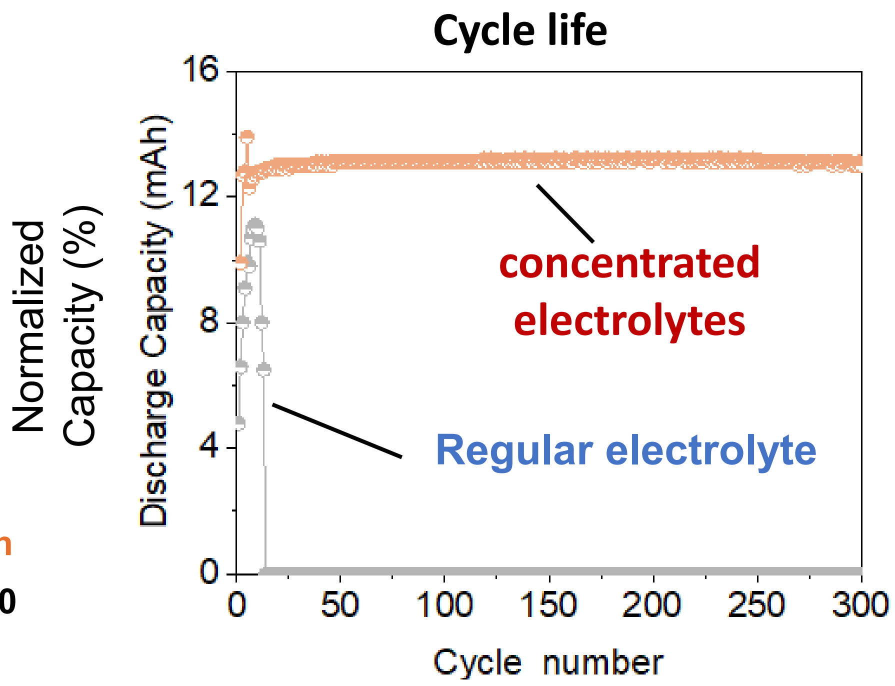
J. Liu, D. Bedrov*, **T. Gao***, et. al., ***ACS Cent. Sci.* 2022**

Fe battery in concentrated electrolytes

All-Fe flow battery (Fe^{3+}/Fe)







Cathode: $2Fe^{3+} + 2e^{-} \rightarrow 2Fe^{2+}$

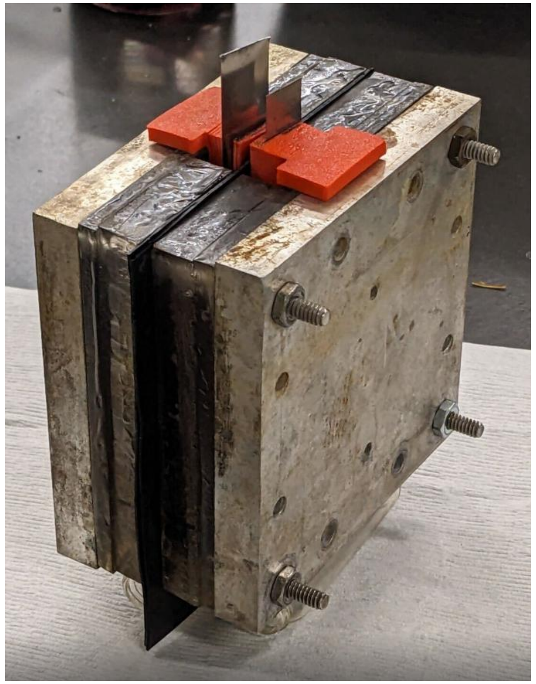
Anode: $Fe - 2e^{-} \rightarrow Fe^{2+}$

- **Significantly better cycle life with concentrated electrolyte**

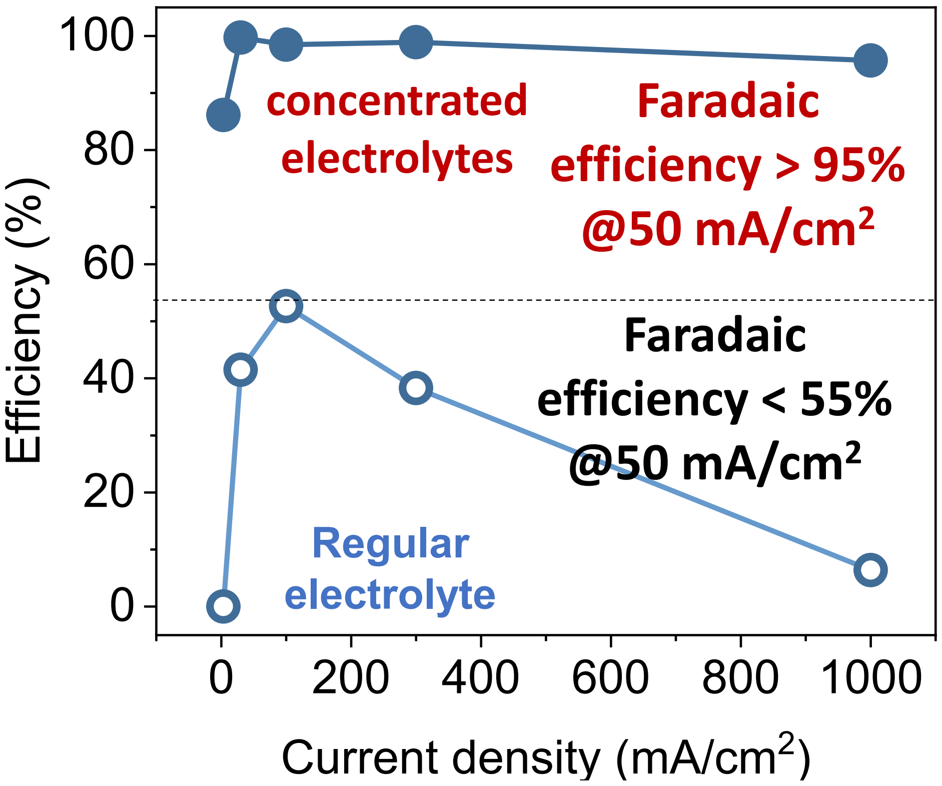
Unpublished results

Fe electrowinning in concentrated electrolytes

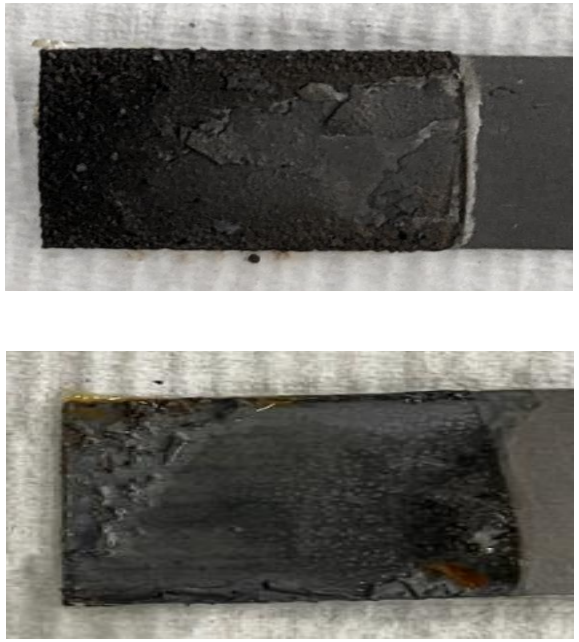
Fe electrowinning cell



Cathode: $Fe^{2+} + 2e^{-} \rightarrow Fe$



Thick and compact



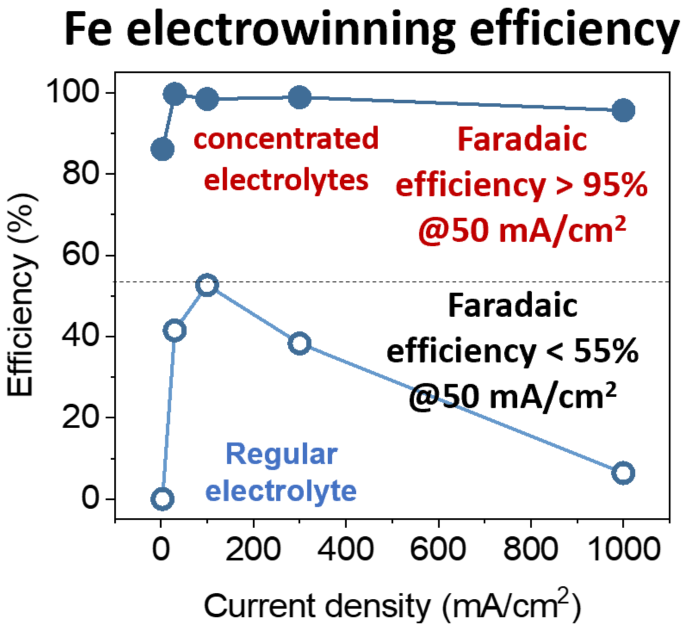
Thin and loose

- **Significantly improved efficiency and deposit quality in concentrated electrolytes**

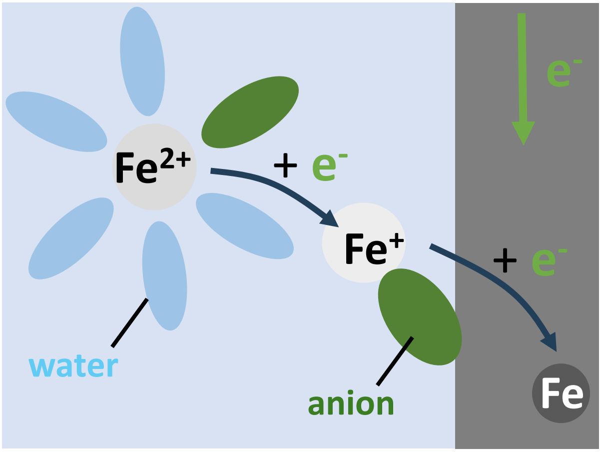
J. Liu, **T. Gao***, *ChemRxiv* **2024**, DOI 10.26434/chemrxiv-2024-stwdn.

Outline

Applications

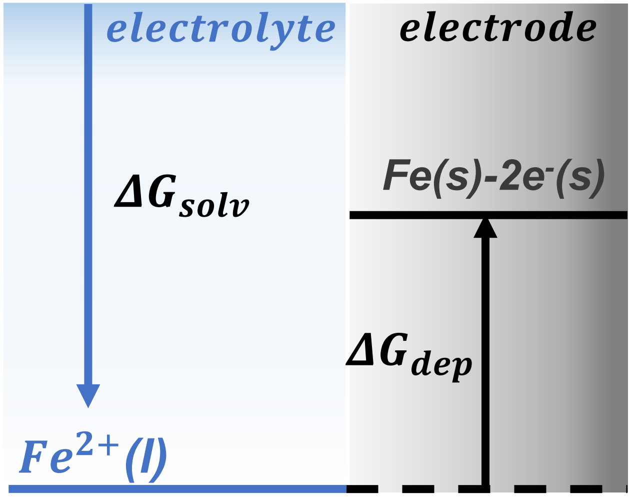


Mechanistic Picture



Why the unprecedented performance?

Theory



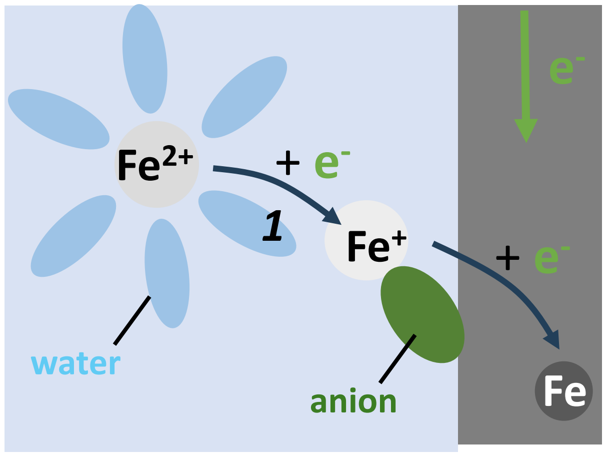
How do we model and predict the electrochemical behavior?

J. Liu, D. Bedrov*, **T. Gao***, et. al., ***ACS Cent. Sci.* 2022**

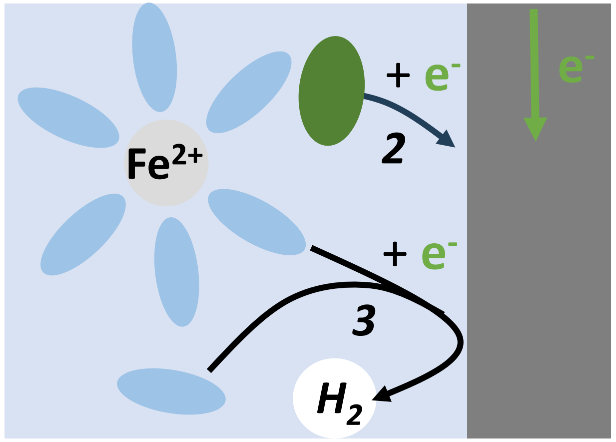
J. Liu, **T. Gao***, *ChemRxiv* **2024**, DOI 10.26434/chemrxiv-2024-stwdn.

Competing reduction reactions

Desired reactions



Parasitic reactions



1. **Reduction of Fe^{2+}**

   $$Fe^{2+} + 2e^{-} \rightarrow Fe$$

2. **Reduction of anion**
   - Inorganic anions: ClO_4^-, NO_3^-
   - Organic anions: OTF^-, $TFSI^-$
   - Halides: can not be further reduced

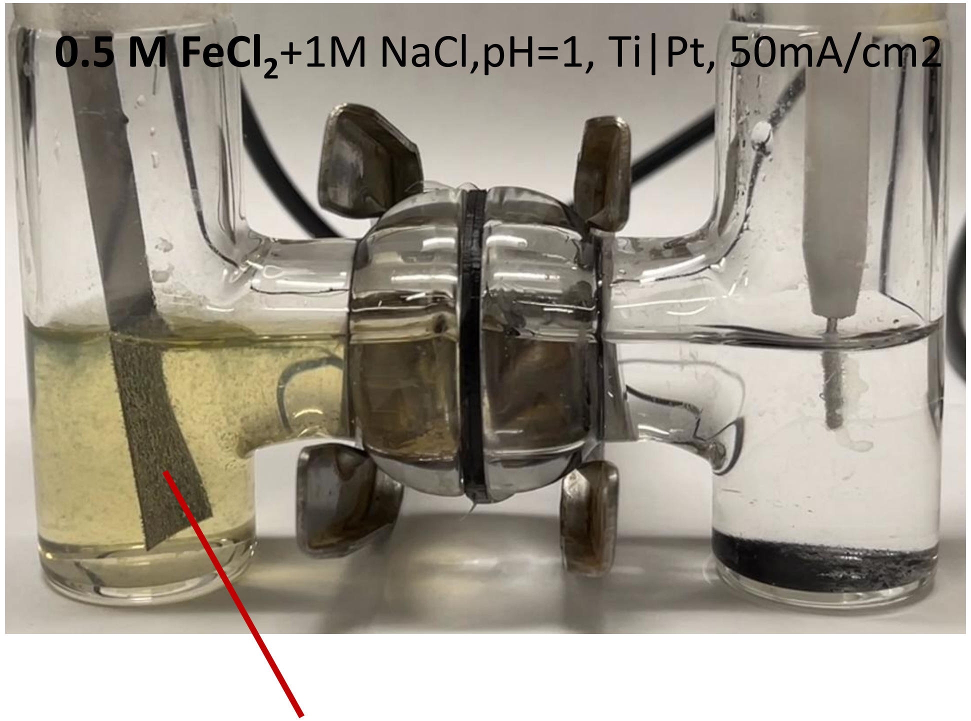
3. **Reduction of solvent (water)**

   $$2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-}$$

Their relative reactivity determines
- Selectivity of reduction reaction (Faradaic efficiency)
- The quality of Fe deposits (morphology, purity, etc.)

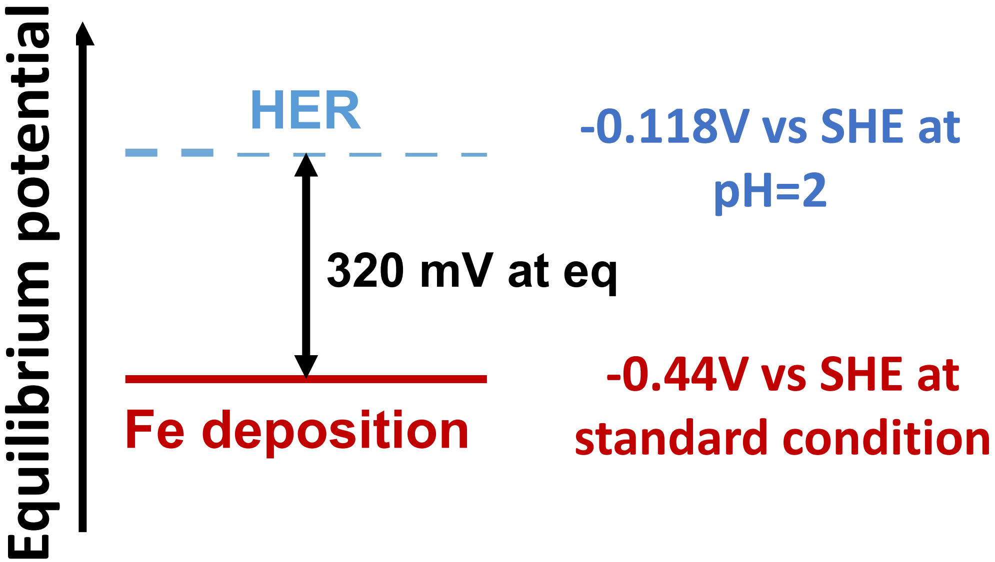
Strong HER in regular electrolytes

Constant current electrolysis



Lots of bubbles

Thermodynamics



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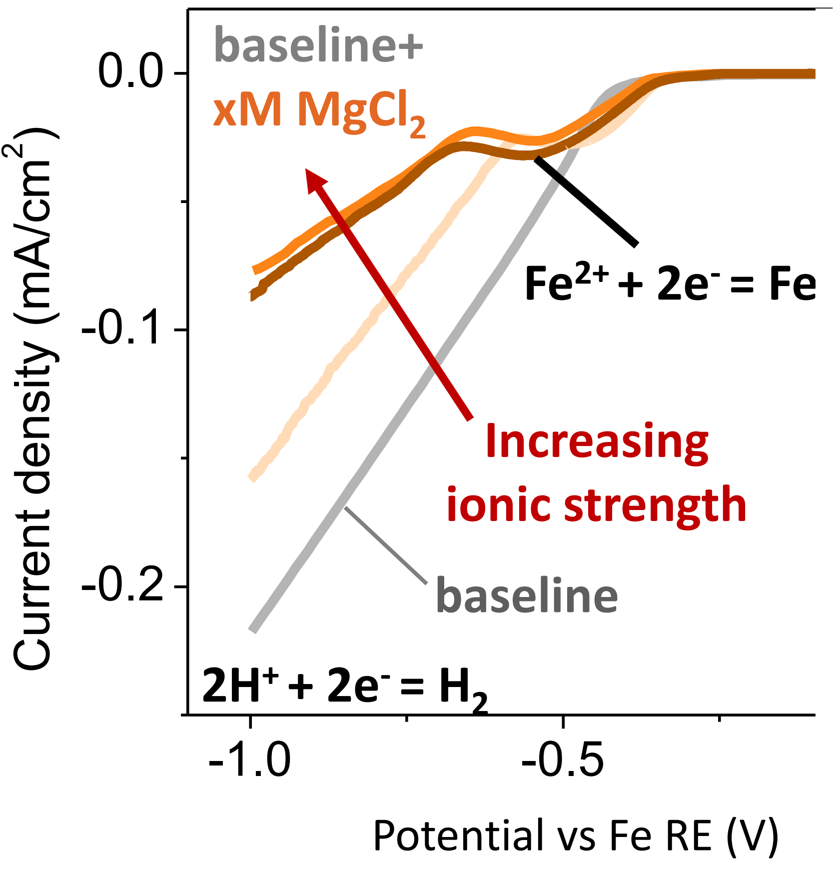
Concentrated electrolytes reduce water reactivity*

Linear scanning voltammetry



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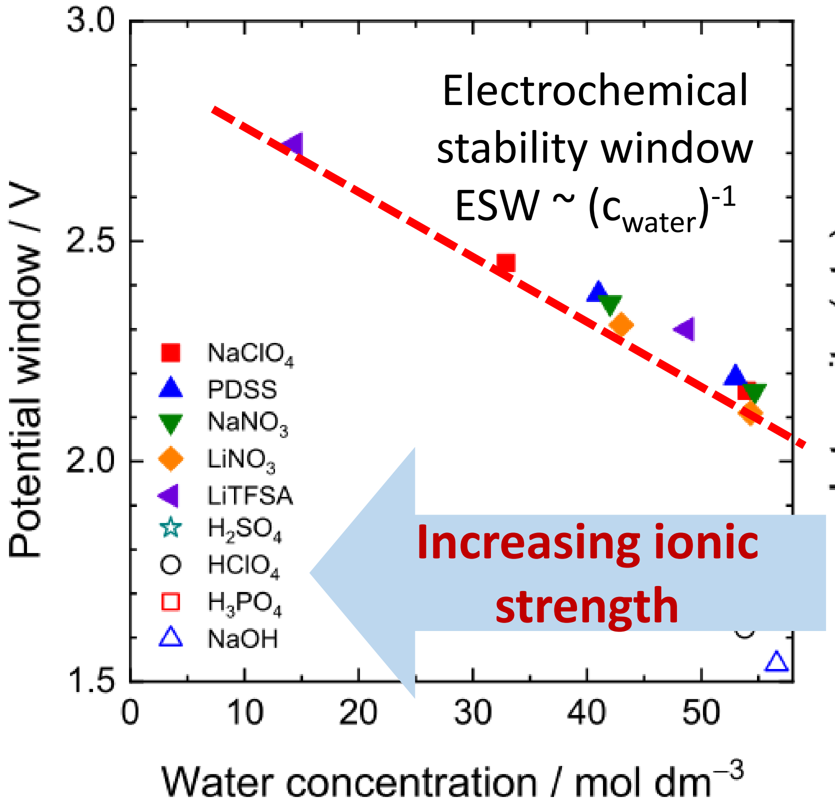
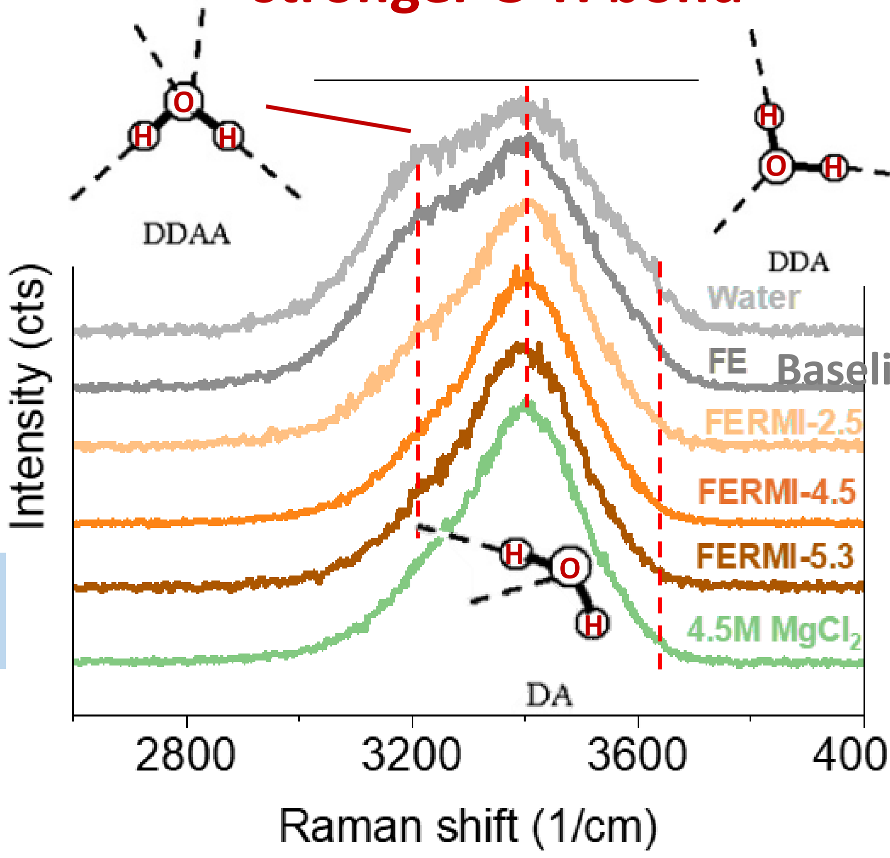
Less water → reduced water activity



T. Fukutsuka, K. Miyazaki, T. Abe, *J. Electrochem. Soc.* **2018**, *165*, A3299.

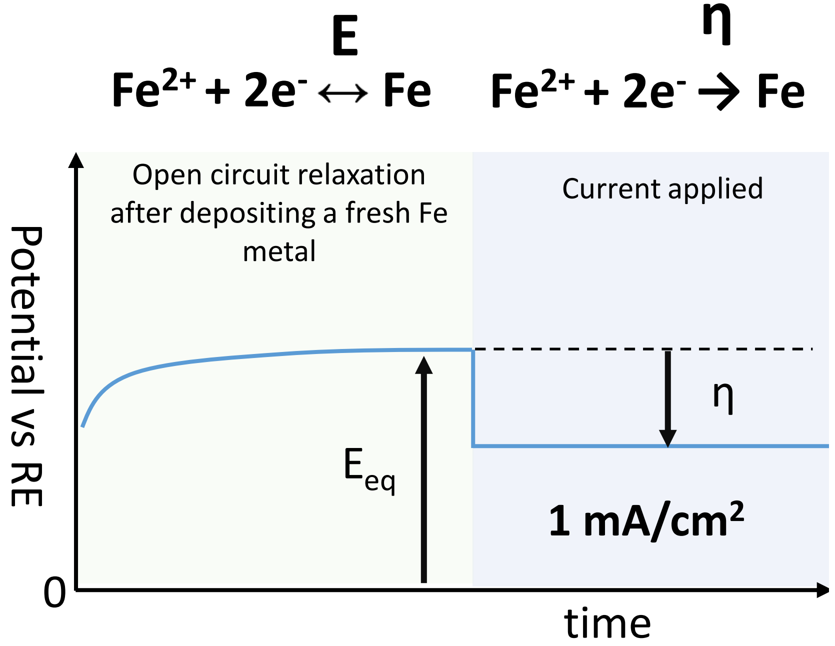
less H-bond → stronger O-H bond



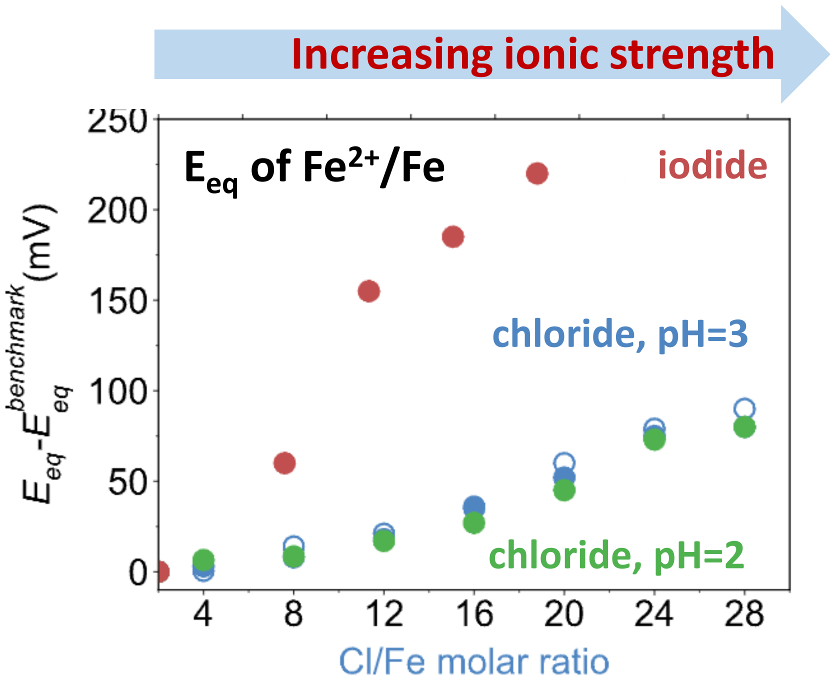
J. Liu, D. Bedrov*, **T. Gao***, et. al., ***ACS Cent. Sci.* 2022**

*also see: X. Ji, *eScience* **2021**, *1*, 99. O. Borodin, *Joule* **2020**, *4*, 69.

Concentrated electrolytes enhance Fe^{2+} reactivity

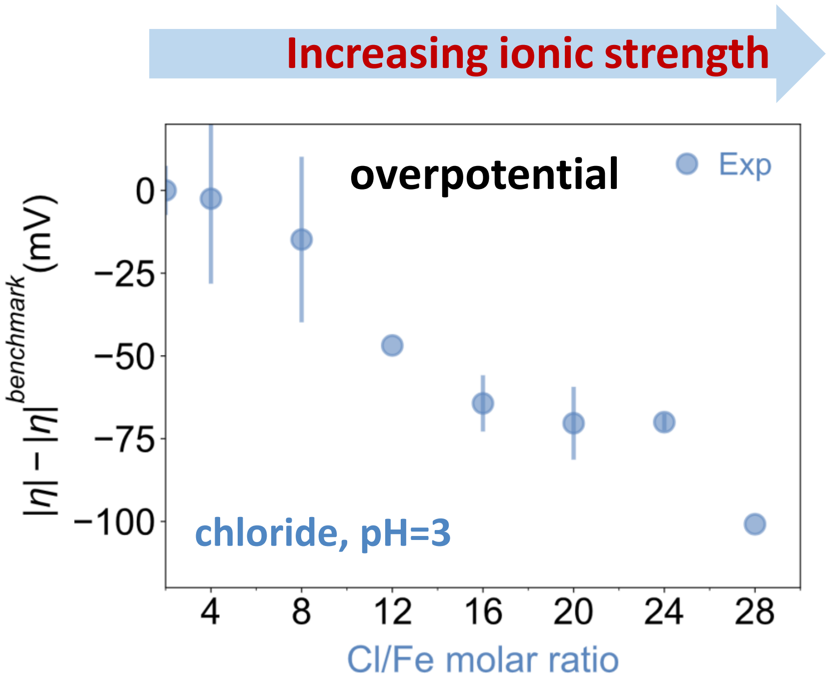


Thermodynamics (E)



E increases by
- > 90 mV in chloride
- >220 mV in iodide

Kinetics (η)



η decreases by > 100 mV in chloride

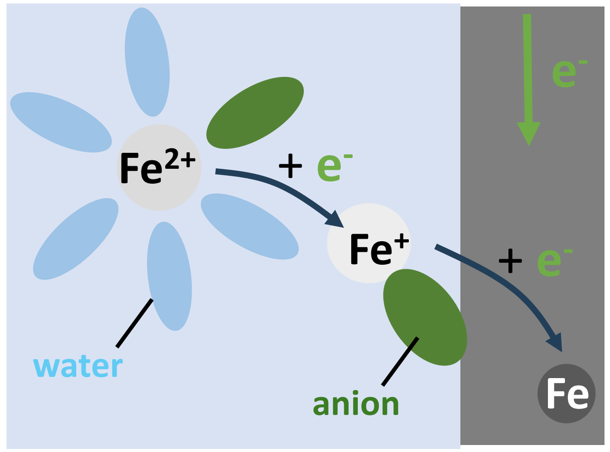
Concentrated electrolytes → promote Fe deposition both thermodynamically and kinetically

Promote Fe^{2+} reactivity by > 190-320 mV

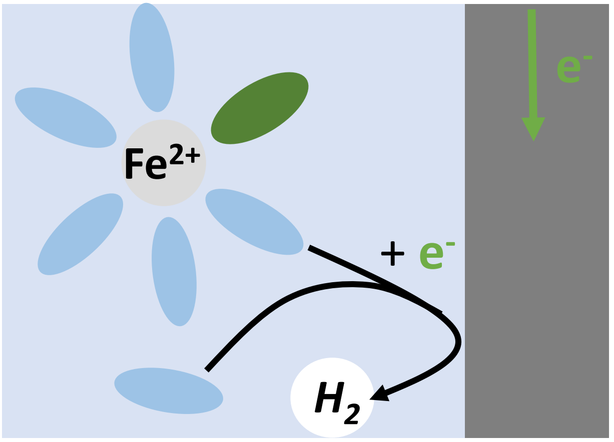
J. Liu, T. Gao*, *et al.*, ***J. Phys. Chem. C****, 2026*

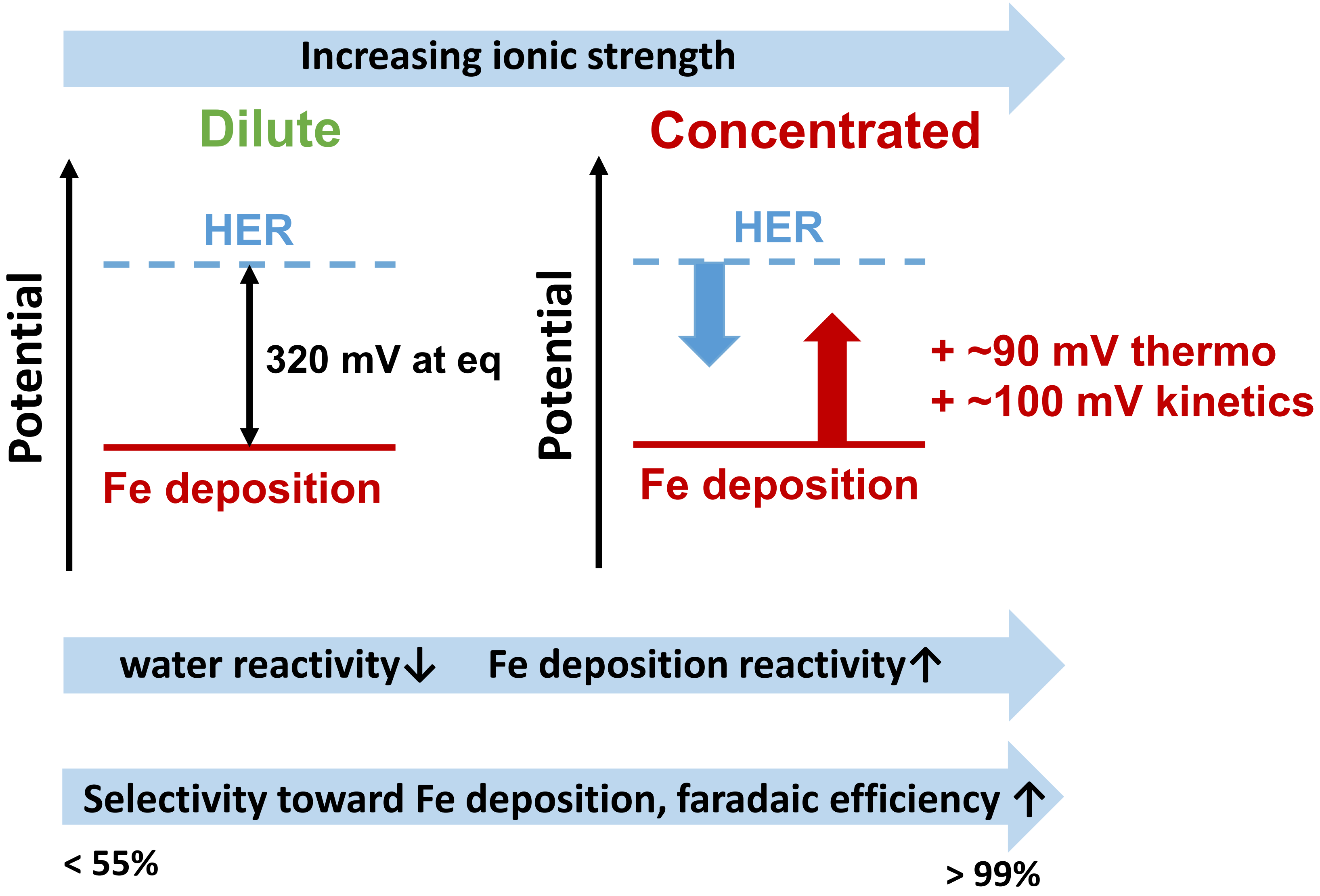
Holistic mechanism underlying enhanced efficiency of Fe deposition

Fe deposition



HER

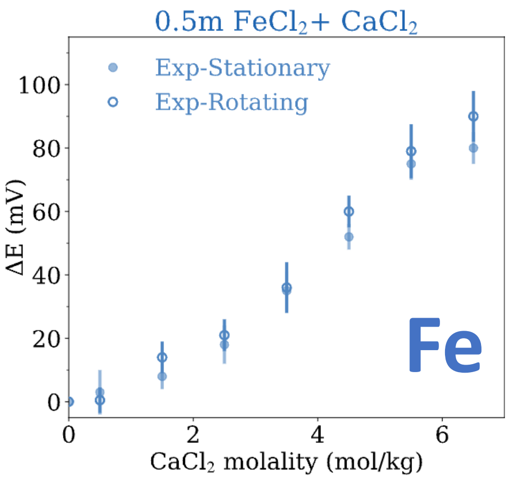


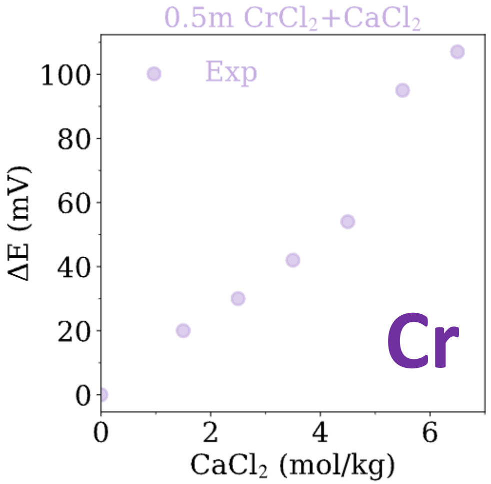


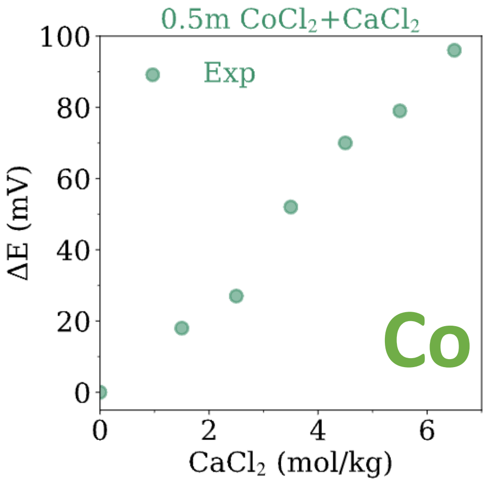
J. Liu, T. Gao*, *et al.*, ***J. Phys. Chem. C***, *2026*

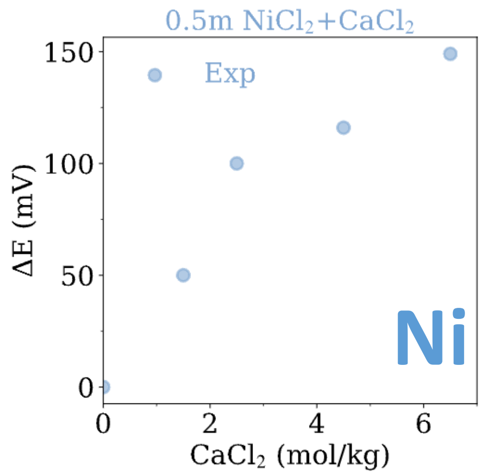
TM deposition potential (E) in aqueous chloride electrolyte

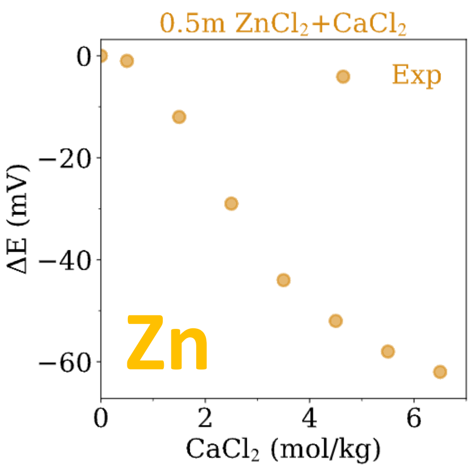
- Examined Period 4 TM metals for their deposition potential in chloride electrolytes
- 5 TM metals that can be electro-deposited in aqueous solutions
  - Including Fe^{2+}/Fe, Cr^{2+}/Cr (-0.9V vs SHE), Co^{2+}/Co(-0.28V vs SHE), Ni^{2+}/Ni(-0.257V vs SHE), Zn^{2+}/Zn(-0.76V vs SHE)

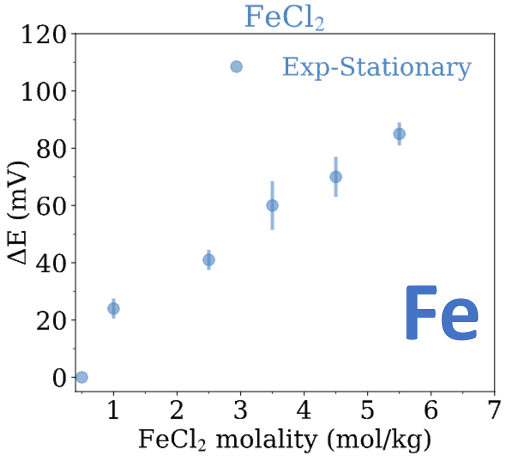




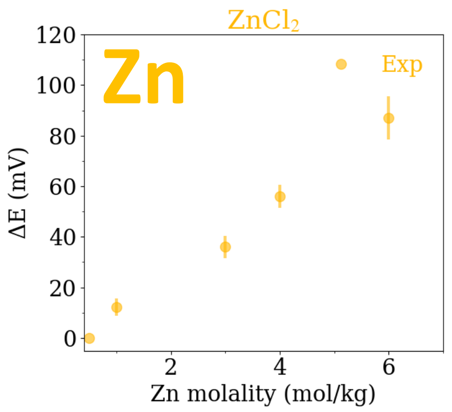








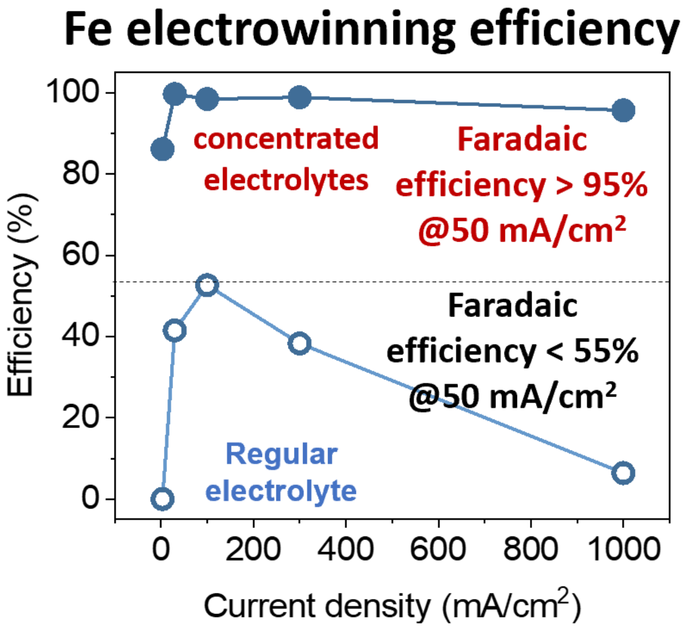
- Deposition potential highly dependent on electrolyte
- E increases with ionic strength by ~80-150 mV
  - Except for $ZnCl_2$+support salt
  - But include concentrated $ZnCl_2$



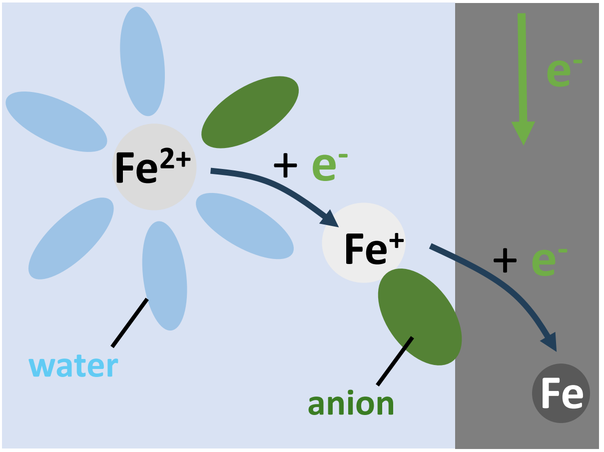
J. Liu, T. Gao*, *et al.*, ***J. Phys. Chem. C***, *2026*

Outline

Applications

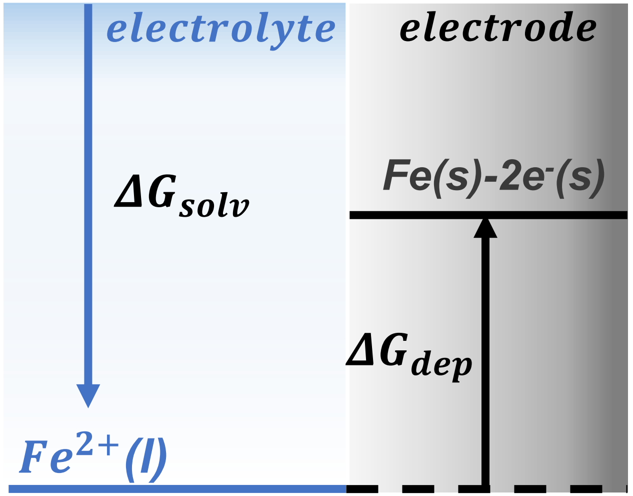


Mechanistic Picture



Why the unprecedented performance?

Theory



How do we model and predict the electrochemical behavior?

J. Liu, D. Bedrov*, **T. Gao***, et. al., ***ACS Cent. Sci.* 2022**

J. Liu, **T. Gao***, *ChemRxiv* **2024**, DOI 10.26434/chemrxiv-2024-stwdn.

Thermodynamics of electro-deposition: classical model

Classical model

$$Fe^{2+}(l) + 2e^{-} \leftrightarrow Fe(s)$$

Deposition energy

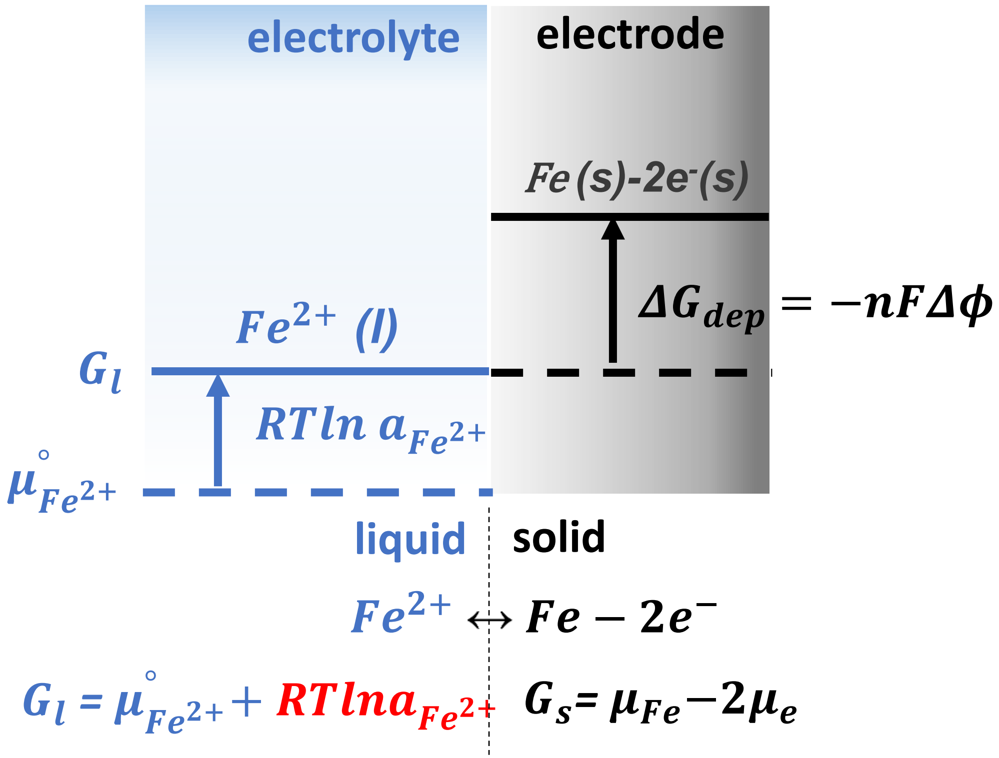
$\Delta G_{dep} = G_s - G_l = -nF\Delta\phi$

Interfacial potential drop

$\Delta\phi = \phi_s - \phi_l$

Measured deposition potential at equilibrium

$E_{eq} = \Delta\phi_{eq} - \Delta\phi_{eq}^{(R)}$

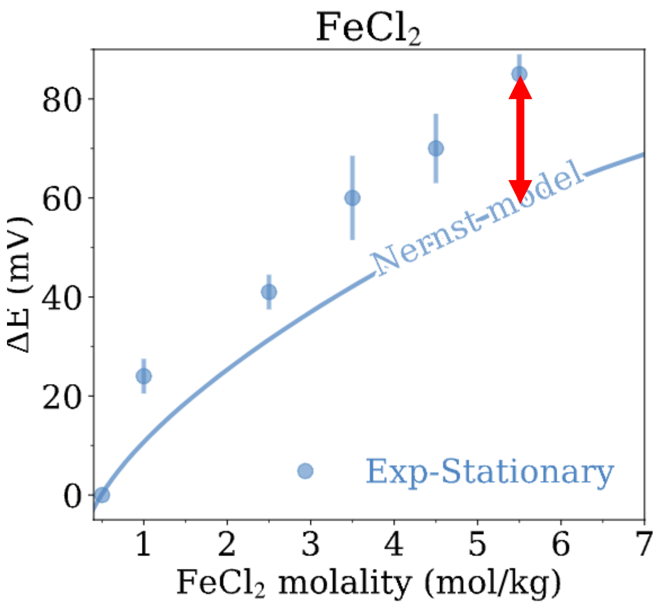


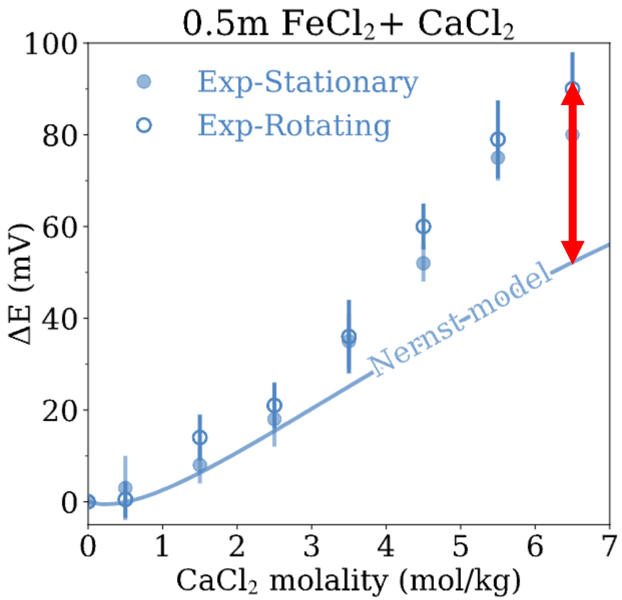
Only this term depends on electrolyte

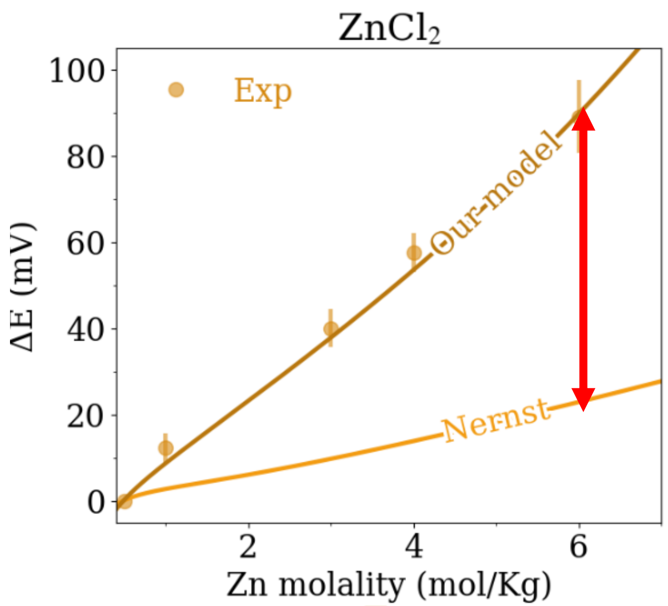
$$\Delta\phi_{eq} = \Delta\phi^0 + \frac{RT\ln(a_{Fe^{2+}})}{2F}$$

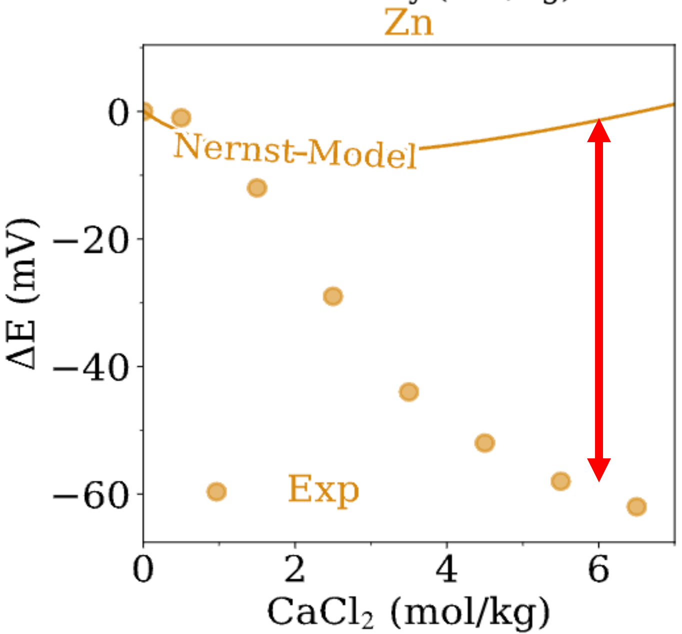
Nernst Equation

Prediction of Nernst Equation









- Nernst equation works well at low ionic strength
- But fails at high ionic strength
  - Big gap between experiment and prediction

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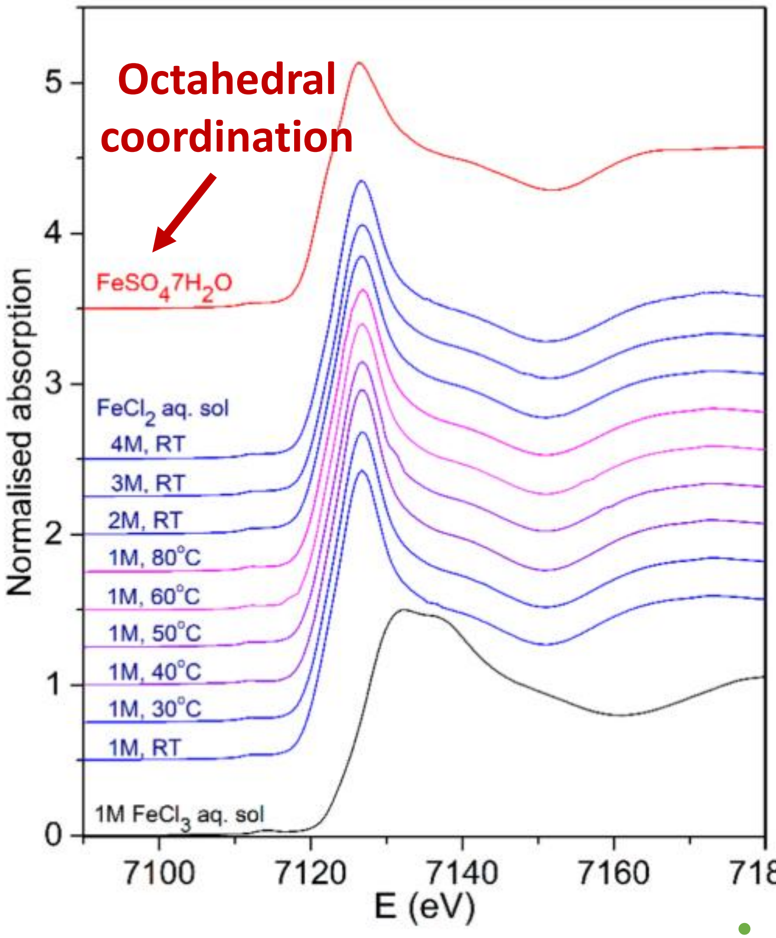
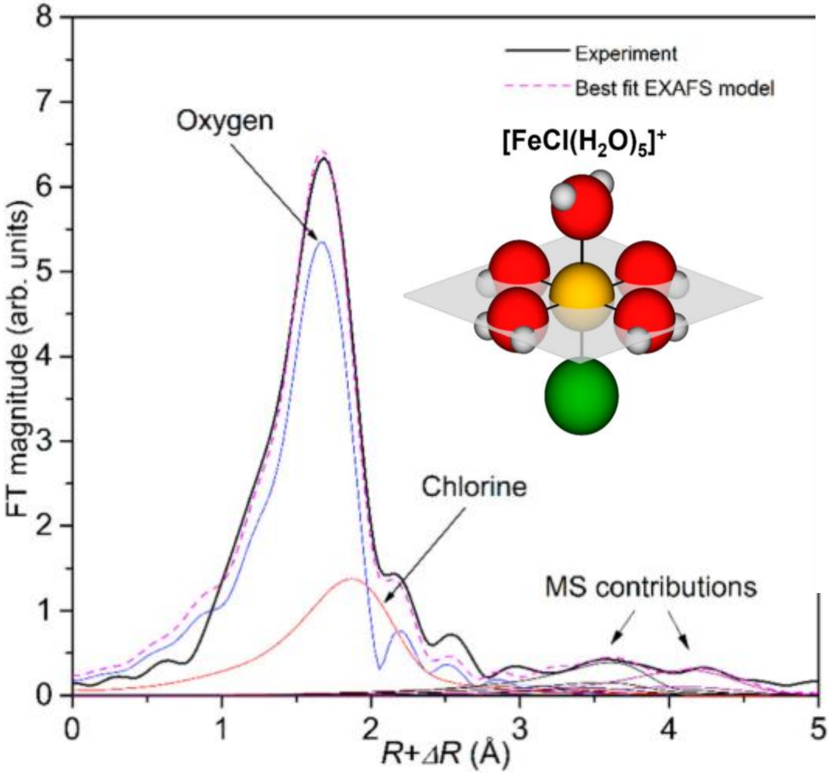
Why? strong Fe-Cl interactions leads to complex formation

X-ray absorption spectroscopy (XAS)

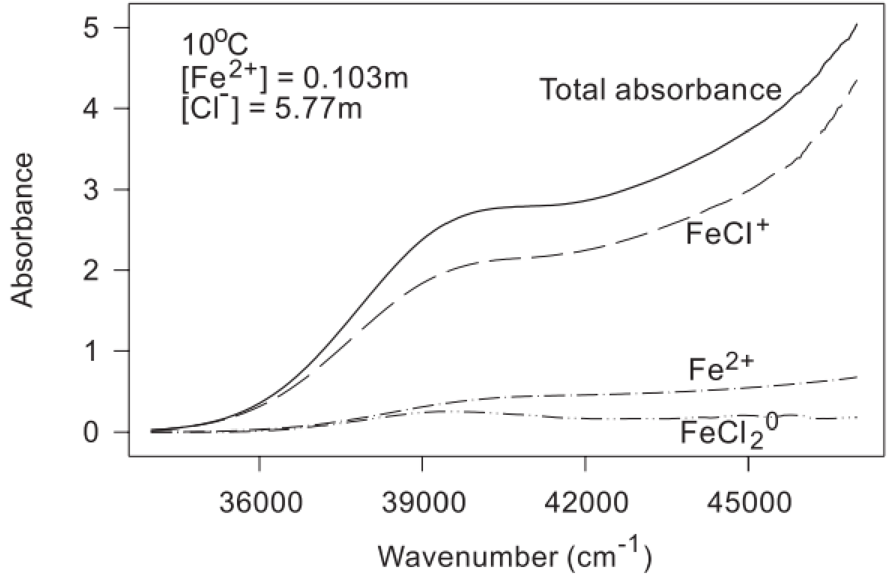
Fe K-edge Near Edge Structure



Extended Fine Structure



UV-vis spectroscopy



Fe-Cl complex at RT

- Octahedral coordination
- $FeCl^{+}$, $FeCl_2$, No FeCl3
- Tetrahedral $FeCl_4$ only at high T

Dilute electrolyte

- < 0.5 m $FeCl_2$
- Water/cation > 100

Concentrated electrolyte

- water/cation → 5-6
- e.g., 0.5m $FeCl_2$ + 8 m $CaCl_2$

M. V. Luin. Uroš, Iztok. Arcon, *Molecules* **2022**, *27*, 1.

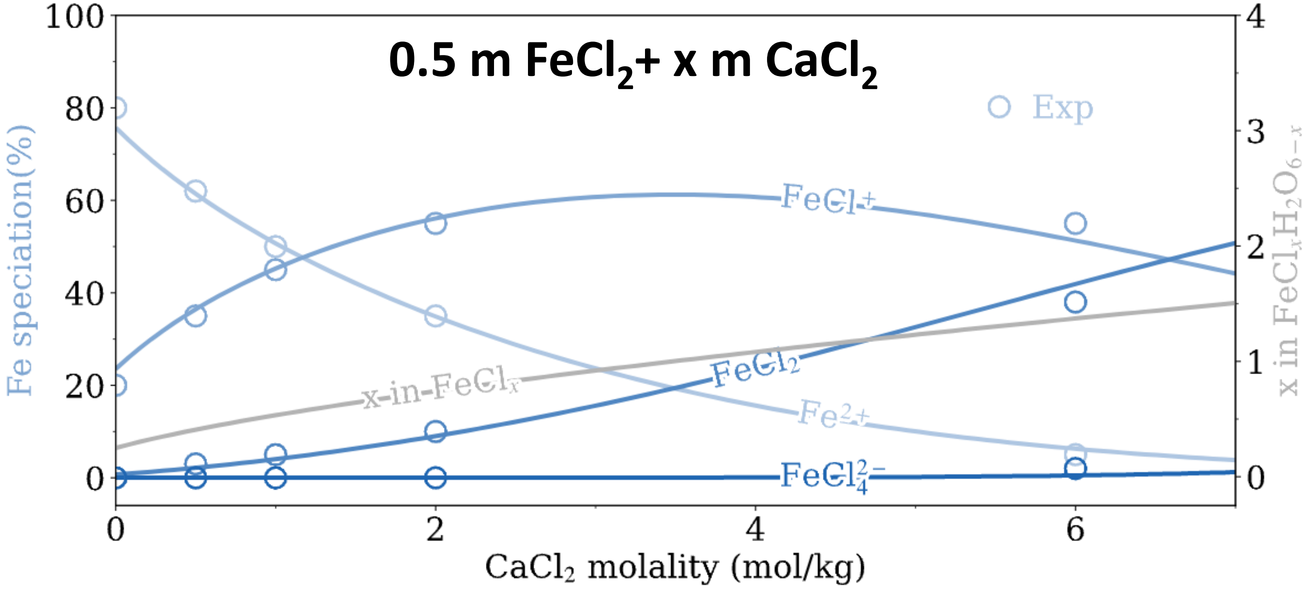
R. Zhao, P. Pan, *Can. J. Chem* **2001**, *79*, 131.

Complex formation equilibria in Fe^{2+} chloride solution

Increasing ionic strength, water/Fe ↓, Cl/Fe ↑

	Fe^{2+} →	$FeCl^{+}$ →	$FeCl_2$ →	$FeCl_4^{2-}$	Average Cl^- number
Dilute: 0.5 m $FeCl_2$	75.4%	23.8%	~0 %	0 %	x=0.25
Concentrated: 0.5 m $FeCl_2$ + 6.5m $CaCl_2$	5.1%	45.2%	48.8 %	<1 %	x=1.42

(water not shown)



Chemical equilibria (with complex stability constant)

$$K_{FeCl_x^{2-x}} = \frac{a_{FeCl_x^{2-x}}}{a_{Fe^{2+}}\ (a_{Cl^-})^x}$$

Mass balance

$$m_{Fe} = m_{Fe^{2+}} + m_{FeCl^+} + m_{FeCl_2} + m_{FeCl_3^-} + m_{FeCl_4^{2-}}$$

Thermodynamics of ions (Pitzer model)

$$ln\gamma_{\pm} = |z_a z_c| f^{\gamma} + \left(\frac{2\upsilon_a \upsilon_c}{\upsilon}\right) mB^{\gamma}$$

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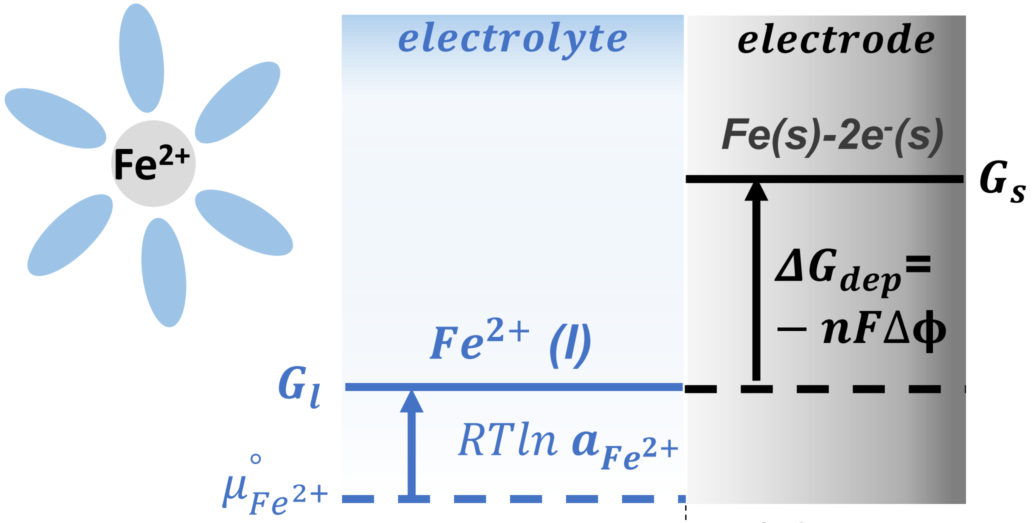
Thermodynamics: model considering complex

Classical model (not consider complex)

$Fe^{2+}(l) + 2e^- \leftrightarrow Fe(s)$

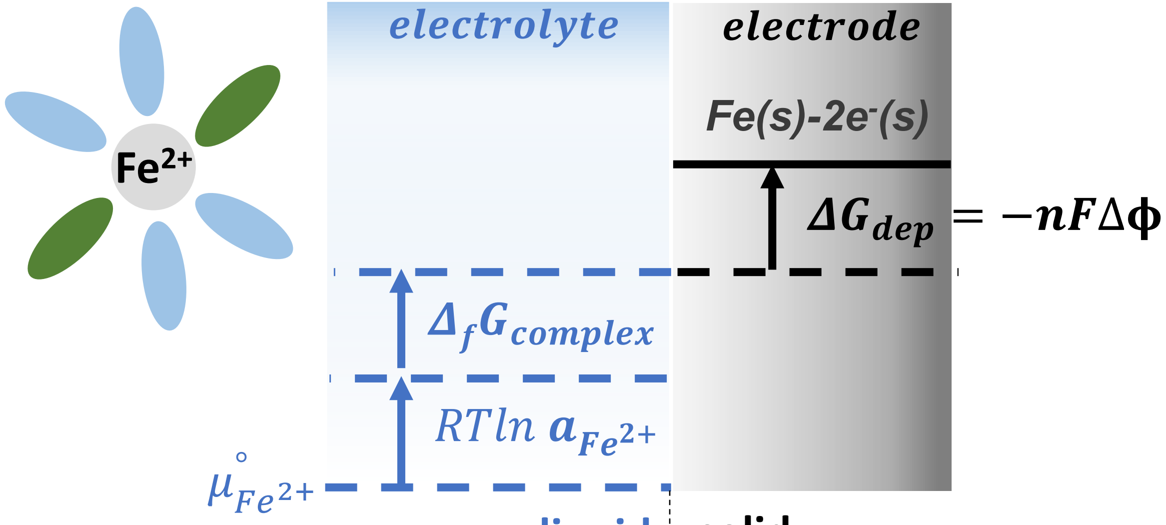


$Fe^{2+} \leftrightarrow Fe - 2e^-$

$G_l = \mu^{\circ}_{Fe^{2+}} + RT\ln a_{Fe^{2+}}$ $G_s = \mu_{Fe} - 2\mu_e$

Consider complex

$Fe(H_2O)_{6-x}Cl_x^{2-x}(l) + 2e^- \leftrightarrow Fe(s) + (6-x)H_2O(l) + xCl^-(l)$



$Fe(H_2O)_{6-x}Cl_x^{2-x} - (6-x)H_2O - xCl^- \leftrightarrow Fe - 2e^-$

$G_l = \mu^{\circ}_{Fe^{2+}} + RT\ln a_{Fe^{2+}} + \Delta_f G_{complex}$ $G_s = \mu_{Fe} - 2\mu_e$

Complex formation

$Fe^{2+}(l) + (6-x)H_2O(l) + xCl^- \rightarrow Fe(H_2O)_{6-x}Cl_x^{2-x}(l)$

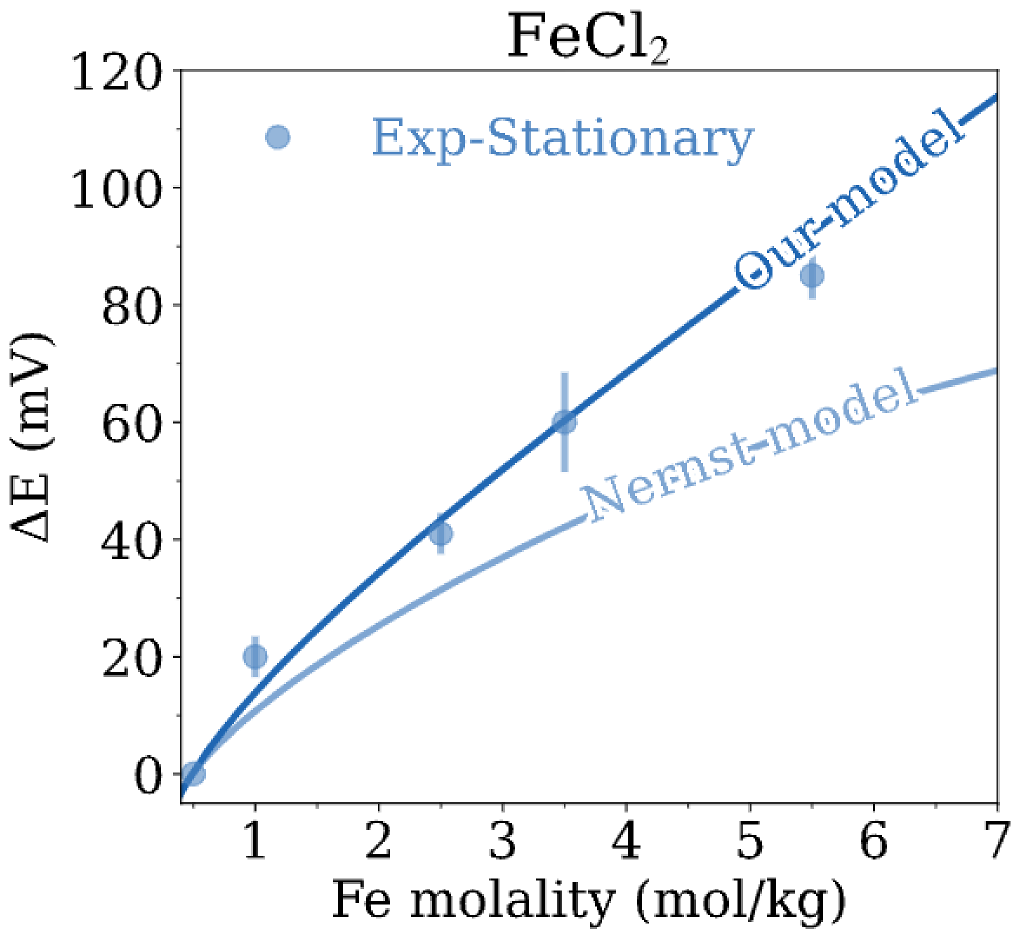
$\Delta_f G_{complex} = \Delta_f G^o{}_{complex} + RT\ln Q$

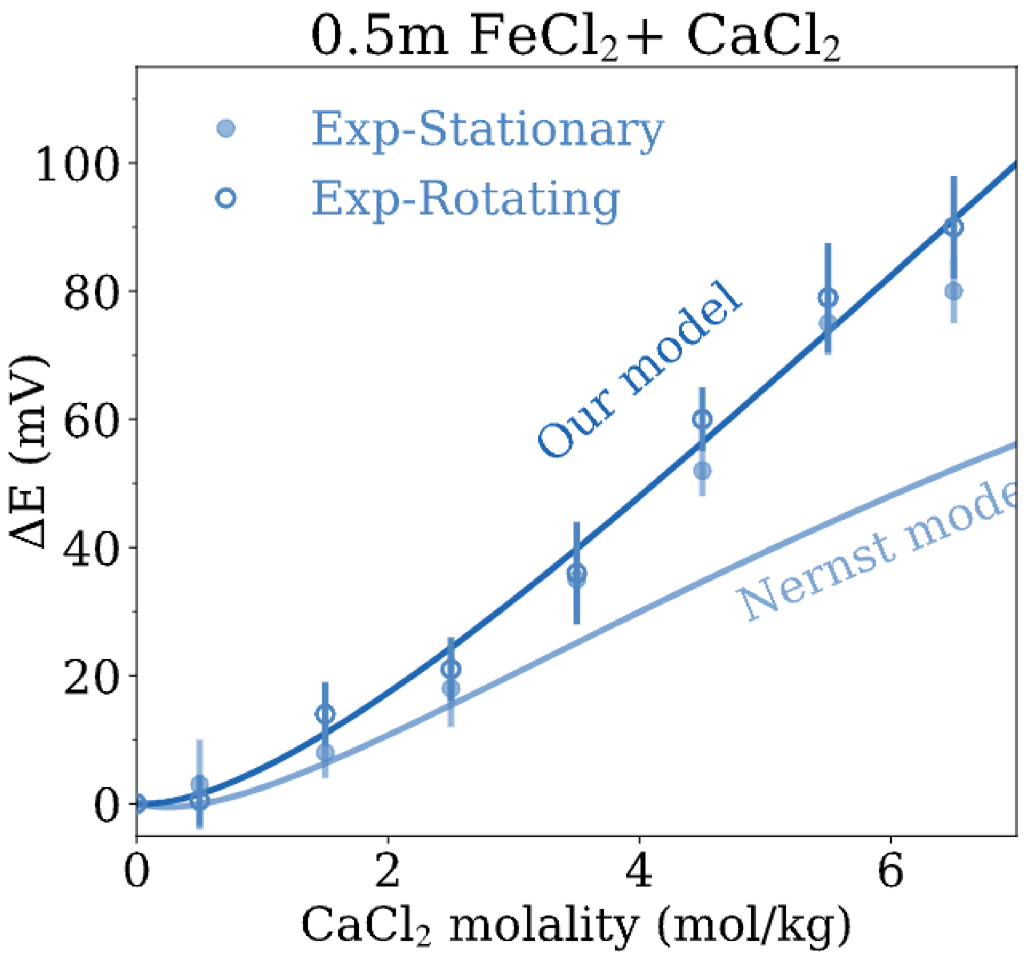
$$\Delta\phi_{eq} = \Delta\phi^0 + \frac{RT\ln\left(a_{Fe^{2+}}\right)}{2F} + \frac{\Delta_f G_{complex}}{2F}$$

$E_{eq} = \Delta\phi_{eq} - \Delta\phi_{eq}^{(R)}$

No fitting parameters — Activity of Fe^{2+} — Complex formation energy

Model prediction: Fe





Our theoretical model is consistent with experimental results in all ionic strength

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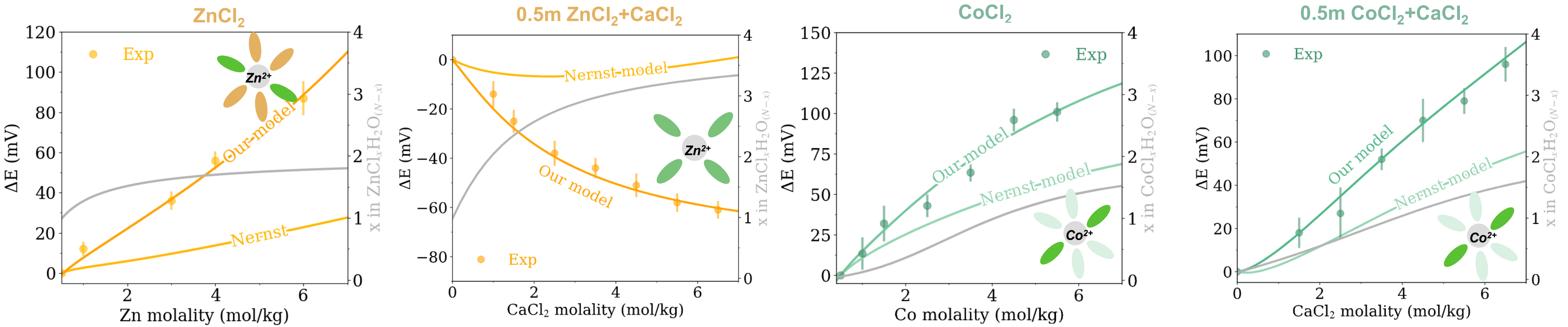
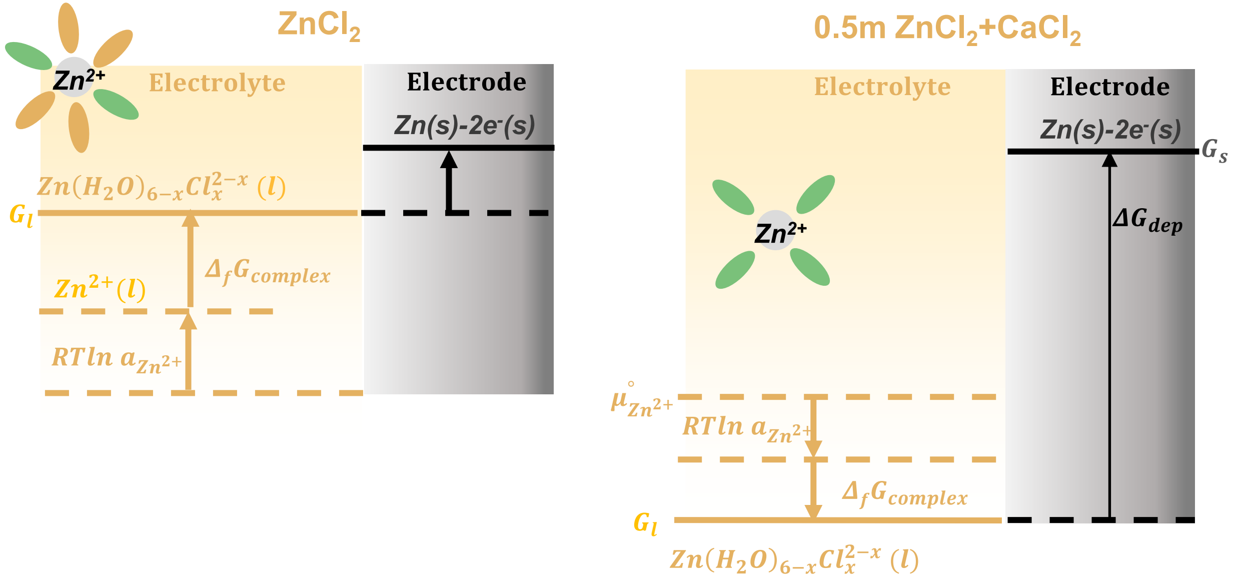
Model generalizability





- **Our theoretical model is generalizable to other TM metals**

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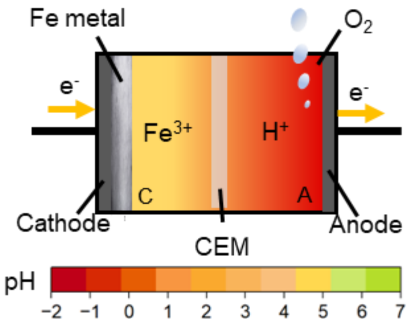
Conclusion



+ ~90 mV thermo
+ ~100 mV kinetics

Fe deposition

- **Concentrated electrolytes offer new opportunities for electrochemical technologies**
  - Fe battery and electrowinning
- **Mechanistic studies discover concentrated electrolytes**
  - Enhance Fe^{2+} reactivity
  - TM deposition potential depends on electrolyte composition
  - Nernst model unable to predict because the strong ion-ion interaction results in complex formation

$$\Delta\phi_{eq} = \Delta\phi^0 + \frac{RT\ln\left(a_{Fe^{2+}}\right)}{2F} + \frac{\Delta_f G_{complex}}{2F}$$

Activity of Fe^{2+} **Complex formation energy**

- **Thermodynamic model considering complex formation**
  - No fitting parameters, chemistry agonistic
  - Accurately predicts deposition potential in concentrated electrolytes

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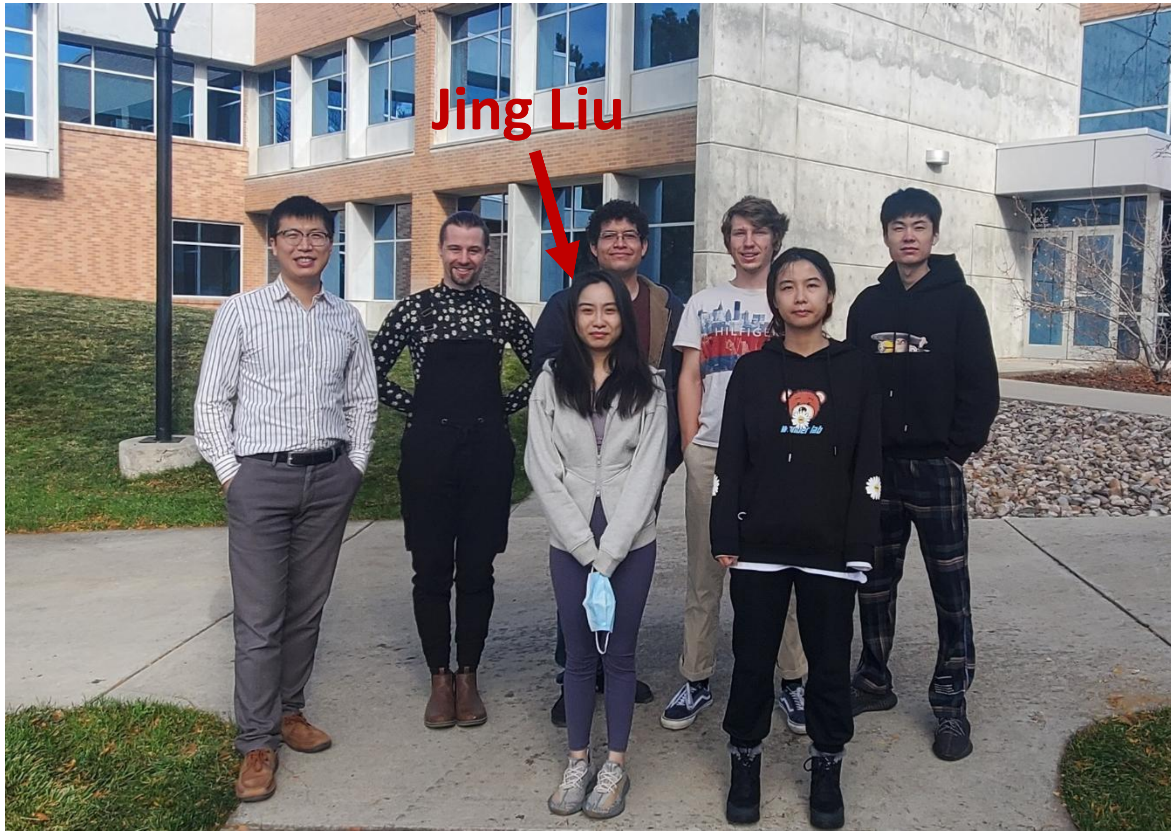
Acknowledgement



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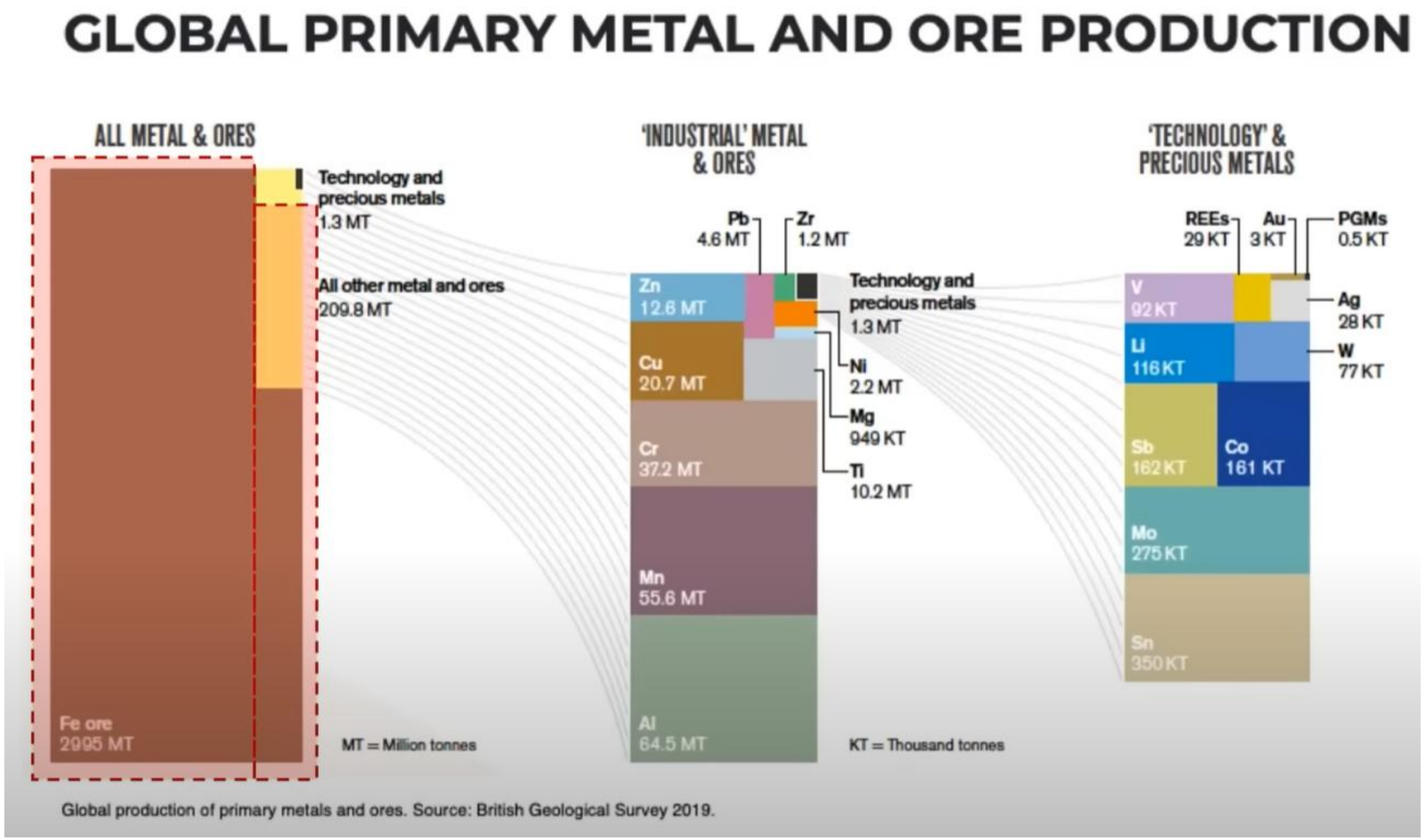
DE-SC0023947

Thank you!
Q&A

Why Fe?



Global production of primary metals and ores. Source: British Geological Survey 2019.

- **The second abundant metal in earth crust**
  - **800 billion tons reserve**
  - **a massive resource**

- **The most produced metal**
  - **Fe: $600/ton**
  - **Zn: $3000/ton**
  - **Li: $100,000/ton**

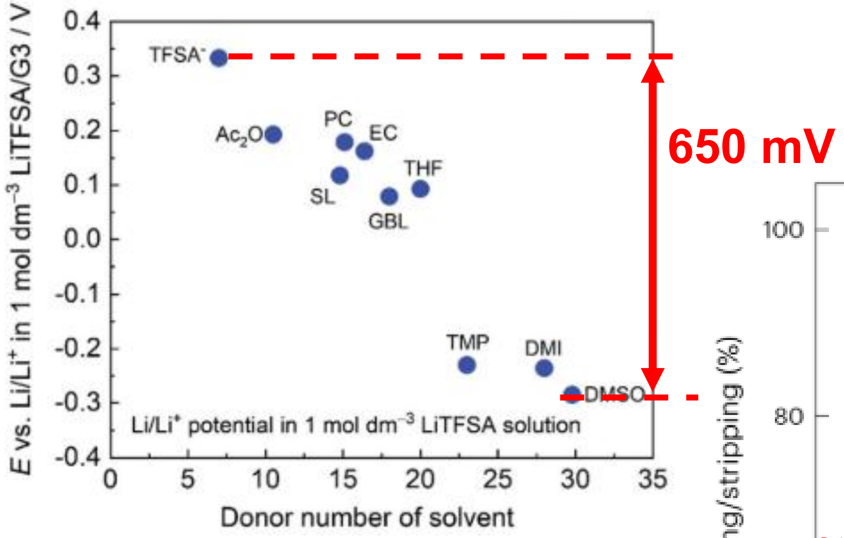
abundant

mass produced

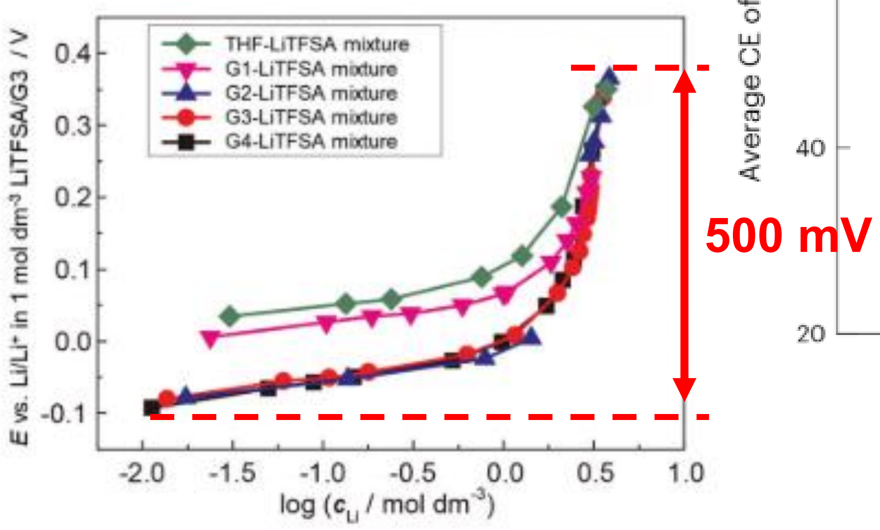
cheap

Lithium deposition potential (E) in non-aqueous electrolytes

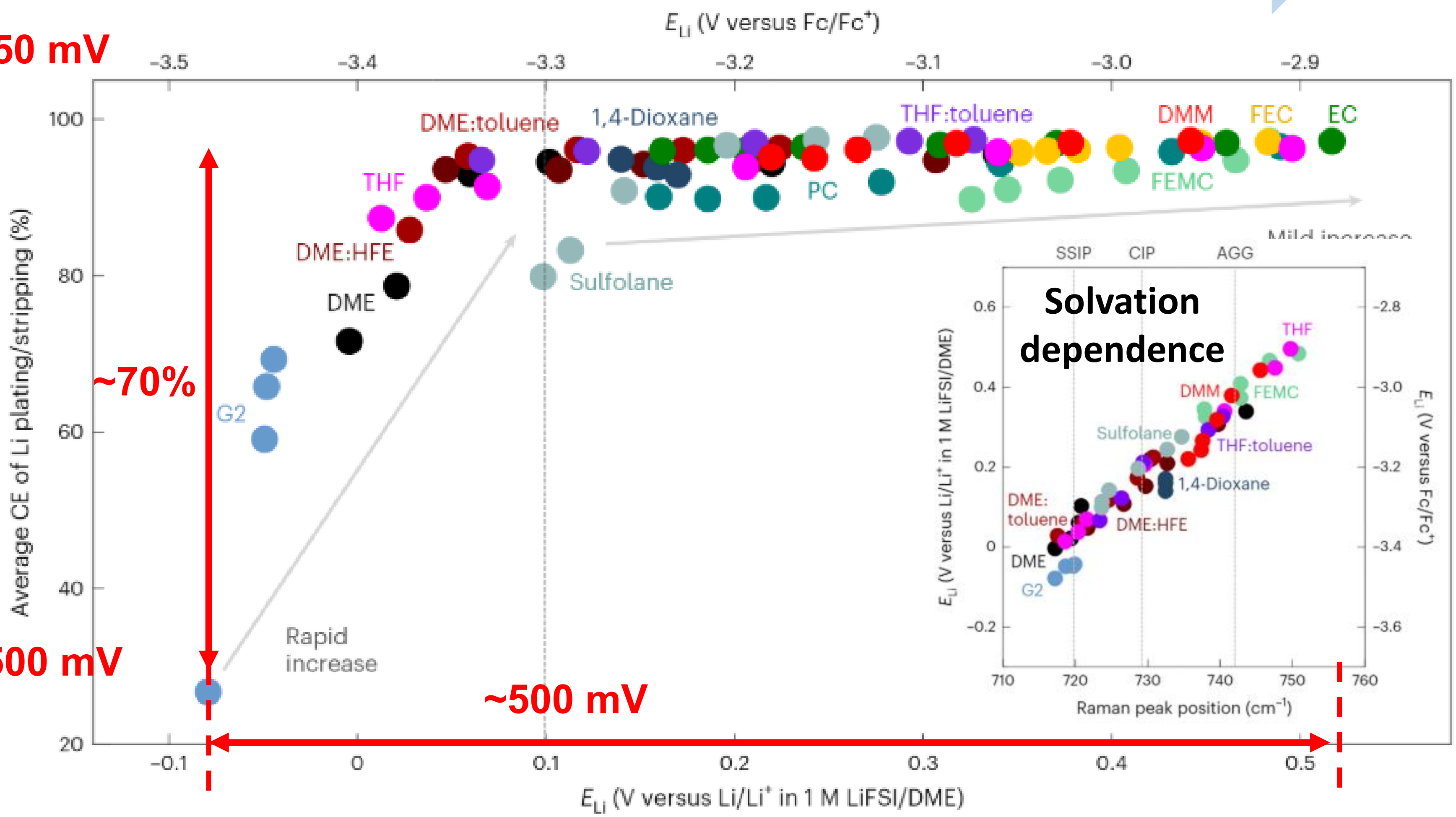
Solvent dependence



Concentration dependence



Increasing E, increasing efficiency



K. Dokko, *Phys. Chem. Chem. Phys.* **2021**, *23*, 21419.

Y. Yamada, *Nat. Energy* **2022**, *7*, 1217.

Thermodynamics of Fe chemistry in aqueous environment

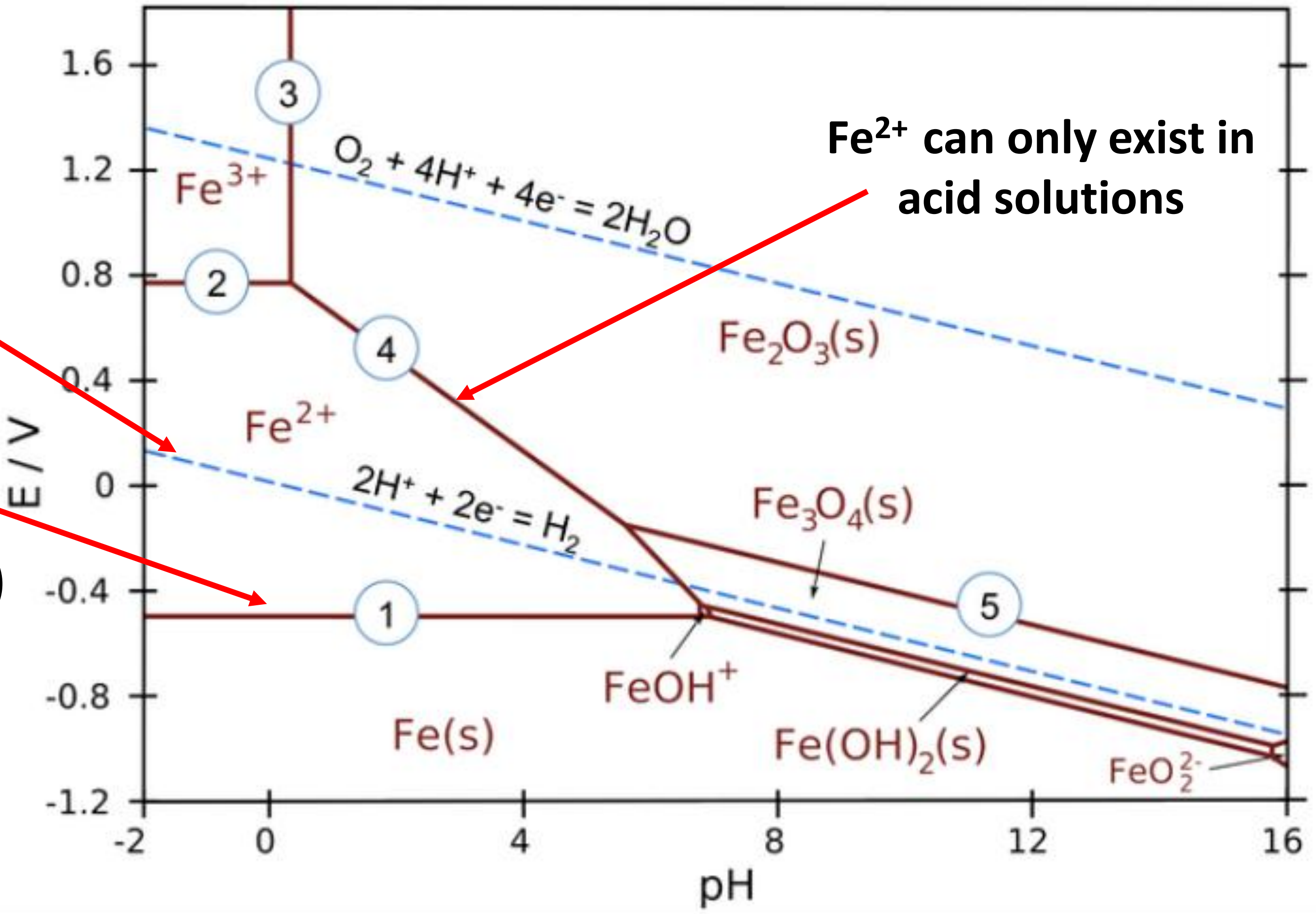
Pourbaix diagram of Fe*

Water reduction

-0.118V vs SHE at pH=2

Fe^{2+} reduction (electro-deposition)

-0.44V vs SHE at standard condition

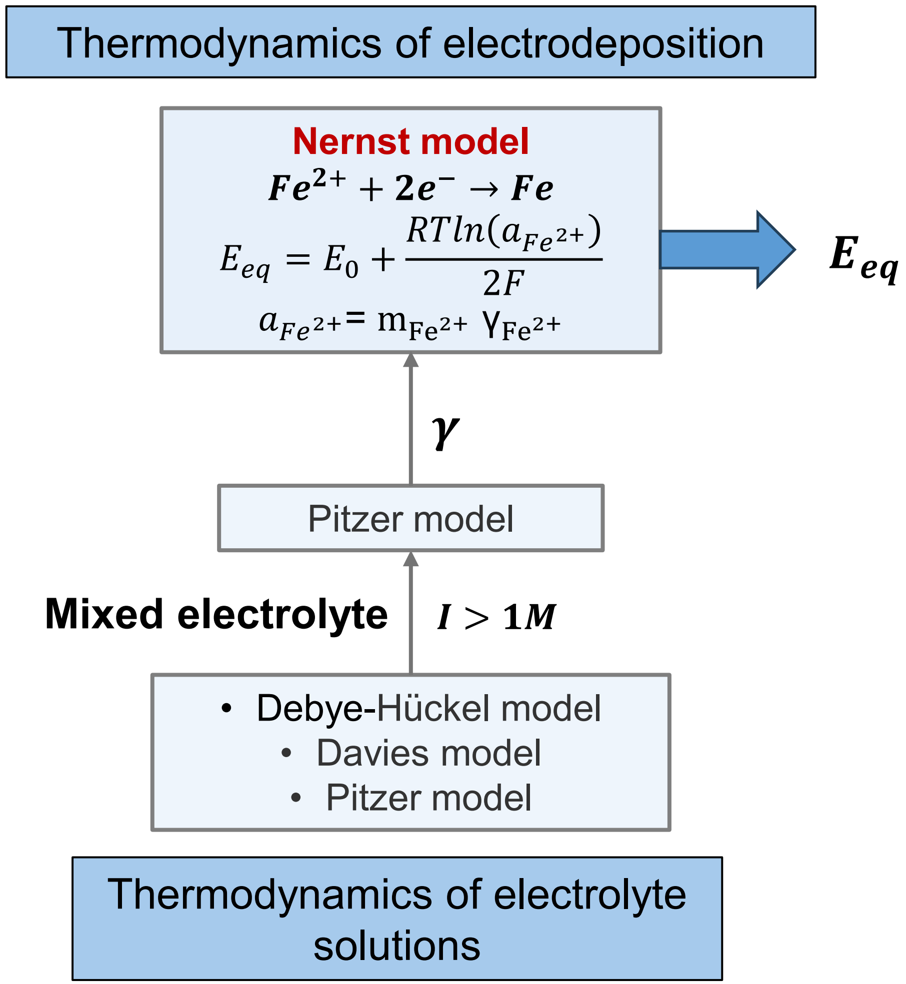


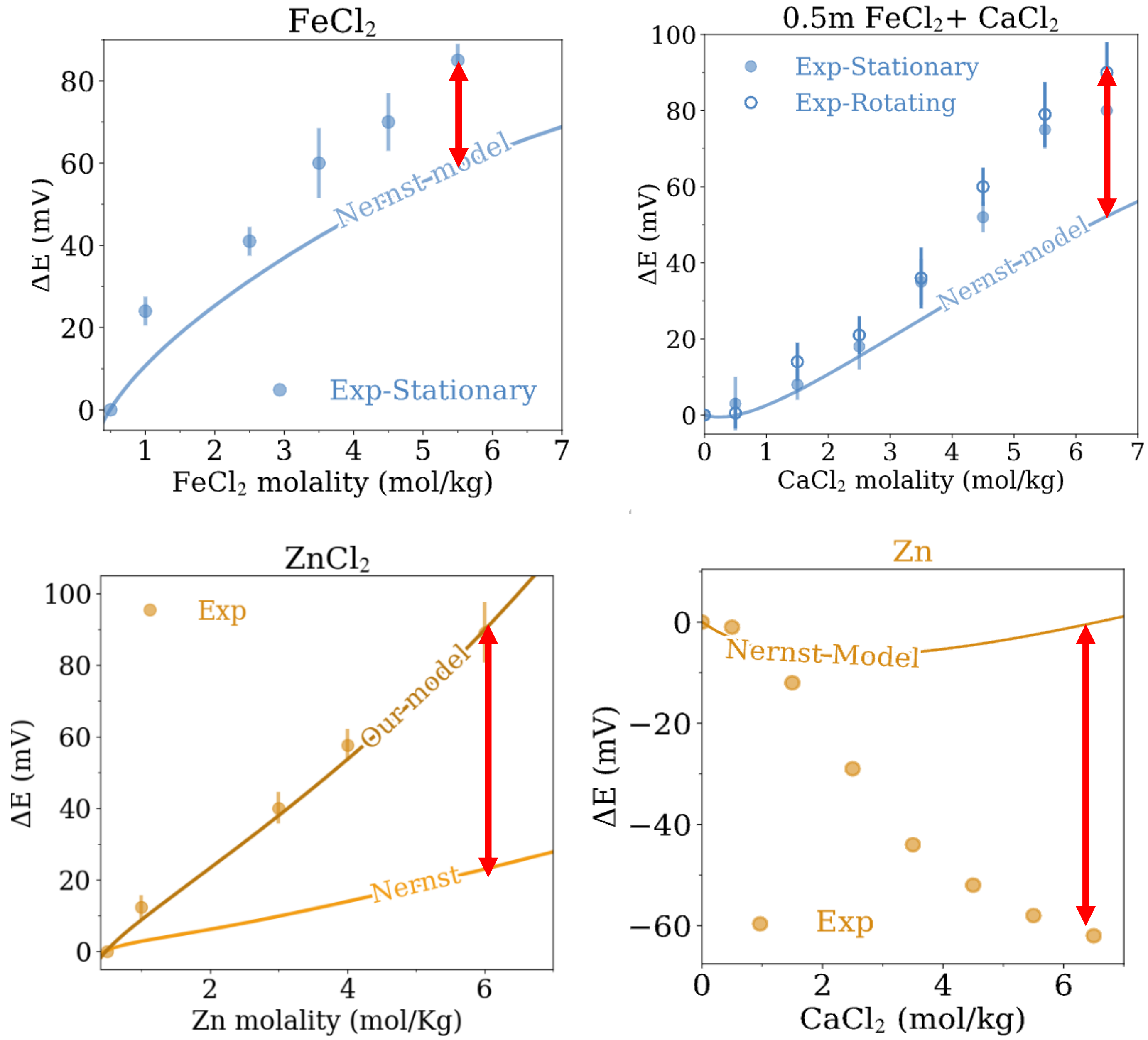
Fe^{2+} can only exist in acid solutions

Water reduction: thermodynamically more favorable → hydrogen evolution reaction (HER)

*https://chem.libretexts.org/, calculated under standard conditions and Fe concentration of 1 μM

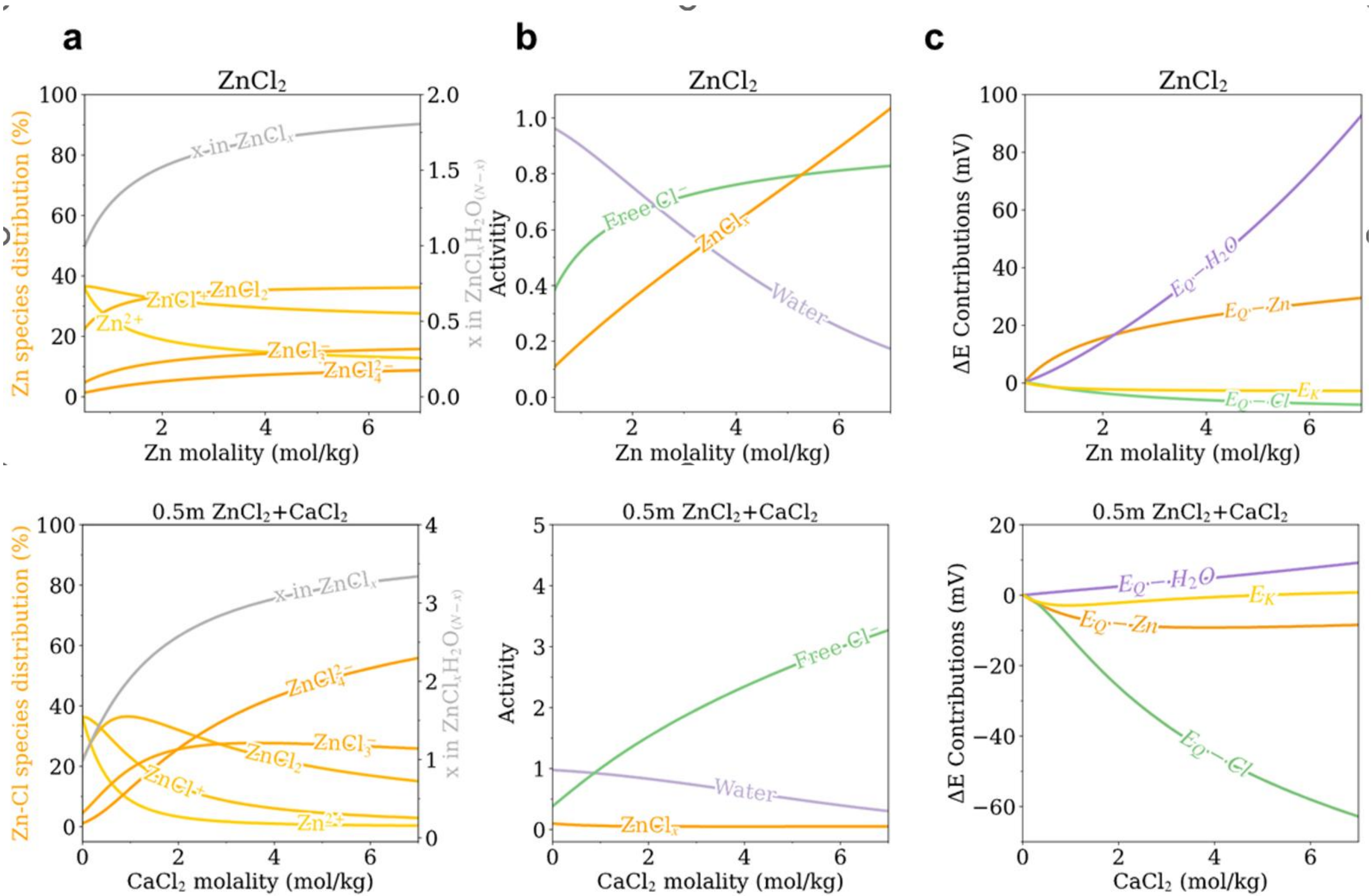
Prediction of Nernst Equation



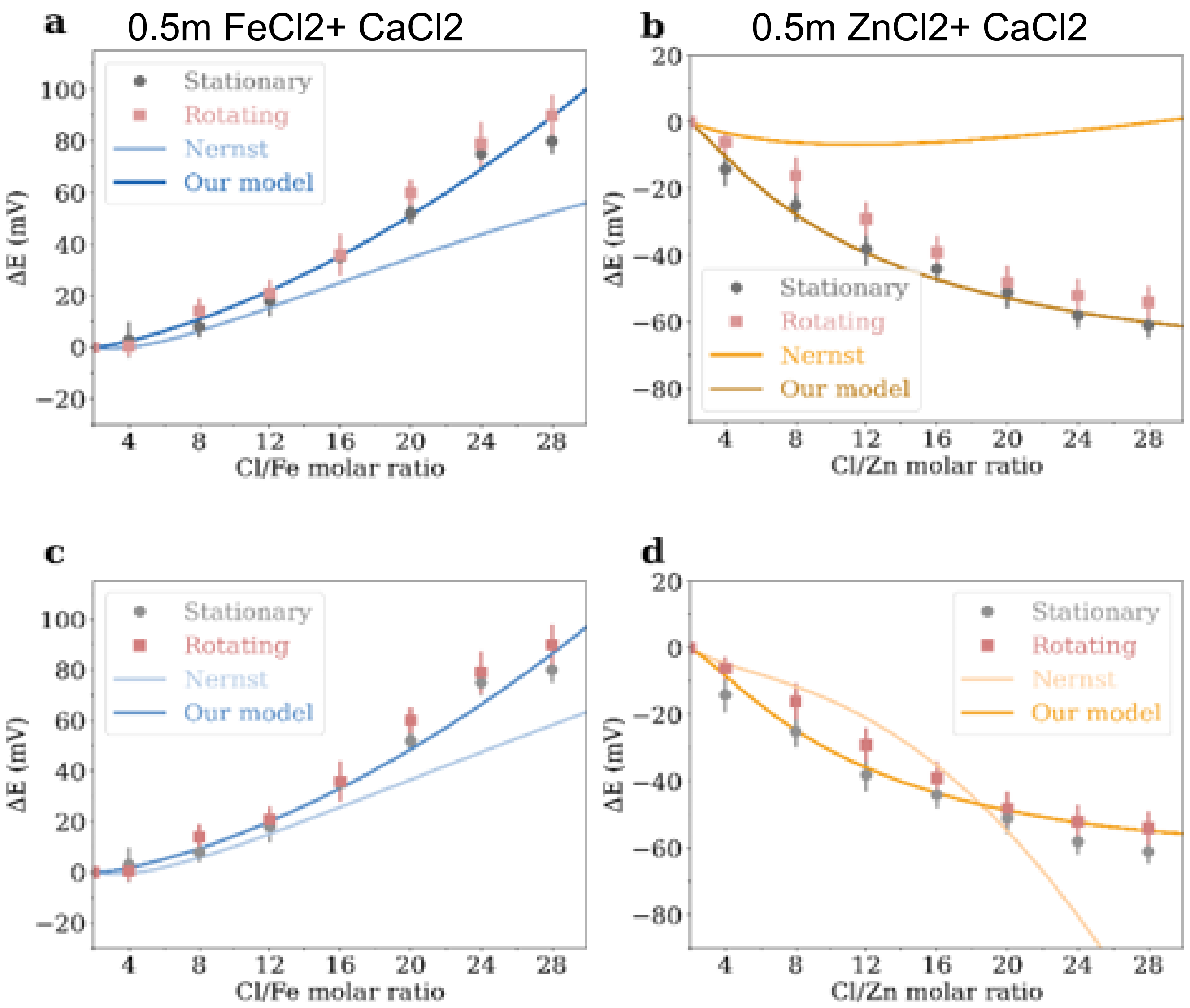


- Nernst Model works well at low ionic strength
- But fails at high ionic strength

J. Liu, **T. Gao***, *in prep, 2025*

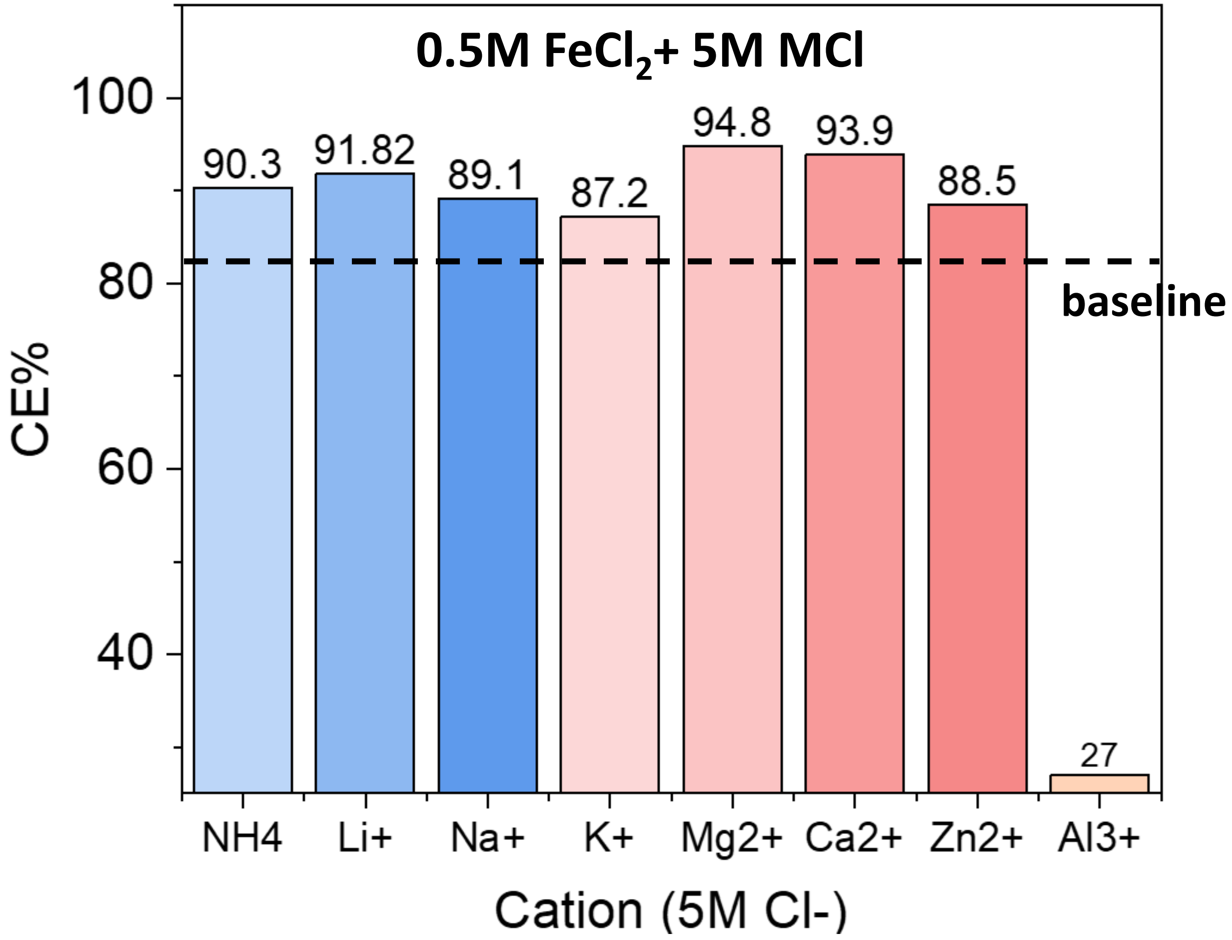

a
b
c
ZnCl₂
Zn species distribution (%)
x in ZnClₓH₂O₍N−x₎
x-in-ZnClₓ
ZnCl+
ZnCl₂
Zn2+
ZnCl₃⁻
ZnCl₄²⁻
Zn molality (mol/kg)
Activity
Free-Cl⁻
ZnClₓ
Water
ΔE Contributions (mV)
E_Q−H₂O
E_Q−Zn
E_K
E_Q−Cl
0.5m ZnCl₂+CaCl₂
Zn-Cl species distribution (%)
CaCl₂ molality (mol/kg)
CaCl₂ (mol/kg)

Model sensitivity to Pitzer parameter



Different Pitzer parameter sets from different literature won't affect the prediction accuracy

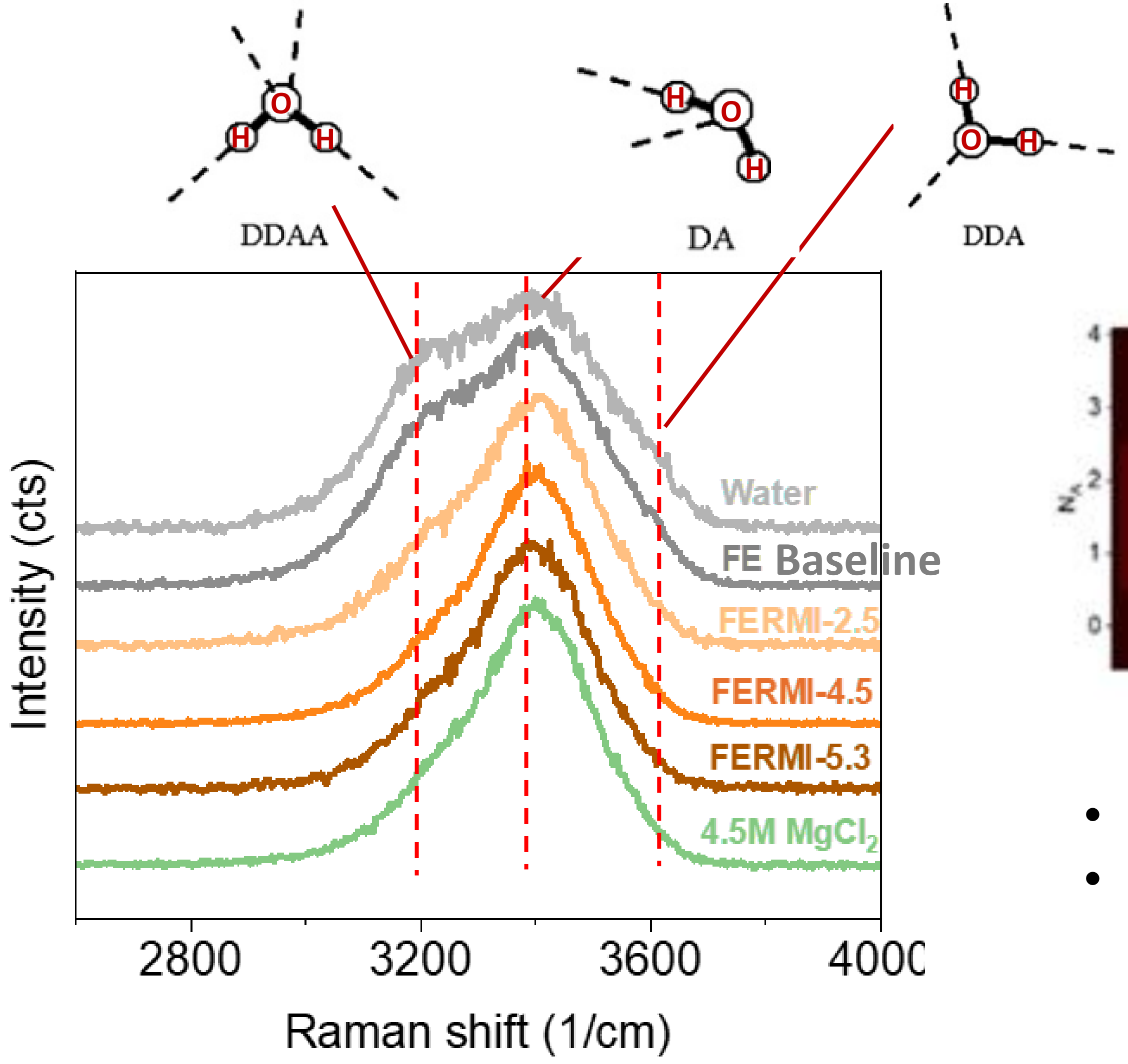
Concentrated electrolyte: w/ different support salt

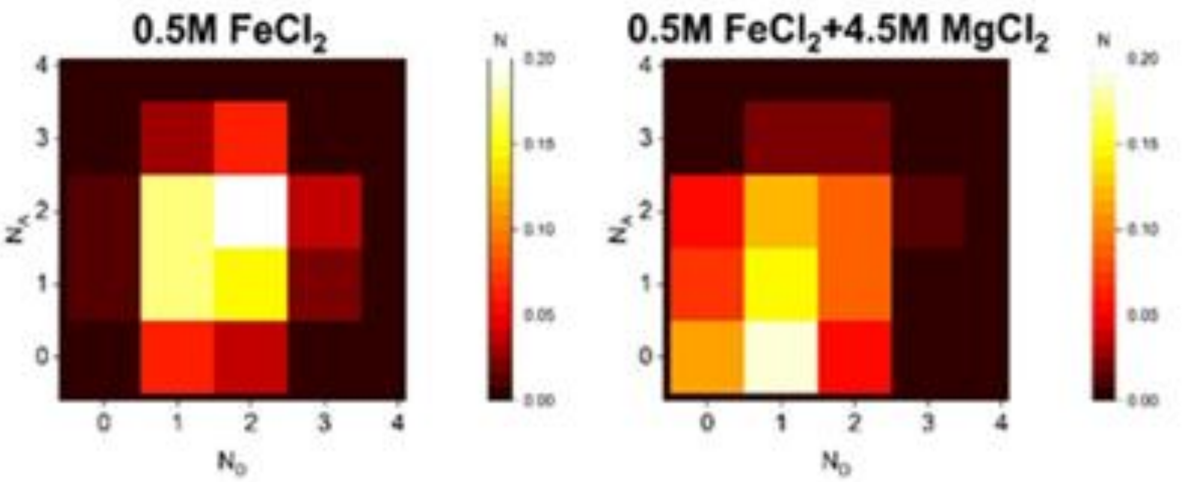


Unpublished results

- Typical Fe inorganic salt has limited solubility
  - $FeCl_2$: 3.57M; $FeSO_4$: 3.0M
- Co-cations have higher solubility
  - Alkali metal: Li, Na, K
  - Alkali earth metal: Mg, Ca
  - Other: Al,NH_4^+ ..
- **Anion-rich electrolytes**
  - anion/Fe ratio >2 by adding co-salt

Less H-bond due to ion-water interaction in concentrated electrolytes





- Less DDAA and DDA water
- H-bond per water reduces from 3.2 to 2.2
  - H-bond length increases (from 2.02 Å to 2.085 Å)
  - Shorter and stiffer O-H covalent bond

Sun, Q. (2009), *Vibrational Spectroscopy*, 51(2), pp. 213–217.

J. Liu, D. Bedrov*, **T. Gao***, et. al., ***ACS Cent. Sci.* 2022**