UCLA Institute for Pure and Applied Mathematics, 10/8/2025

Unified Quantum Theory of Electrochemical Kinetics by Coupled Ion-Electron Transfer

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Professor of Mathematics

Massachusetts Institute of Technology

MZB, *Faraday Discussions* (2023).
Zhao,… Chueh, Braatz, MZB, *Nature* (2023).
Zhang, Fraggedakis, Gao, Pathak,… Shao-Horn, MZB, *Science* (2025)

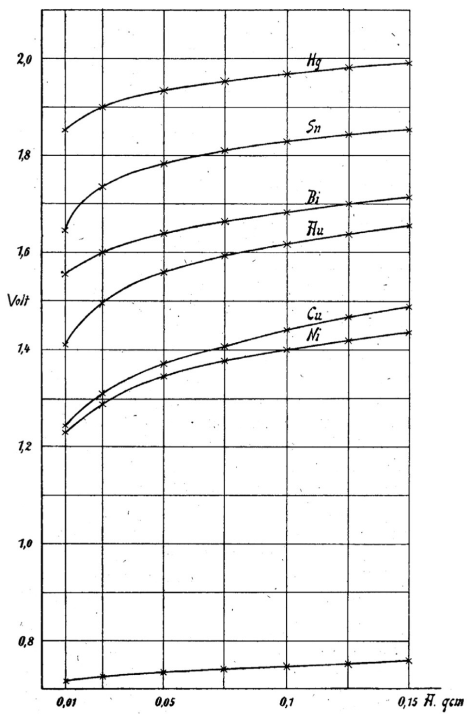
History of Charge Transfer Theory

MZB, *Faraday Discussions* 246, 60-124 (2023).

Tafel's Law of Electrolysis

J. Tafel, *Zeit. Physik. Chem.* (1905).

$$\ln I = a + b\,\eta$$



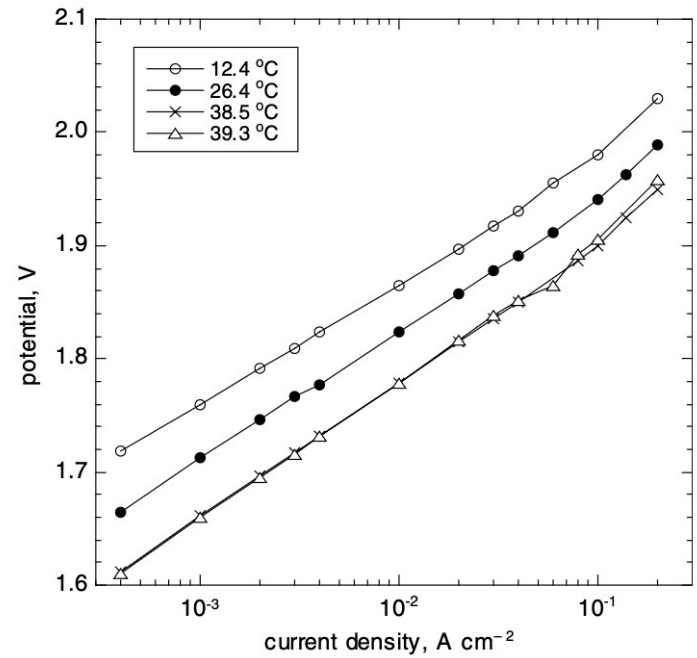
Tafel's data for hydrogen evolution reaction (HER) in acid on different metals…

Über die Polarisation
bei kathodischer Wasserstoffentwicklung.

Von

Julius Tafel.

Julius Tafel (1862-1918)

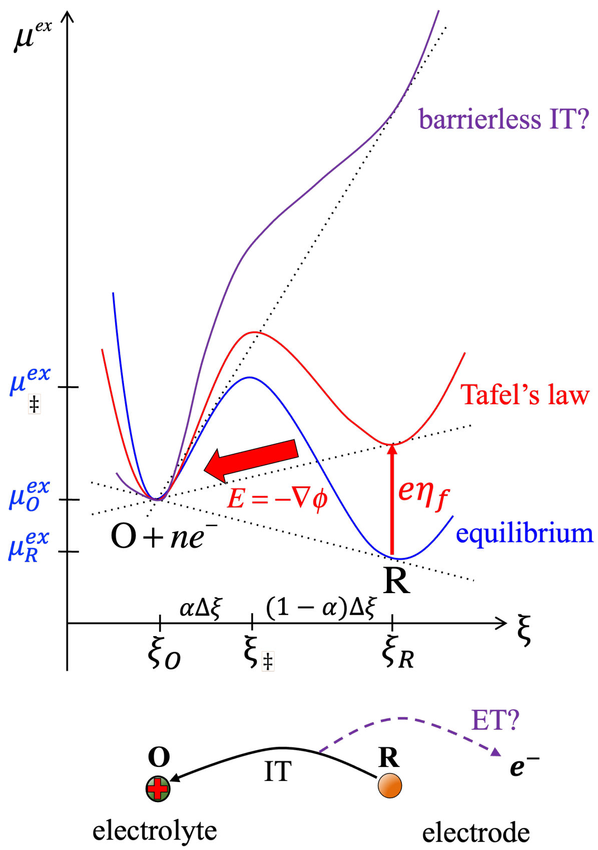


… shown on (slightly curved) "Tafel plot".

Burstein, Corrosion Science (2005).

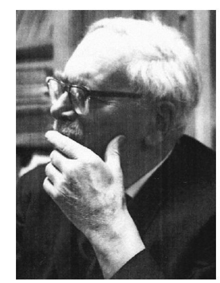
The Butler-Volmer Equation

T. Erdey-Gruz & M. Volmer, Z. Phys. Chem. (1931). J.A.V. Butler, Trans. Faraday Soc. (1932)



$$I = I_0\left(e^{-\alpha\, e\eta/k_BT} - e^{(1-\alpha)\, e\eta/k_BT}\right)$$

Max Volmer (1885-1965)



John A. V. Butler (1899-1977)

Pros:

- Simple
- Interpolates Tafel's Law for oxidation & reduction
- Intuitive *classical physics* of **ion transfer (IT)** biased by E field

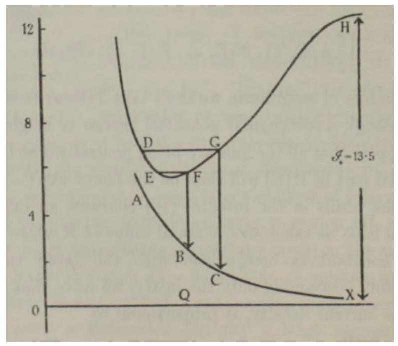
Cons:

- Parameters (I_0,α) fitted, not predicted
- Often must fit an empirical "film resistance"
- Fails at large overpotentials (barrierless IT)
- Neglects *quantum physics* of **electron transfer (ET)**

The original Gurney-Butler mechanism for electrolysis:
"Ion-coupled electron transfer" (ICET)

MZB, *Faraday Discussions* 246, 60-124 (2023).

Ronald Wilfrid Gurney (1898-1953)



Making use of this distribution, the integral (6), representing the current flowing, must now be replaced by

$$\int_{E_0+}^{E_1-\epsilon V} n\,(E, V)\,.\,N_+\,(E)\,.\,P\,(E)\,,dE, \qquad (10)$$

where E_1 is the value of E corresponding to w_1 when V is zero. The corresponding integral at the anode will be

$$\int_{E_1+\epsilon V}^{E_0-} \nu\,(E, V)\,.\,N_-\,(E)\,.\,P\,(E)\,.\,dE, \qquad (11)$$

where ν (E, V) is the number of vacant levels in the metal, which falls

R. W. Gurney, "Quantum theory of electrolysis",
Proc. Roy. Soc. A (1931). ***The nearly forgotten seminal paper.***

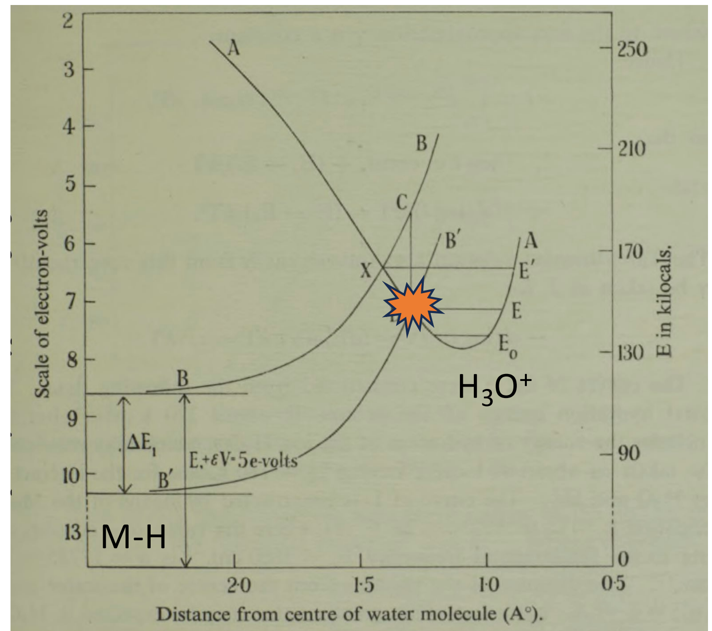


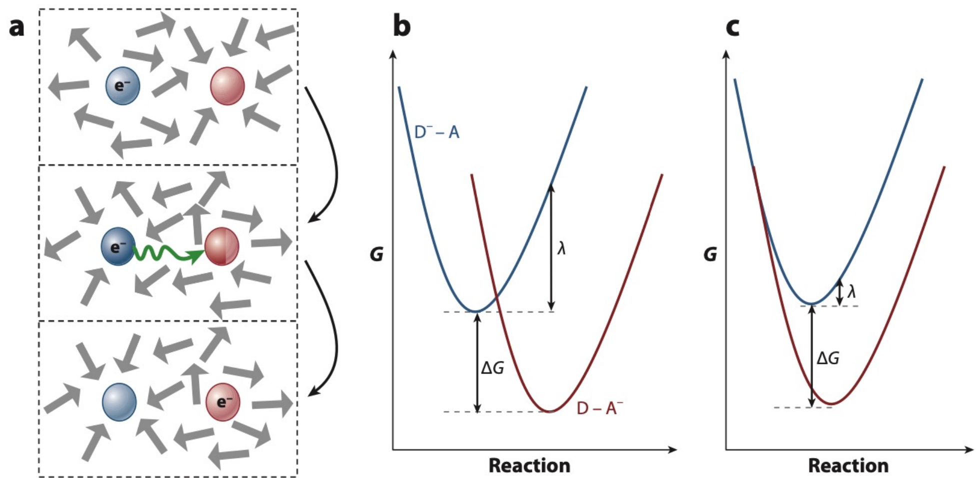
FIG. 1—Discharge of proton in H_3O^+. AA, curve of $\mathcal{J} - L$; BB, curve of $E_1 + \epsilon V + R$.

$$i = k_0\,(1 - x)\,e^{-\epsilon\,.\,\Delta V/\gamma kT} - k'_0 x\,e^{\epsilon\,.\,\Delta V/\gamma kT}$$

J. A. V. Butler, Proc. Roy. Soc. A (1936)

Marcus Theory of Electron Transfer

R. Marcus, J. Chem. Phys. (1956); Rev. Mod. Phys. (1993).



Van Voorhis et al, Ann. Rev. Phys. Chem. (2010)

Rudolf Arthur Marcus (1923-)

Non-adiabatic ET rate:

$$k_{ET} = \frac{|H_{DA}|^2}{\sqrt{4\pi\lambda k_B T}} \exp\left(\frac{-(\Delta G + \lambda)^2}{4\lambda k_B T}\right)$$

$\Delta G = e\,\eta_f + \epsilon_F - \epsilon$ for Faradaic reactions

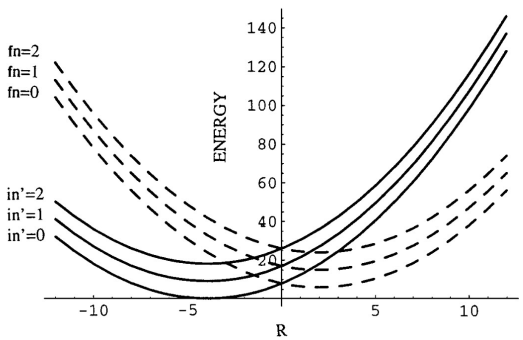
Predicts:

- Quantum prefactor (Fermi's Golden Rule)
- Pure ET barrier ~ **reorganization energy** λ
- Curved Tafel plots
  - Marcus "inverted region" for localized states
  - Limiting current for metal electrodes (MHC)

Neglects:

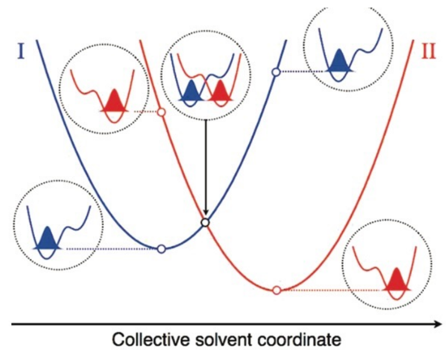
- **Bond-breaking (**IT) in electrochemistry

Proton-Coupled Electron Transfer (PCET) Theory



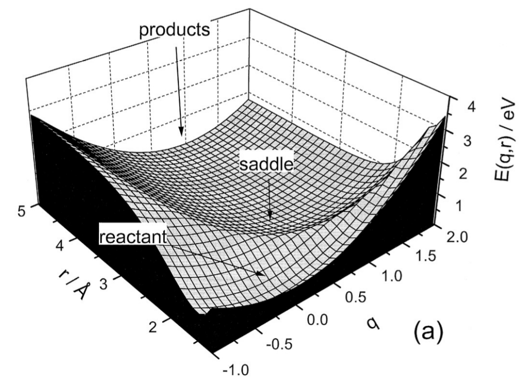
$$k_{ETPT} = \frac{V_{el}^2}{\hbar^2}\sqrt{\pi\hbar^2/\lambda_s^{ETPT}k_BT}\sum_{n'}\rho_{in'}\sum_{n\in b}|\langle\chi_{fn}|\chi_{in'}\rangle|^2$$
$$\times\, e^{-(\lambda_s^{ETPT}+\Delta E^{el}+\varepsilon_{fn}-\varepsilon_{in'})^2/4\lambda_s^{ETPT}K_BT}.$$

Cukier & Nocera, Ann. Rev. Phys. Chem. (1998)
R. I. Cukier, *J. Phys. Chem.* (1994).
V. A. Benderskii & S. Yu. Grebenshchikov,
J. Electronanal. Chem. (1994).



$$k = \sum_{\mu} P_{\mu}\sum_{\nu}\frac{|V^{el}S_{\mu\nu}^{(0)}|^2}{\hbar}\sqrt{\frac{\pi}{\lambda_{\mu\nu}k_BT}}\exp\left[-\frac{(\Delta G_{\mu\nu}^0+\lambda_{\mu\nu})^2}{4\lambda_{\mu\nu}k_BT}\right]$$

J. Y. Fang & S. Hammes-Schiffer, J. Chem. Phys.(1997).
S. Hammes-Schiffer, Acc. Chem. Res.. (2001).
S. Hammes-Schiffer & A. A. Stuchebrukhov, Chem. Rev. (2010)



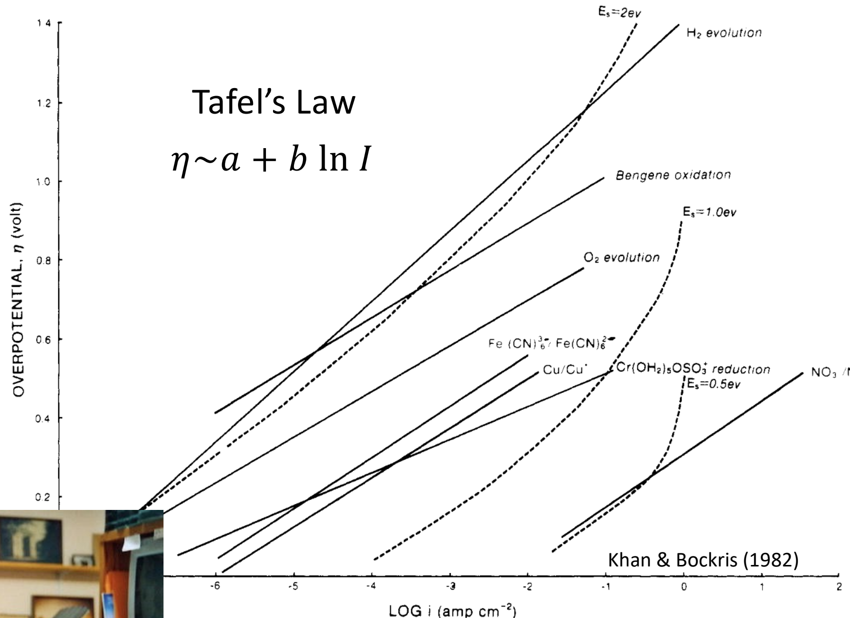
J. B. Strauss, A. Calhoun & A. Voth, J. Chem. Phys. (1995).
A. Calhoun & G. A. Voth, J. Phys. Chem. (1996).
Koper & Voth, "BBET", Chem Phys. Lett. (1998)

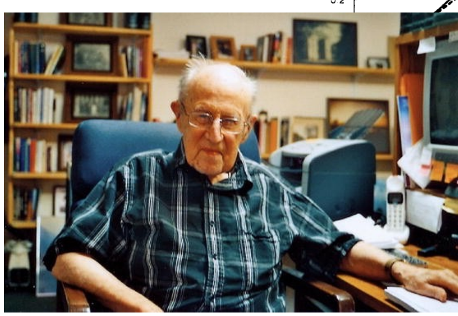
Schmickler, Chem. Phys. Lett. (1995).
Santos & Schmickler, Chem. Rev. (2010).

Many rate expressions for PCET with both protons and electrons treated quantum mechanically,
but still no derivation of a simple formula to replace or extend the BV equation.

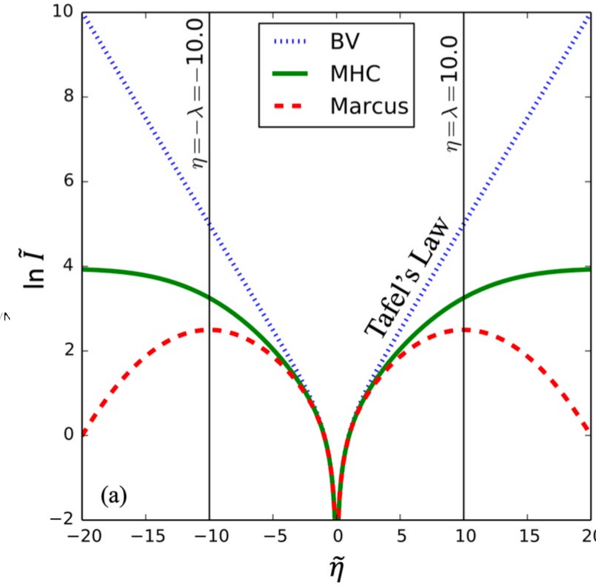
Despite Nobel Prizes for ET theory (Marcus, 1992) and quantum chemical simulations (Kohn & Poppel 1998), there is still no quantum theory of Tafel's law (1905)!

Julius Tafel (1862-1918)





John O'M. Bockris (1923-2013)
Faraday Medal (1981), Ig Nobel Prize (1997)



Limiting current for a metal electrode

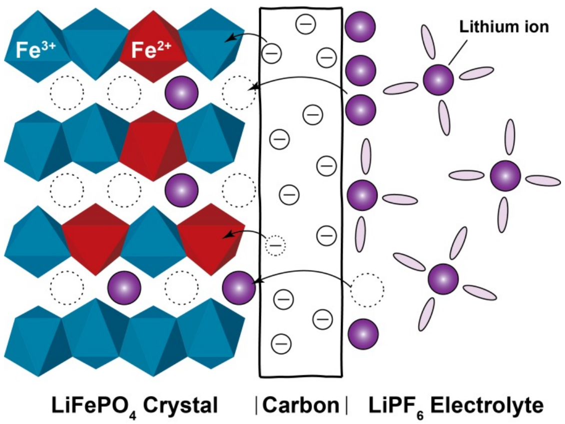
"Inverted region" for localized electrons

The quantum mechanical formulation of electrode reactions still possesses the Achilles' heel that it cannot replicate Tafel's law,… one of the most tested and verified laws of nature. - J. O'M. Bockris

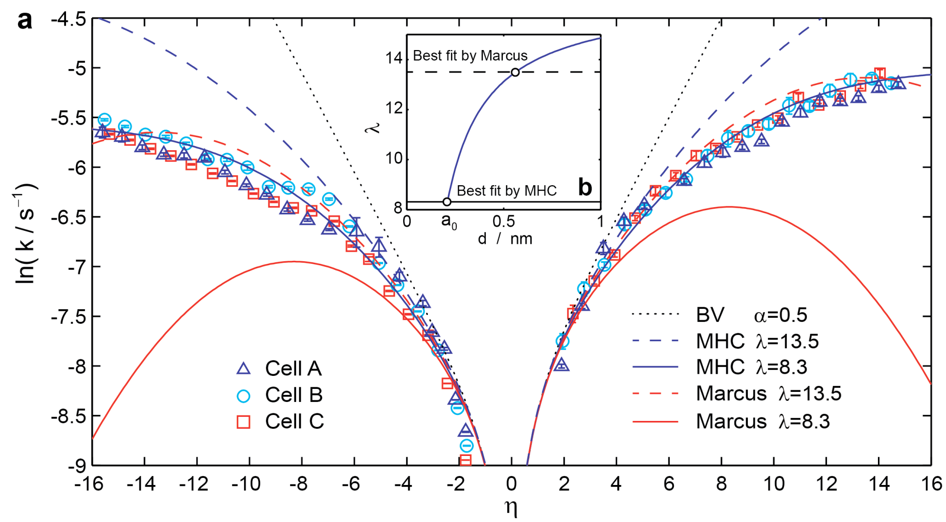
A new mechanism for lithium intercalation:
“Electron-coupled ion transfer” (ECIT)

MZB, *Faraday Discussions* 246, 60-124 (2023).

Peng Bai & M. Z. Bazant, *Nature Communications* (2014)



Peng Bai
MIT → WUSTL



$$\lambda \approx \lambda_o = \frac{e^2}{8\pi\varepsilon_0 k_B T}\left(\frac{1}{a_0} - \frac{1}{2d}\right)\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s}\right)$$

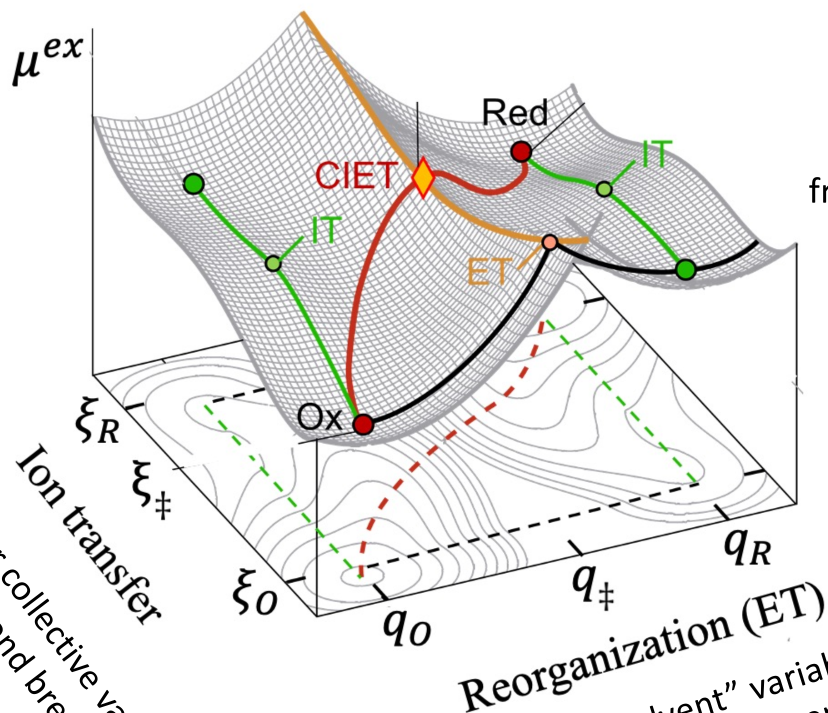
Marcus outer-sphere reorganization energy
for $Fe^{3+} + e^- \rightarrow Fe^{2+}$ in the solid LFP crystal

$$k^{MHC}_{ox/red}(\eta) = A \int_{-\infty}^{\infty} \exp\left(-\frac{(x - \lambda \pm e\eta)^2}{4\lambda k_B T}\right) \frac{dx}{1 + \exp(x/k_B T)}$$

Marcus-Hush-Chidsey (MHC) kinetics for ET at a metal electrode

A general framework for Faradaic reaction kinetics:
“Coupled Ion-Electron Transfer” (CIET)

Dimitrios Fraggedakis et al., *Electrochimica Acta* (2021)



Diabatic Red/Ox free energy surfaces

Gurney-Butler collective variable for classical “bond breaking”

Marcus “solvent” variable setting red/ox electron energies

Dimitrios Fraggedakis
MIT → Princeton

$$\mu_1^{ex}(q,\xi) = \mu_1^{ex}(q_O,\xi_O) + f_1(q,\xi) + \frac{k_O}{2}(q-q_O)^2$$

$$\mu_2^{ex}(q,\xi) = \mu_2^{ex}(q_R,\xi_R) + f_2(q,\xi) + \frac{k_R}{2}(q-q_R)^2$$

IT ET

Unified theory of
Coupled Ion-Electron Transfer (CIET)

MZB, *Faraday Discussions* 246, 60-124 (2023).

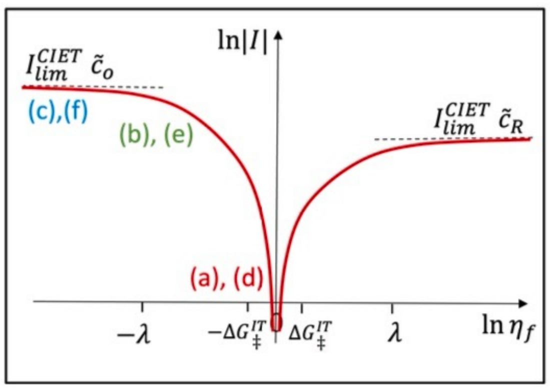
Marcus kinetics for ET-limited Faradaic Reactions (ECIT)

MZB, *Faraday Discussions* 246, 60-124 (2023).

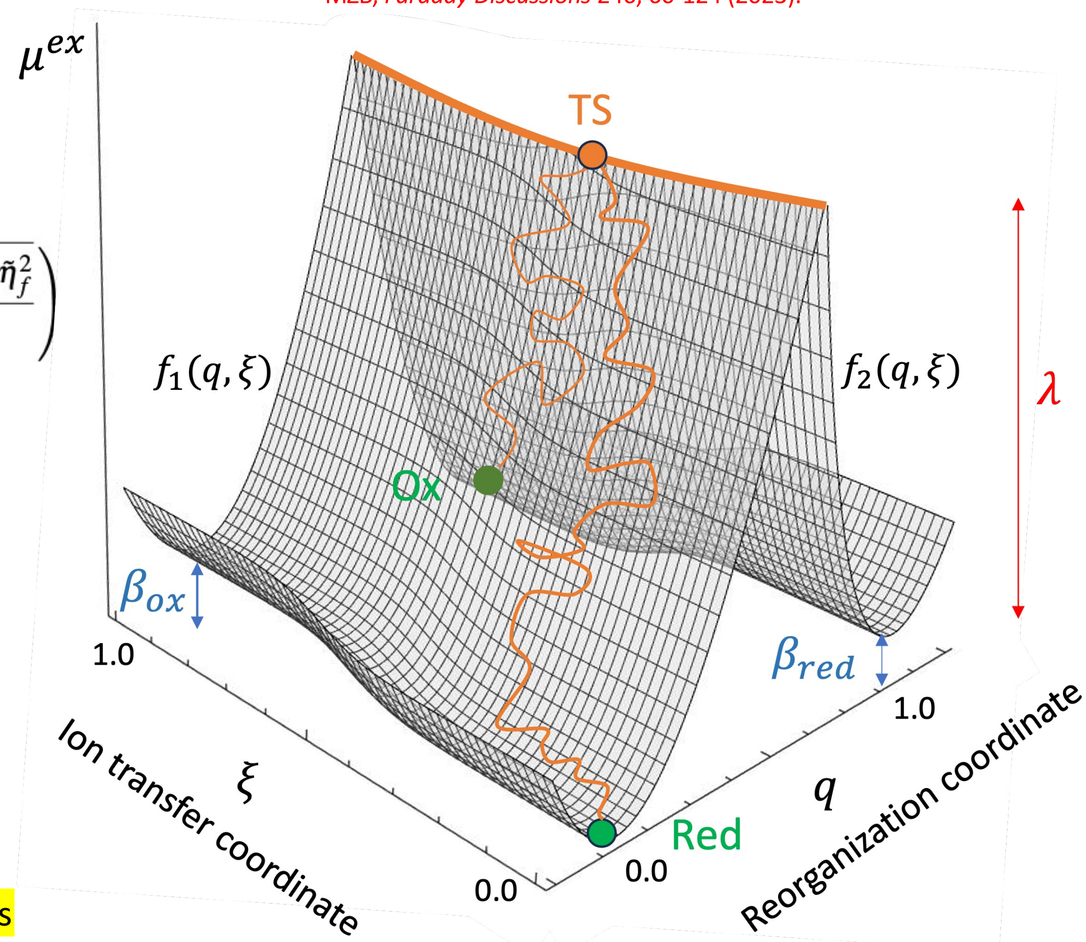
$\lambda \gg \beta_{red}, \beta_{ox}, |e\eta_f|, \Delta_e, k_B T$

$$I_{ECIT} = \frac{e\Delta_e}{h}\frac{A}{A_s}\frac{e^{-\Delta\tilde{G}_{\ddagger}^{IT}}}{\gamma_{\ddagger}^{IT}} \times \left(\frac{\tilde{c}_+}{1+e^{\tilde{\eta}_f}} - \frac{\tilde{c}}{1+e^{-\tilde{\eta}_f}}\right) \operatorname{erfc}\left(\frac{\tilde{\lambda} - \sqrt{1+\sqrt{\tilde{\lambda}}+\tilde{\eta}_f^2}}{2\sqrt{\tilde{\lambda}}}\right)$$

$$\Delta G_{\ddagger}^{IT} = \frac{1}{2}\min_{\xi}\{f_1(q_O,\xi)+f_2(q_R,\xi)\} - \Delta_e$$



Curved Tafel plots with reaction-limited currents



Butler-Volmer kinetics for IT-limited Faradaic reactions (ICET)

MZB, *Faraday Discussions* 246, 60-124 (2023).

$\beta_{red}, \beta_{ox} \gg \lambda, |e\eta_f|, \Delta_e, k_BT$

$I = I_0^{ICET}\left(e^{-\alpha\, e\eta/k_BT} - e^{(1-\alpha)\, e\eta/k_BT}\right)$

Gurney-Butler symmetry factor

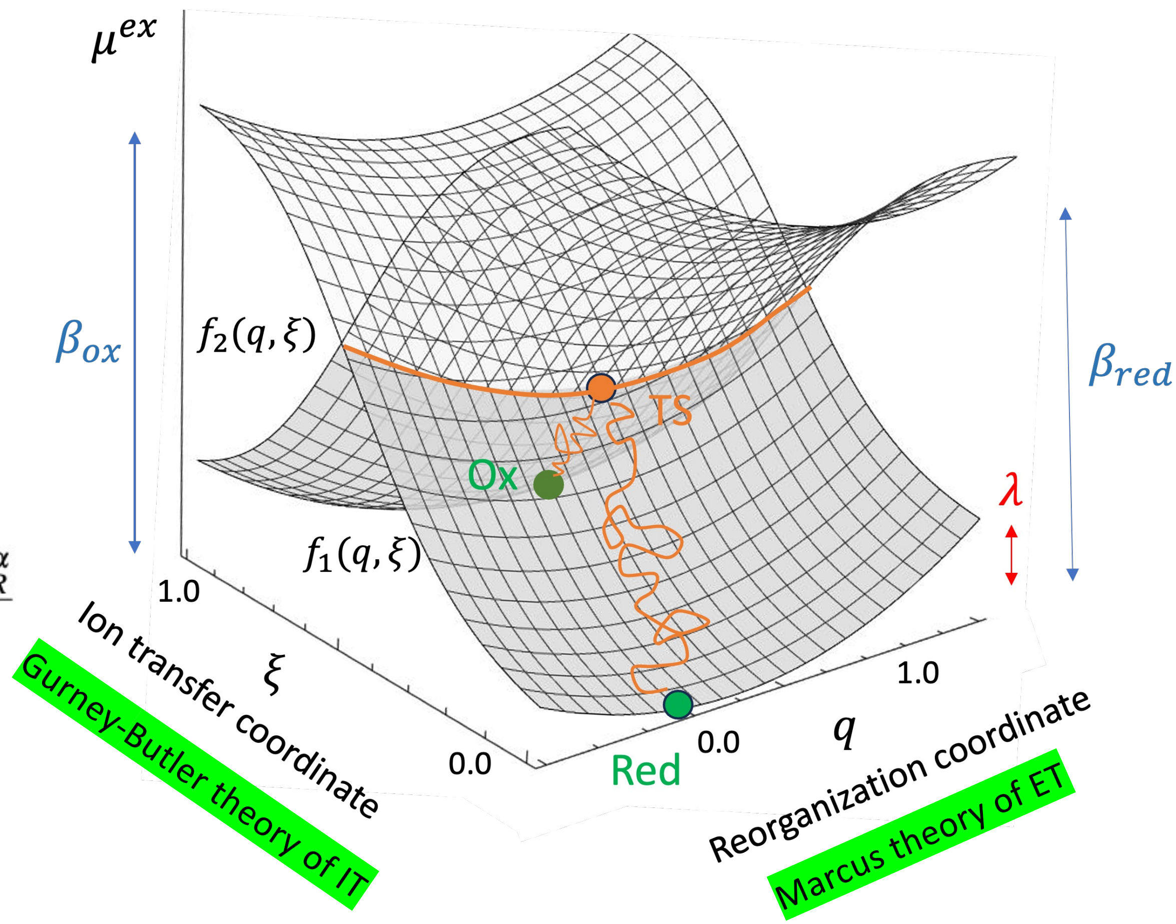
$$\alpha = \frac{\beta_{red}}{\beta_{red}+\beta_{ox}}$$

New quantum formula for the exchange current

$$I_0^{ICET} = \frac{e\Delta_e}{h}\frac{A}{A_s}\left(\frac{M(0)}{\sqrt{\pi\alpha(1-\alpha)\tilde{\lambda}}}\right) e^{-\Delta\tilde{G}_{\ddagger}^{ICET}} \frac{\tilde{c}_O^{1-\alpha}\tilde{c}_R^{\alpha}}{\gamma_{\ddagger}^{IT}}$$

ICET activation energy

$$\Delta G_{\ddagger}^{ICET} = \alpha(1-\alpha)(\beta_{red}+\beta_{ox}+\lambda)-\Delta_e$$



Butler-Volmer kinetics for IT-limited Faradaic reactions (ICET)

MZB, *Faraday Discussions* 246, 60-124 (2023).

$\beta_{red}, \beta_{ox} \gg \lambda, |e\eta_f|, \Delta_e, k_B T$

$I = I_0^{ICET}\left(e^{-\alpha\, e\eta/k_B T} - e^{(1-\alpha)\, e\eta/k_B T}\right)$

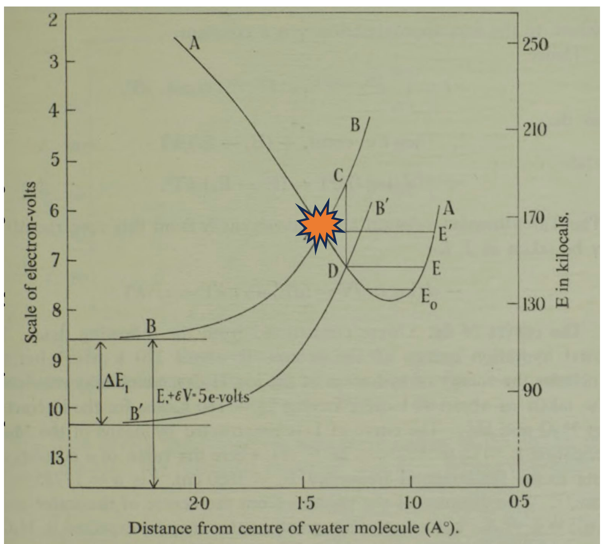
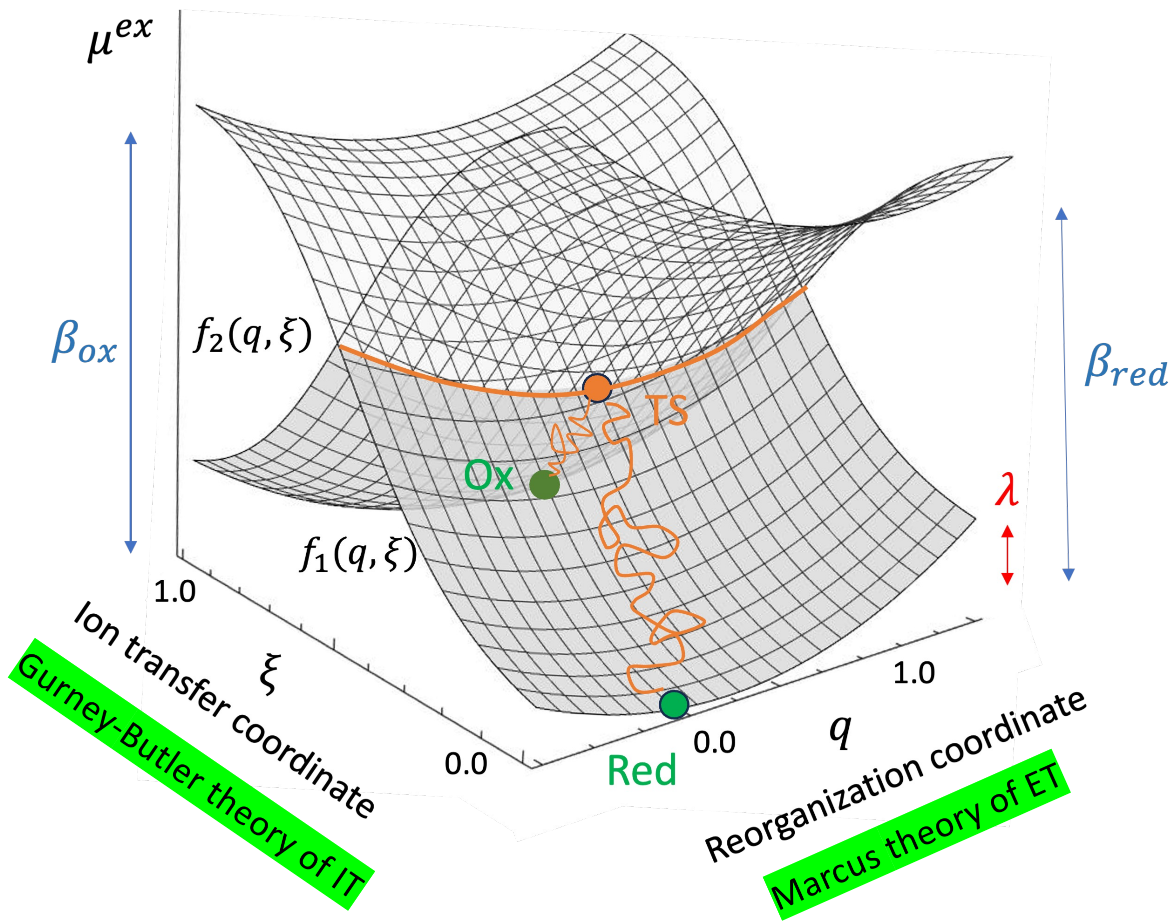


FIG. 1—Discharge of proton in H₃O⁺. AA, curve of $\mathcal{J}$ − L; BB, curve of E₁ + εV + R.

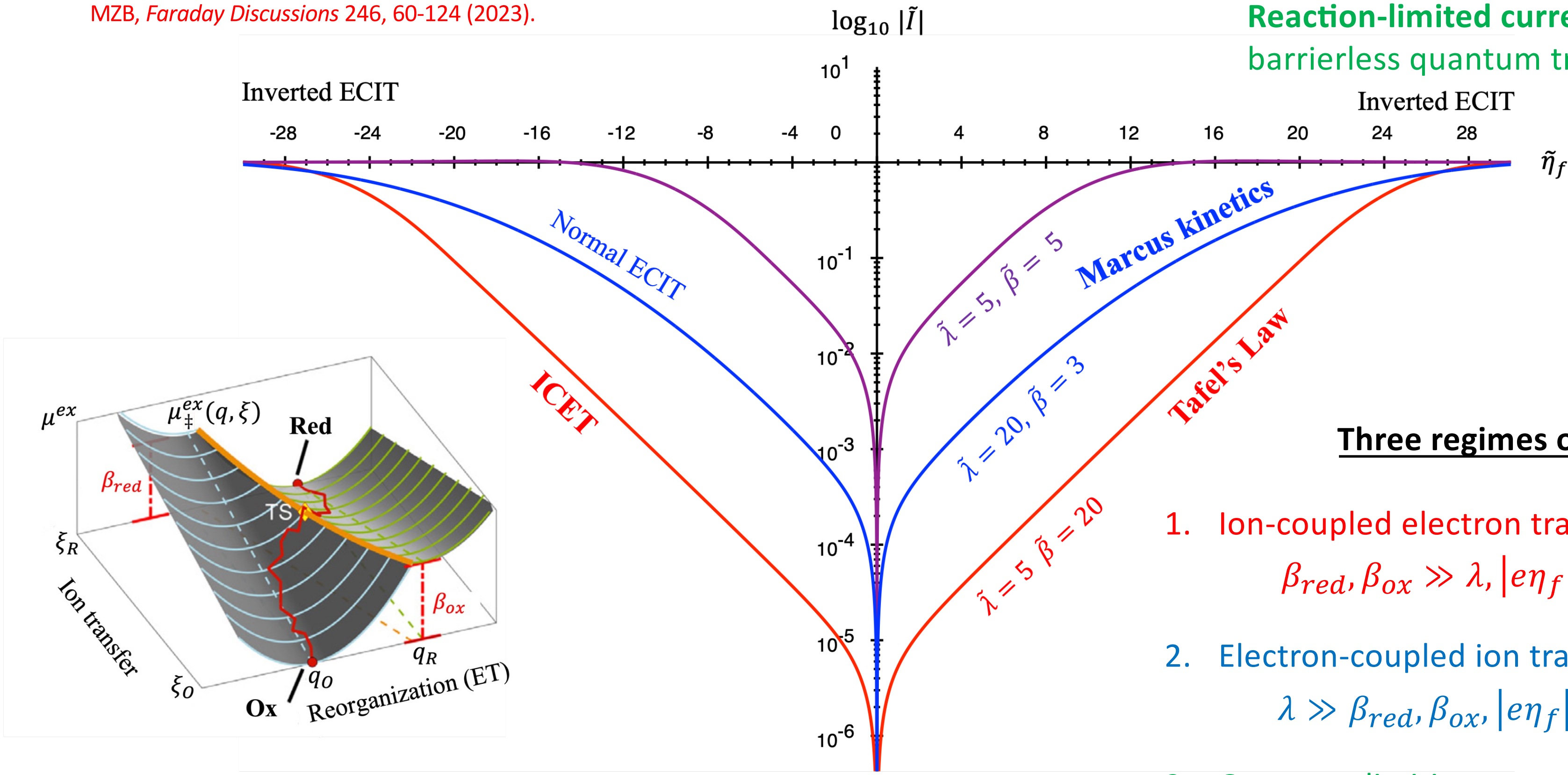
J. A. V. Butler, Proc. Roy. Soc. A (1936)



Unified theory of Faradaic current by non-adiabatic CIET

MZB, *Faraday Discussions* 246, 60-124 (2023).

Reaction-limited current from barrierless quantum transitions

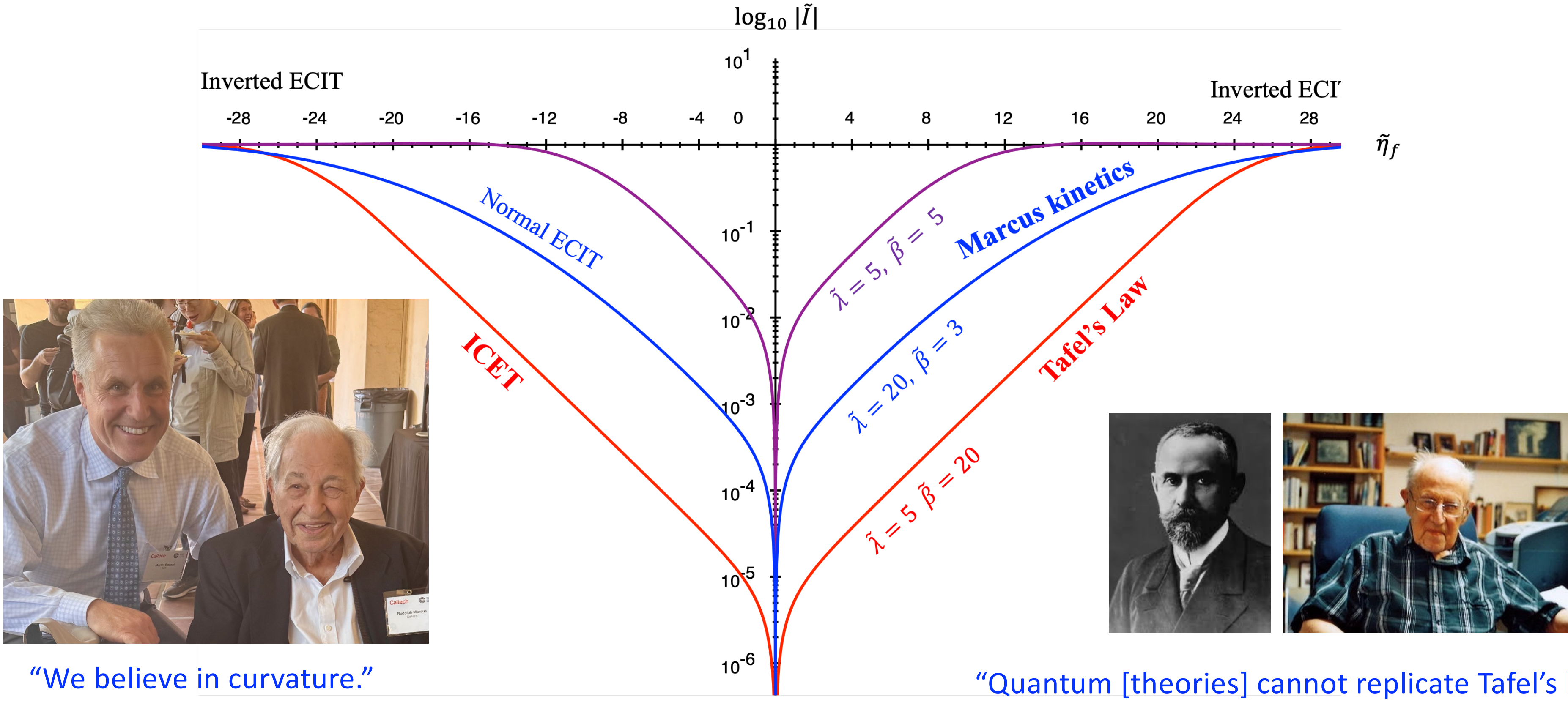


Truncated linear (IT) & harmonic (ET) diabatic free energy landscapes → simple, uniformly valid formula.

Three regimes of CIET:

1. Ion-coupled electron transfer (ICET)
   $\beta_{red}, \beta_{ox} \gg \lambda, |e\eta_f|, \Delta_e, k_B T$
2. Electron-coupled ion transfer (ECIT)
   $\lambda \gg \beta_{red}, \beta_{ox}, |e\eta_f|, \Delta_e, k_B T$
3. Quantum limiting current (Inverted ECIT)
   $|e\eta_f| \gg \beta_{red}, \beta_{ox}, \lambda, \Delta_e, k_B T$

Unified theory of Faradaic current by non-adiabatic CIET

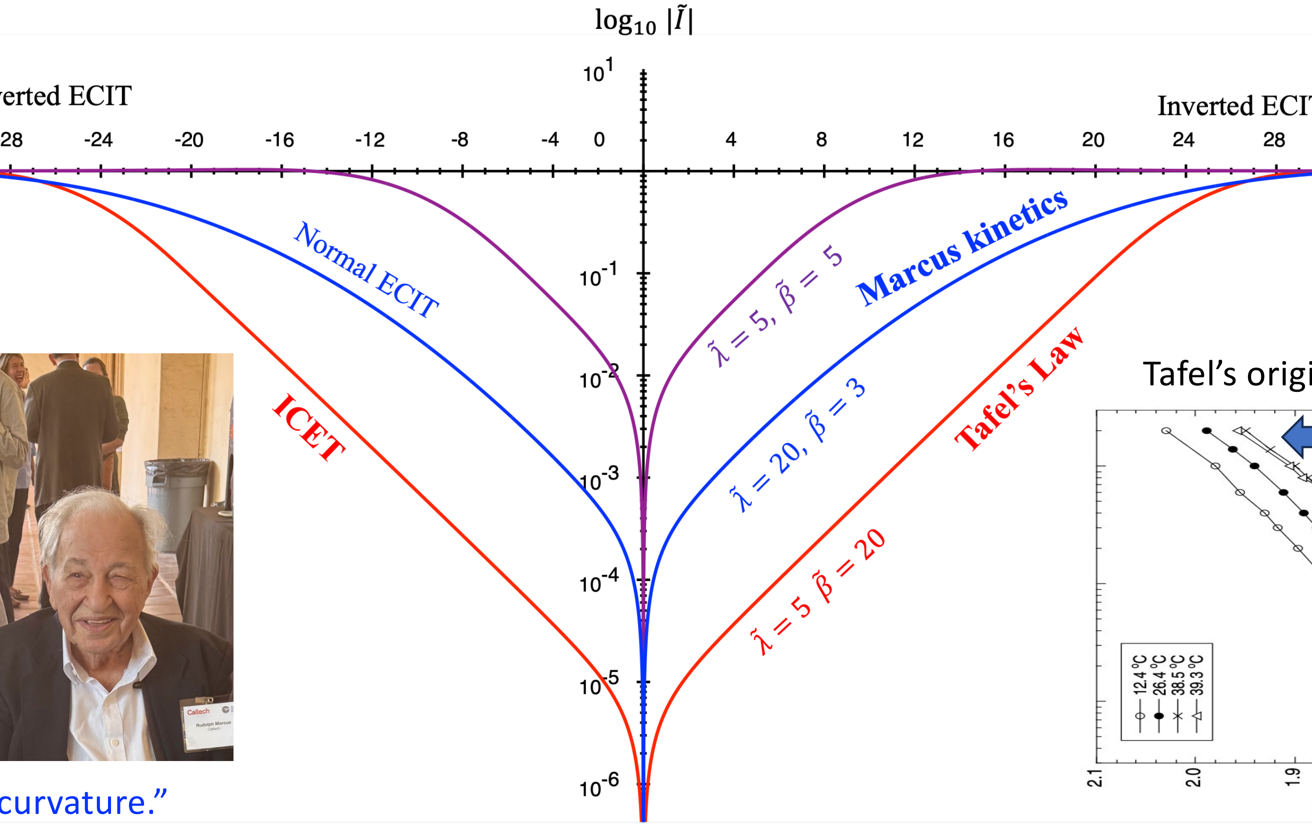


"We believe in curvature."
- Rudy Marcus
on his 102nd birthday (7/22/2025)

"Quantum [theories] cannot replicate Tafel's law, one of the most verified laws of nature."
- J. O'M. Bockris

MZB, *Faraday Discussions* 246, 60-124 (2023).

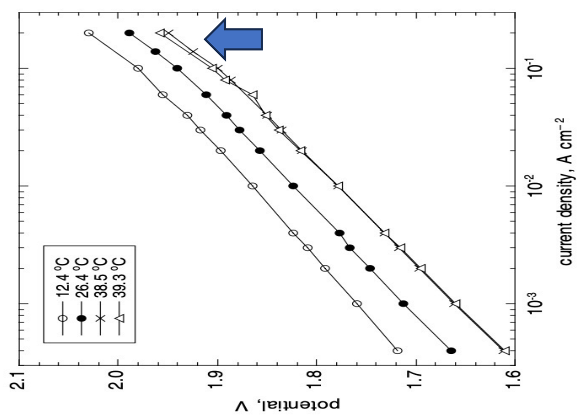
Unified theory of Faradaic current by non-adiabatic CIET



"We believe in curvature."
- Rudy Marcus
on his 102^{nd} birthday (7/22/2025)

MZB, *Faraday Discussions* 246, 60-124 (2023).

Tafel's original data for HER



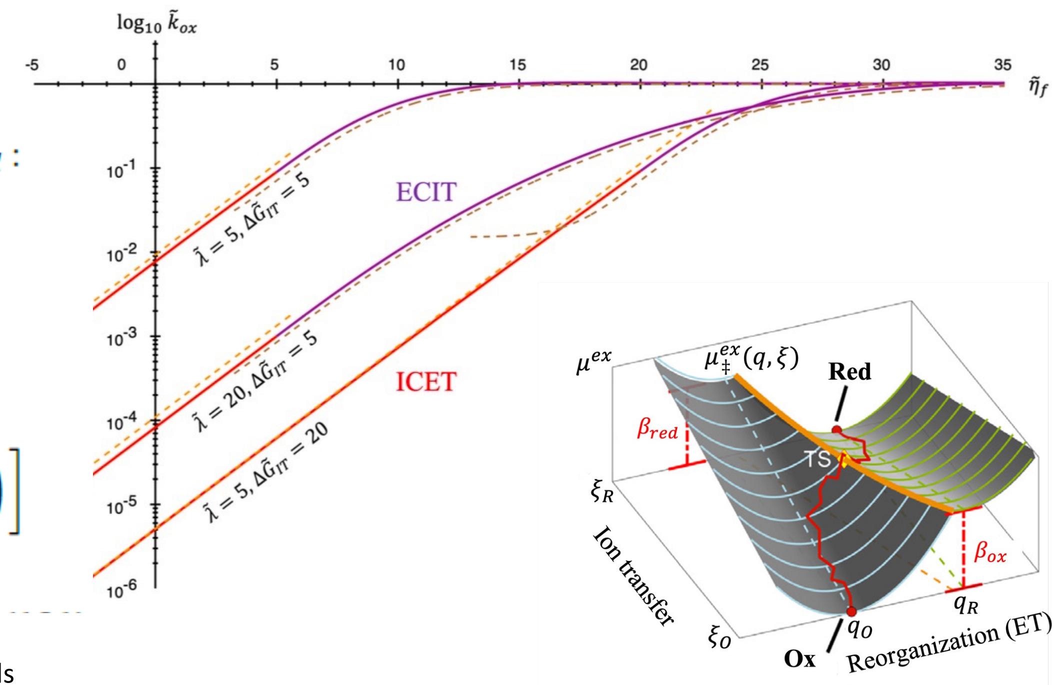
J. Tafel, *Zeit. Physik. Chem.* (1905).

Burstein, Corrosion Science (2005).

Uniformly valid approximation

MZB, *Faraday Discussions* 246, 60-124 (2023).

$$\frac{k_{ox}^{uni}}{k_0 M(\tilde{\eta}_f)} = \begin{cases} \text{Butler-Volmer ICET kinetics for } \tilde{\eta}_f < \tilde{\beta}_{red}: \\ \dfrac{e^{-(1-\alpha)(\alpha\tilde{\lambda}+\tilde{\beta}_{red})}}{\sqrt{4\alpha(1-\alpha)\pi\tilde{\lambda}}} e^{(1-\alpha)\tilde{\eta}_f} \\ \text{Marcus ECIT kinetics for } \tilde{\eta}_f > \tilde{\beta}_{red}: \\ \dfrac{1}{2}\left[\mathrm{erf}\left(\sqrt{\alpha(1-\alpha)\tilde{\lambda}}\right) - \mathrm{erf}\left(\dfrac{2\alpha\tilde{\lambda}+\tilde{\beta}_{red}-\tilde{\eta}_f}{2\sqrt{\alpha\tilde{\lambda}/(1-\alpha)}}\right)\right] \\ \quad + \dfrac{e^{-\alpha(1-\alpha)\tilde{\lambda}}}{\sqrt{4\alpha(1-\alpha)\pi\tilde{\lambda}}} \end{cases}$$



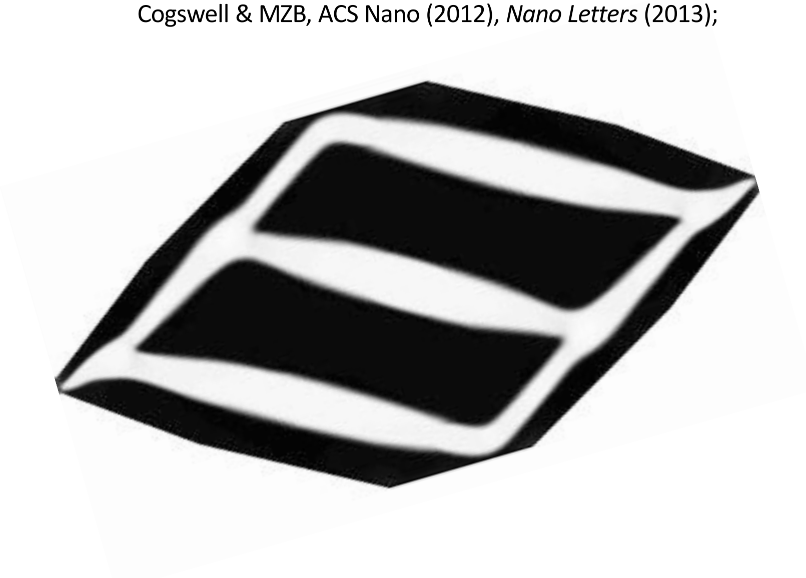
Derived by asymptotic matching of limits of high and low overpotentials

CIET in Li-ion Batteries

Challenge: Battery reaction kinetics are masked by heterogeneity

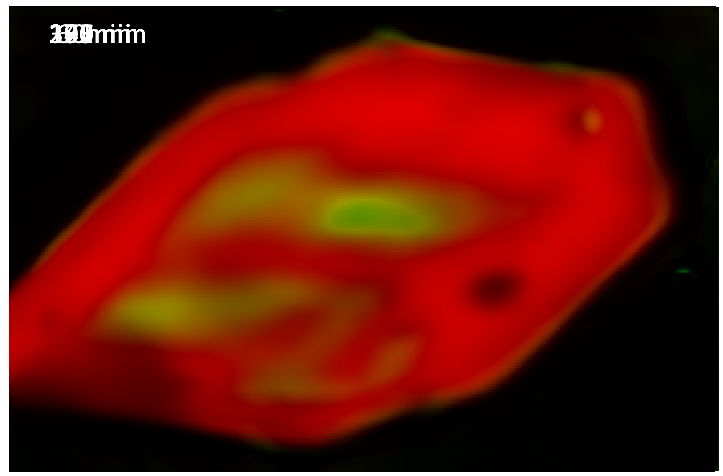
Simulations @ MIT (2006-2013)

MZB, *Accounts of Chemical Research* (2013)
Bai, Cogswell, MZB, *Nano Letters* (2011)
Cogswell & MZB, ACS Nano (2012), *Nano Letters* (2013);



Experiments @ Stanford (2011-2016)

William Chueh et al, Nano Letters (2013)
Jongwoo Lim, Yiyang Li,…MZB, William Chueh, *Science* (2016).
Scanning transmission x-ray microscopy (STXM) of LiFePO4 platelets



Jongwoo Lim
Stanford → Seoul National Univ.

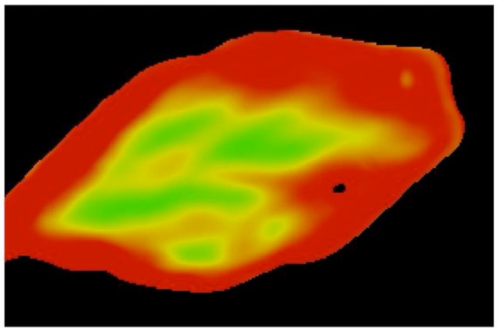
GCEP Sabbatical Chair @ Stanford (2015-2016)→
D3BATT Center for Data-Driven Design of Batteries (Toyota Research Institute, 2017-2025)

Can we learn the reaction kinetics directly from images?

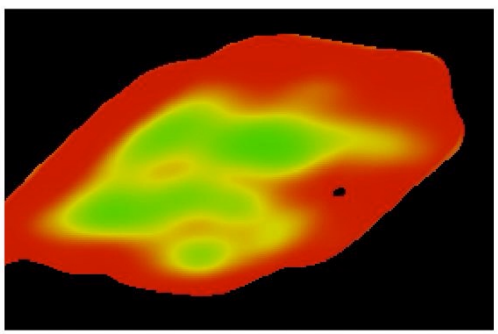
Image Inversion Reveals Physics + Surface Heterogeneity !

Hongbo Zhao et al, Learning heterogeneous reaction kinetics from X-ray movies pixel-by-pixel, *Nature* (2023)

Experiment



Simulation

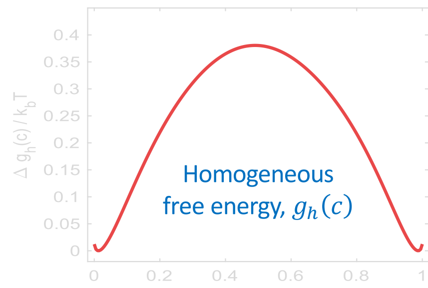


Only 7 images per cycle!

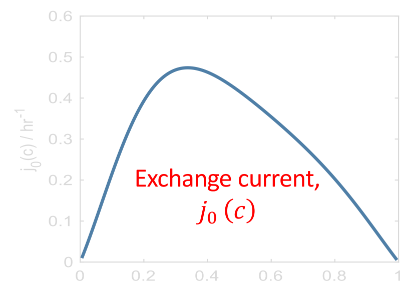
$$\frac{\partial c}{\partial t} = f(x)\, j_0(c) \sinh\left(\mu_{ox} - \frac{\partial}{\partial c} g_h(c) + \kappa \nabla^2 c + \boldsymbol{\sigma}: (\epsilon^0 c - \boldsymbol{u})\right)$$

$$\nabla \cdot \sigma = 0, \qquad \sigma_{ij} = \lambda_{ijkl}(u_{kl} - \epsilon^0_{kl} c)$$

(Chemo-mechanics from DFT simulations, not fitted.)

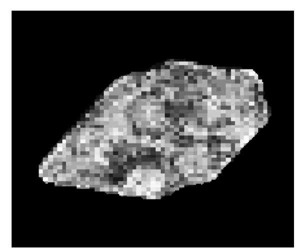


Thermodynamics

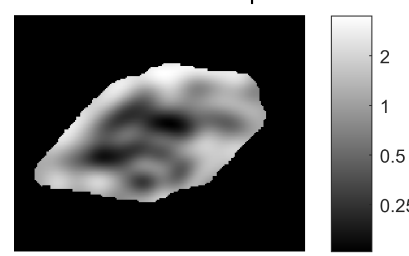


Reaction Kinetics

Carbon coating thickness



Rate constant map



Surface Heterogeneity

Learning heterogeneous reaction kinetics from X-ray videos pixel by pixel

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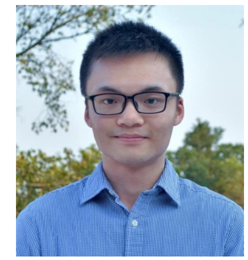
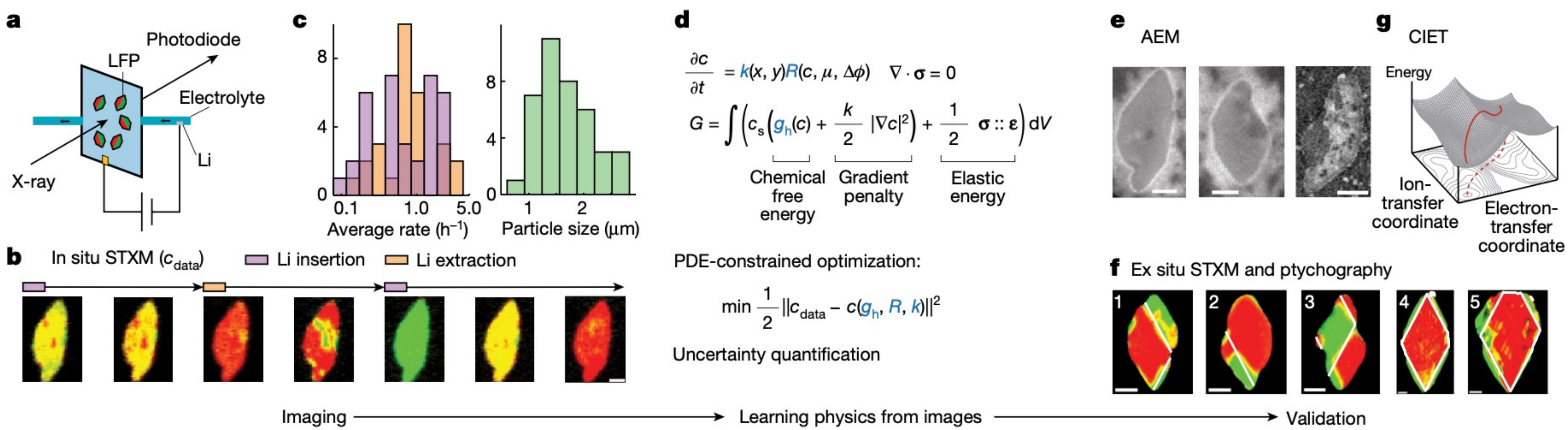
Hongbo Zhao[1], Haitao Dean Deng[2], Alexander E. Cohen[1], Jongwoo Lim[2], Yiyang Li[2], Dimitrios Fraggedakis[1], Benben Jiang[1], Brian D. Storey[3], William C. Chueh[2,4], Richard D. Braatz[1] & Martin Z. Bazant[1,5]✉

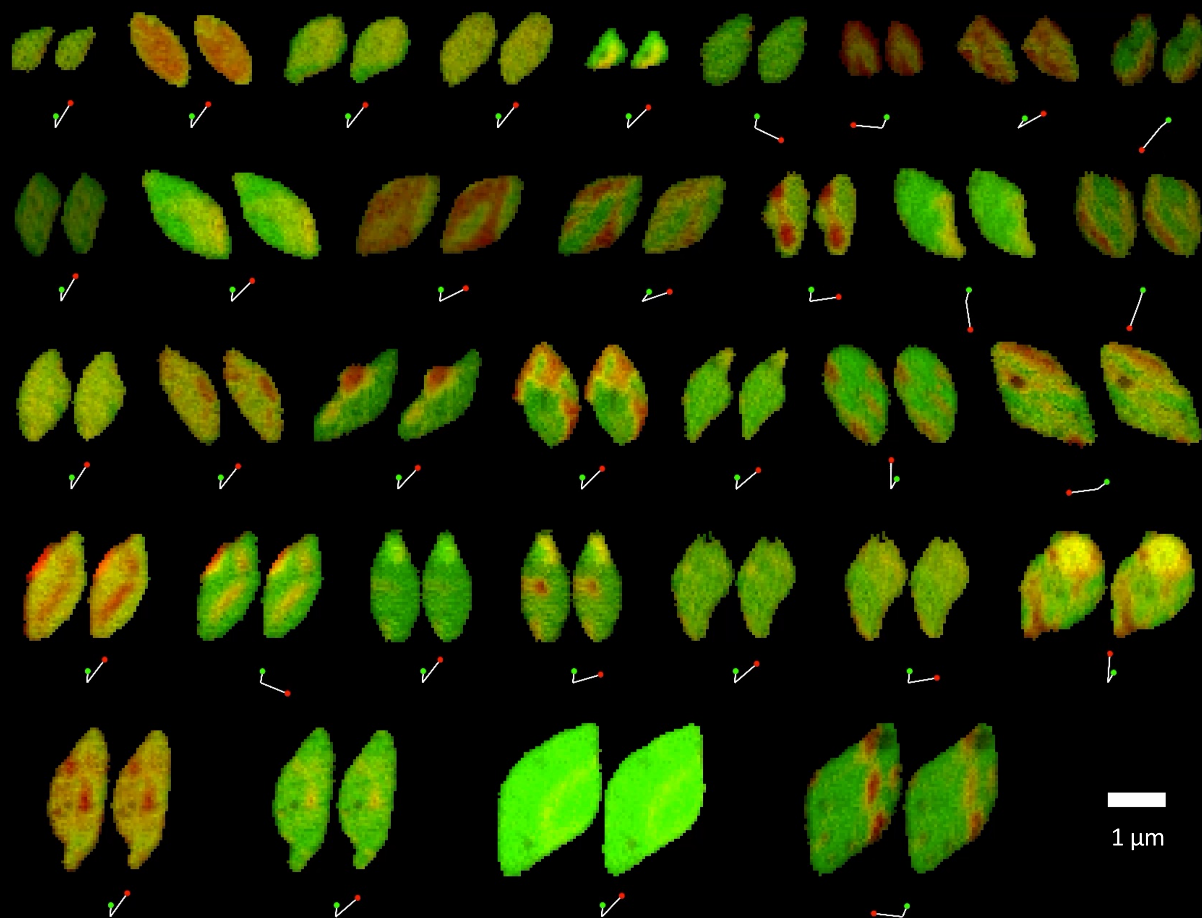
Nature | Vol 621 | 14 September 2023 | 289

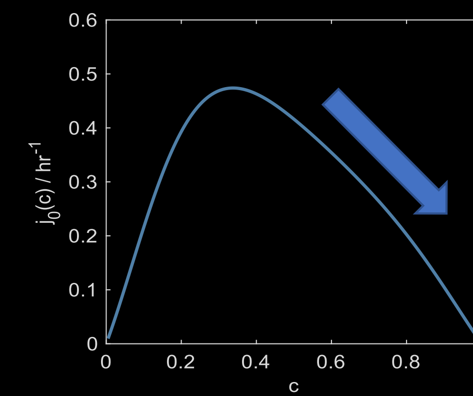


Hongbo Zhao
MIT → UCSD

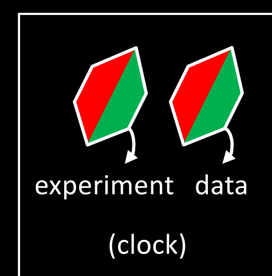


STXM images vs. the trained model (180,000 pixels, 63 particles)





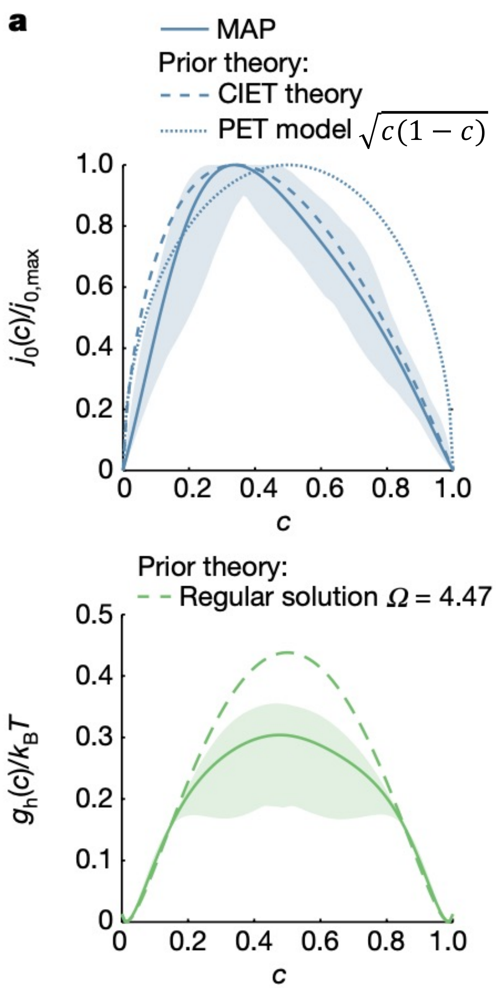
Auto-inhibitory Li insertion:
Stable at high rates



Experiment: Jongwoo Lim, Yiyang Li,…MZ Bazant, WC Chueh, *Science* (2016).

Image inversion: Hongbo Zhao, … Bazant, Braatz, Chueh, *Nature* (2023)

Learning reaction kinetics and nonequilibrium thermodynamics from x-ray images



H. Zhao, H. D. Deng…, R. D. Braatz, W. C. Chueh & MZB, *Nature* (2023).

$$i_0 \simeq \frac{i_r^*}{2}\frac{\tilde{c}_+ c(1-c)}{\tilde{c}_+ + c}\operatorname{erfc}\left(\frac{1}{2} - \frac{1}{2\lambda/k_BT}\sqrt{1+\sqrt{\lambda/k_BT}+(\ln c)^2}\right)$$

Prior theory

- Coupled ion-electron transfer (ECIT)
- Metallic electron donor, ion intercalation in a lattice
- λ fitted to *curved* Tafel plots

Fraggedakis…& Bazant, *Elec. Acta* (2021)
Bazant, *Faraday Discussions* (2023)

$$\Delta g_h(c) = k_BT\,(c\ln c + (1-c)\ln(1-c)) + \Omega\, c(1-c)$$

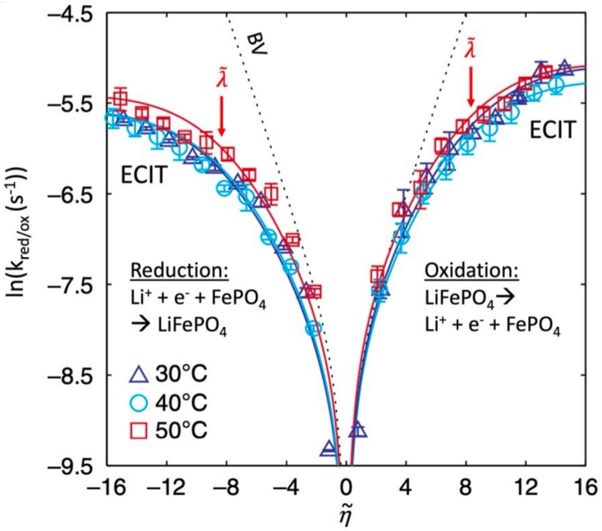
Prior theory

- Regular solution model $\Delta g_h(c)$
- *Ab initio* elastic constants + Vegard's law
- Ω, κ fitted to miscibility gap + elastic stripe spacing

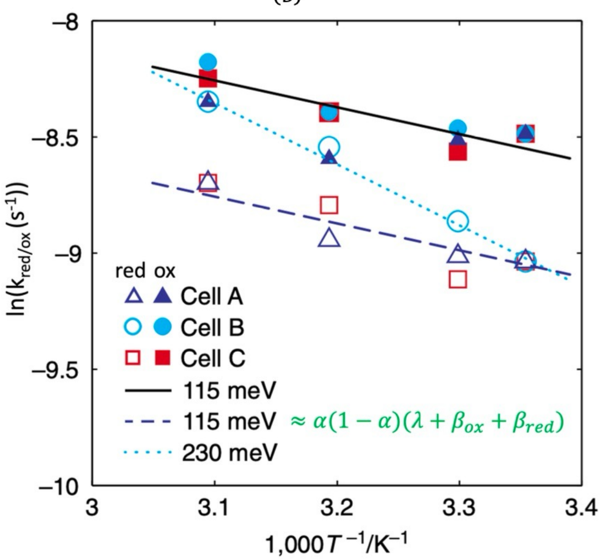
Cogswell & Bazant, *ACS Nano* (2012)

CIET in Lithium Iron Phosphate

(a)



(b)



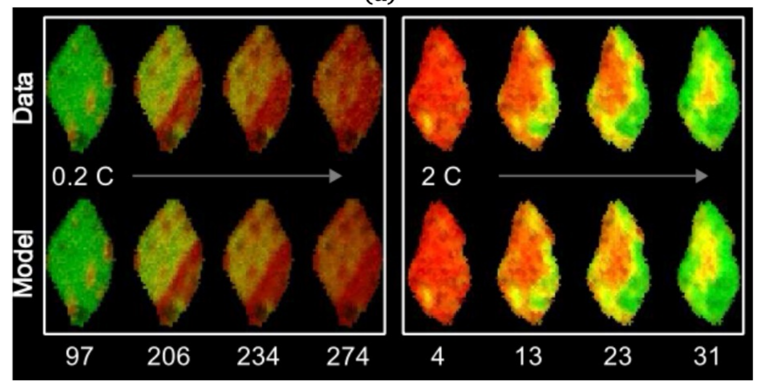
← Overpotential and temperature dependence consistent with ECIT:

$\lambda = 214 \pm 1$ meV [Bai (2014)]

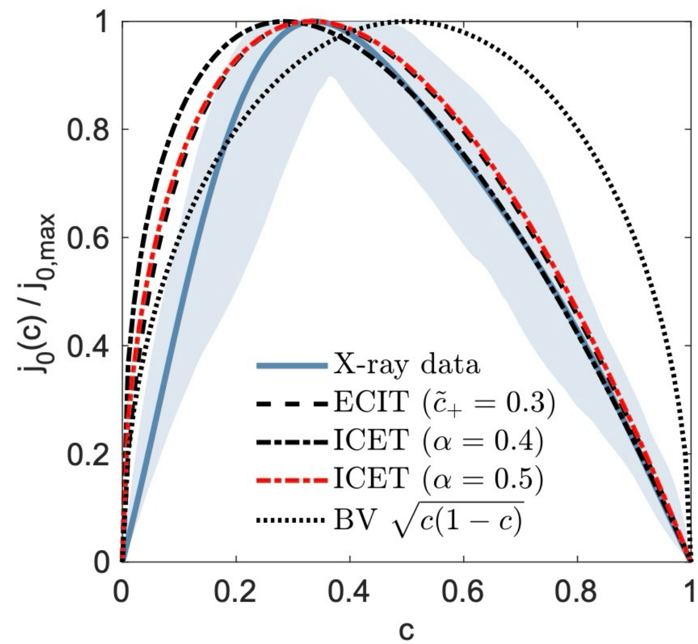
$\beta_{red} \approx \beta_{ox} \approx 120$ meV

Both regimes of CIET predict exchange current versus intercalated Li concentration learned of x-ray images →

(a)

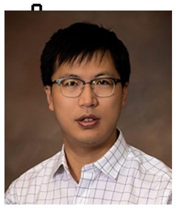


(b)



Li-ion battery data collapse with CIET theory

Yirui Zhang
MIT → Rice



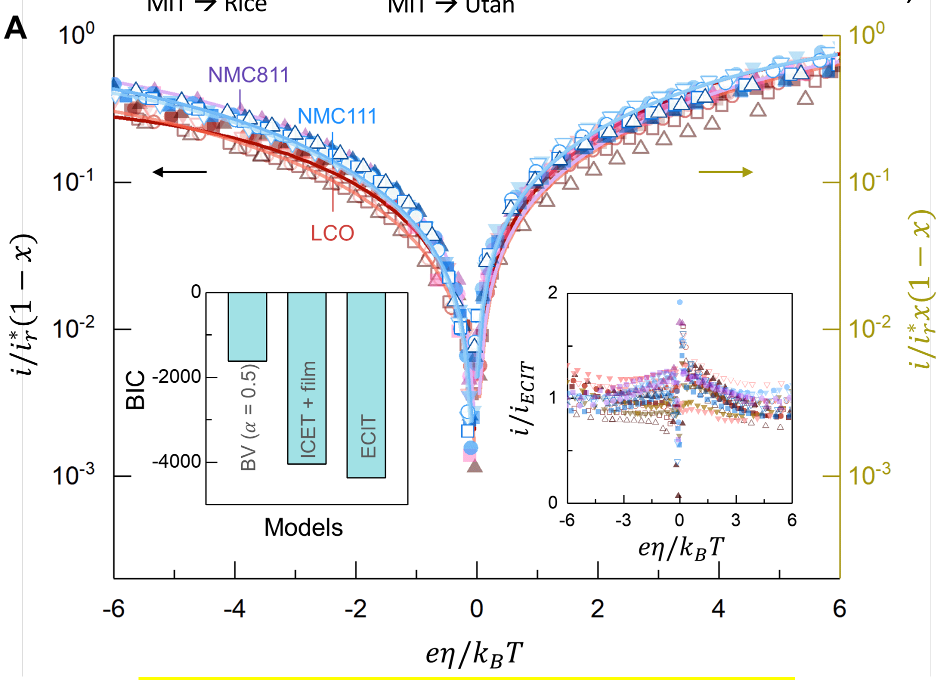
Tao Gao
MIT → Utah

"Lithium intercalation by coupled ion-electron transfer"
Zhang, Fraggedakis, Gao, Pathak… Bazant & Shao-Horn,
Science (2025)

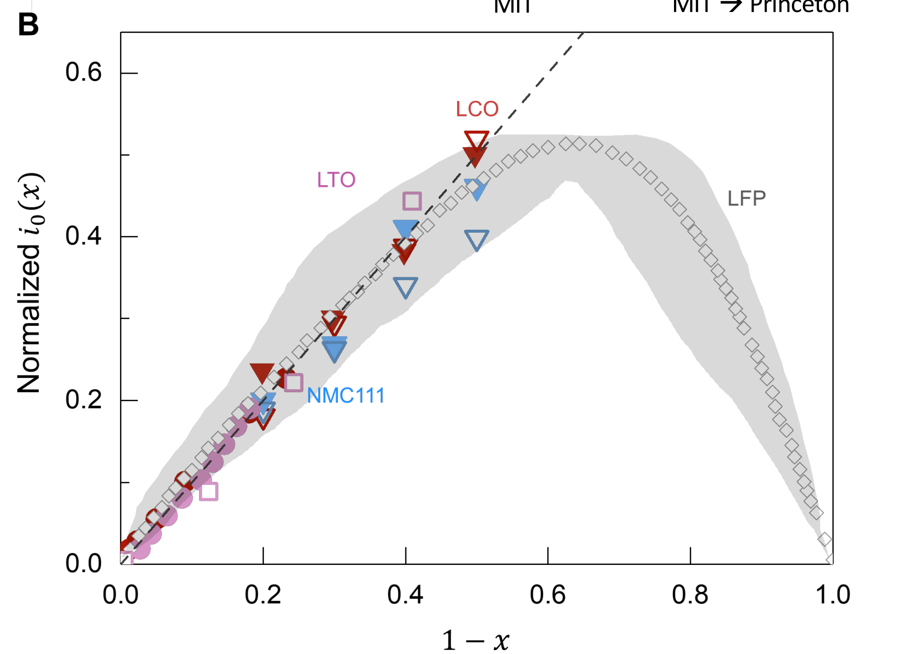
Shakul Pathak
MIT

Dimitrios Fraggedakis
MIT → Princeton

50+ datasets, 8 materials, 2 electrolytes,



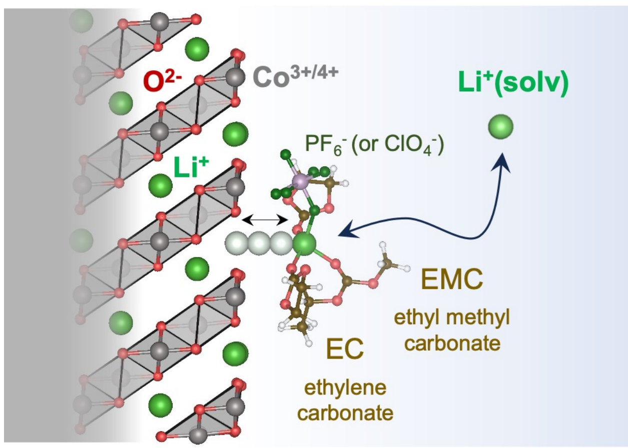
Universal ECIT Overpotential Dependence



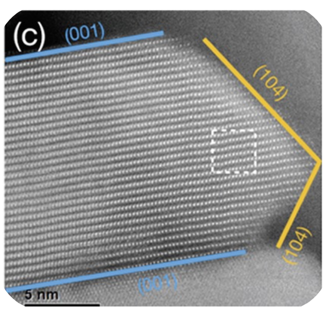
Universal Solid Vacancy Dependence

Quantum prediction of Li+ intercalation rates in LCO

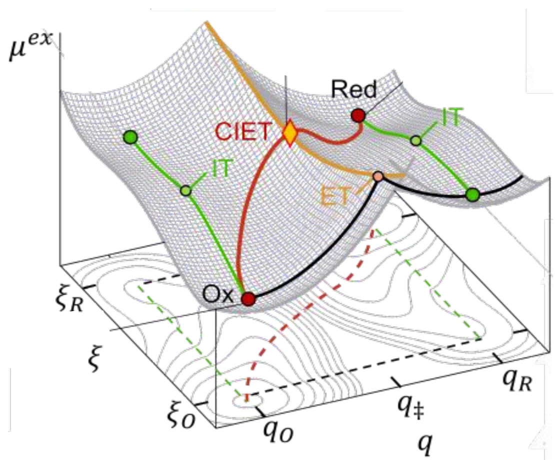
Cathode–electrolyte interface



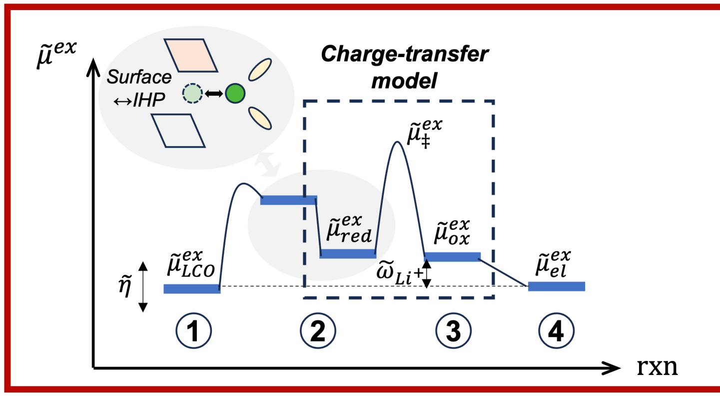
Cathode (Li_xCoO_2) **Electrolyte** (EC/EMC:Li{PF_6,ClO_4})

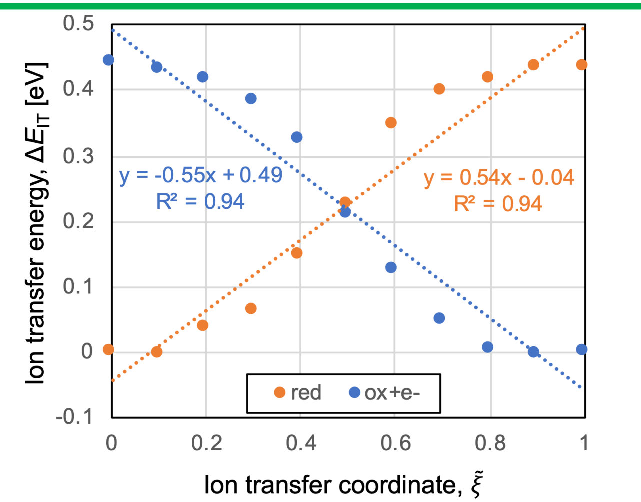


Coupled ion-electron transfer ▶



Ion transfer diabatic surfaces from constrained DFT ▶

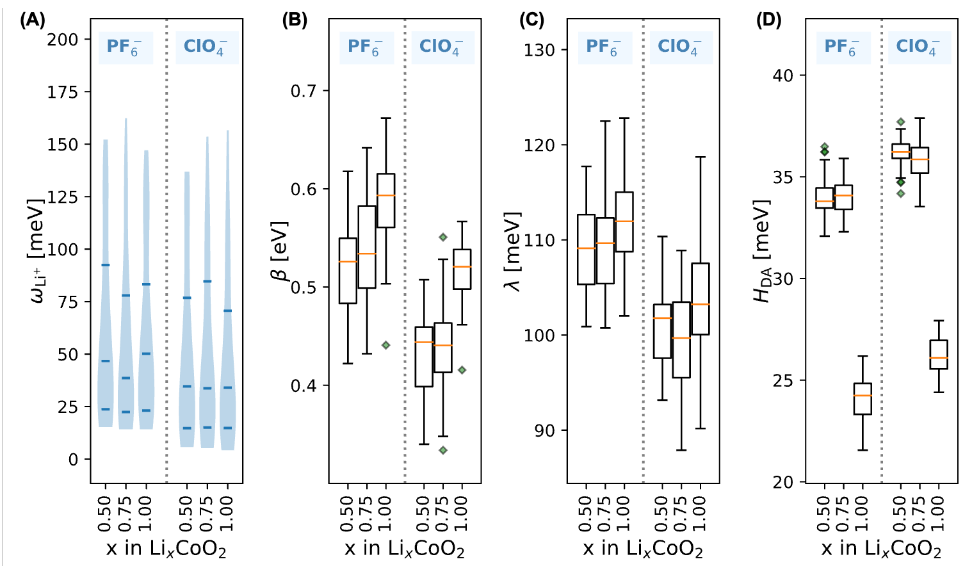




Joakim Stenlid, et al., ACS Energy Letters (2024)

Ab Initio prediction of Li+ intercalation rates in LCO

CIET parameters from quantum simulations for two different anions in 1M EC/EMC electrolyte

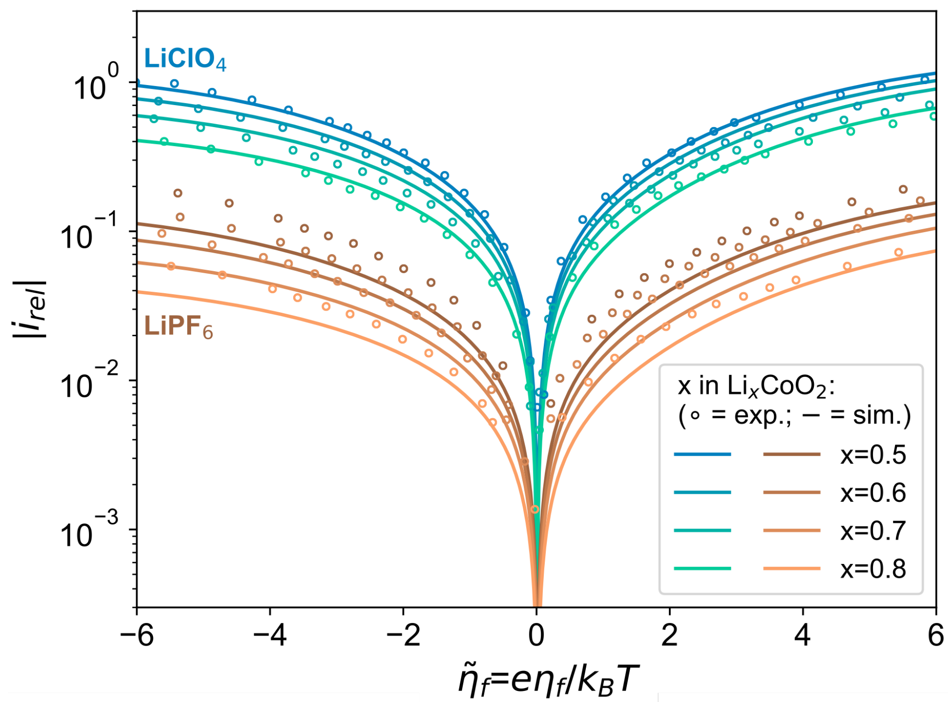


β neglects IT entropy at finite T…

λ closely matches experiment

Sum of currents from 3 Li+ surface adsorption states

$$i_{tot} = \frac{1}{Z}\sum_j i_j^{\mathrm{CIET}}(\mathbf{p}_j)\, exp\left(\frac{-\Delta\omega_{\mathrm{Li}^+,j}}{k_{\mathrm{B}}T}\right)$$



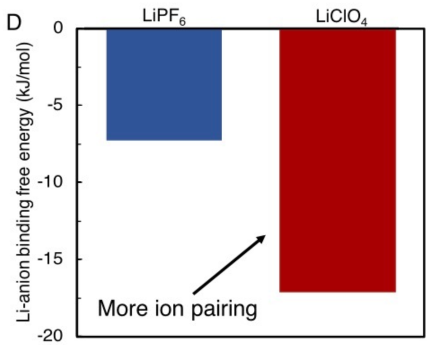
Joakim Stenlid, et al., ACS Energy Letters (2024)

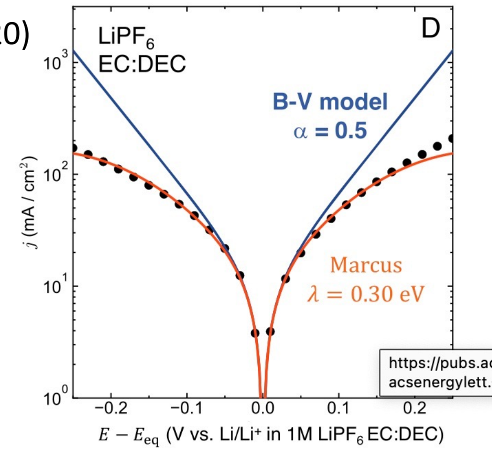
CIET kinetics of electrodeposition & electrocatalysis

Some Examples of CIET in Electrodeposition

ECIT in lithium metal electrodeposition:

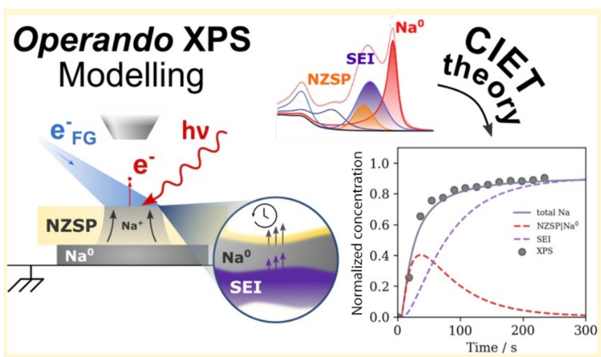
D. Boyle,… Yi Cui, ACS Energy Lett. (2020)





ECIT in sodium metal interphase growth in solid-state batteries:

N. Williams…, Skinner, Aguadero, Chem Mater. (2023).



ECIT in zinc metal electrodeposition:

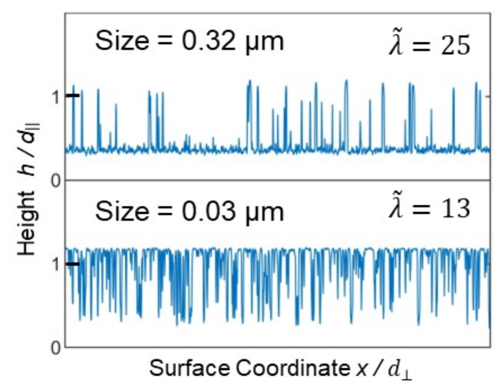
D. Cogswell, Phys Rev E. (2015)

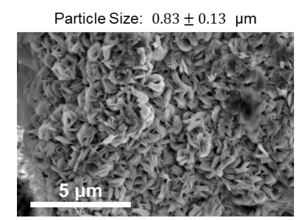
ICET in SEI growth on copper:

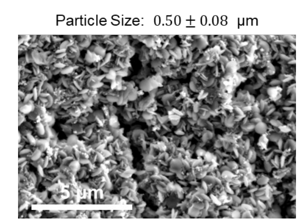
H. Thaman, M. Li, … MZB, Chueh, Nano Letters (2025).

ECIT in lithium peroxide electrodeposition:

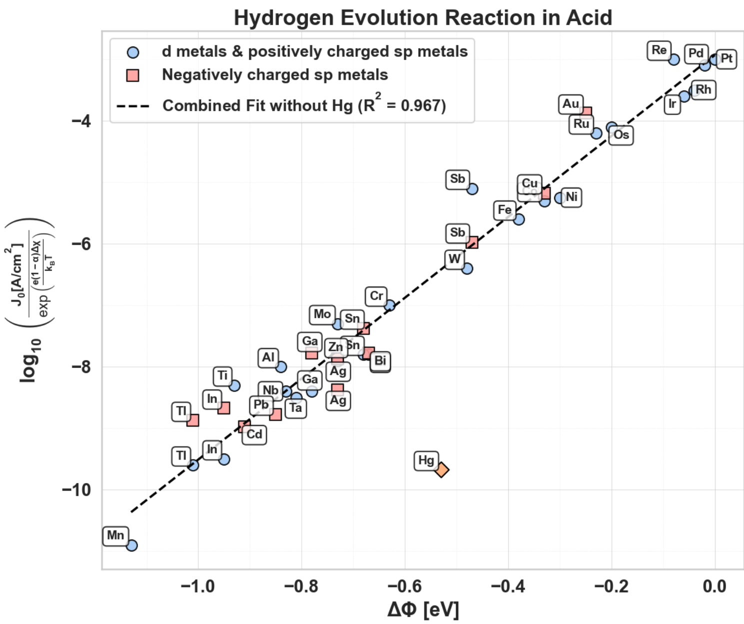
P. Zhang, S. Pathak, MZB and P. Bai, ACS Appl. Mater. Interfaces (2025)



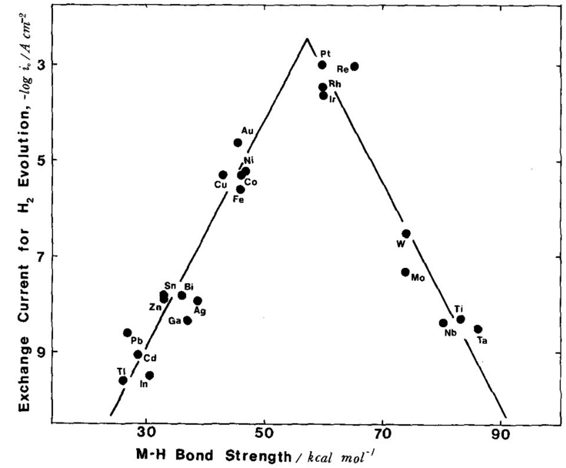




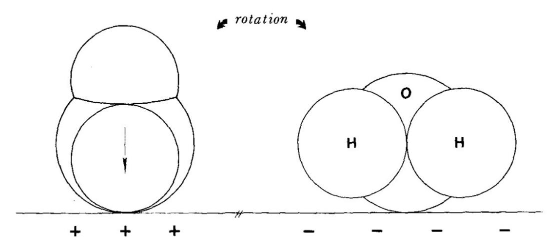
CIET in Electrocatalysis: Metal Dependence of HER



Junghyun Yoon
SNU→MIT



- Bockris (1947), Trasatti (1972):
  ← linear trend of ln(current) vs. metal work function
  → Or "volcano plot" vs. H adsorption energy
- Buckley & Leddy, JECS (2024): modified BV derivation
- J. Yoon & MZB (2025): CIET theory



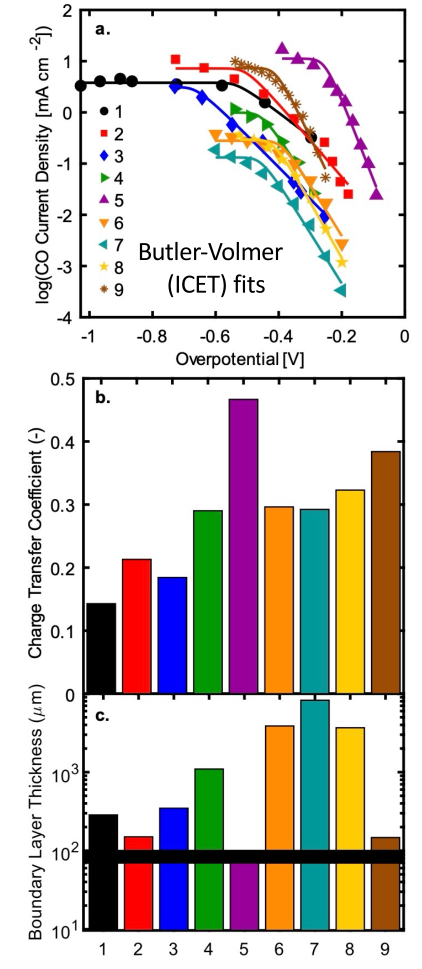
d & (+) sp metals
$\alpha = 0.608, \chi = 0.4\ V$

(-) sp metals
$\alpha = 0.611, \chi = 0\ V$

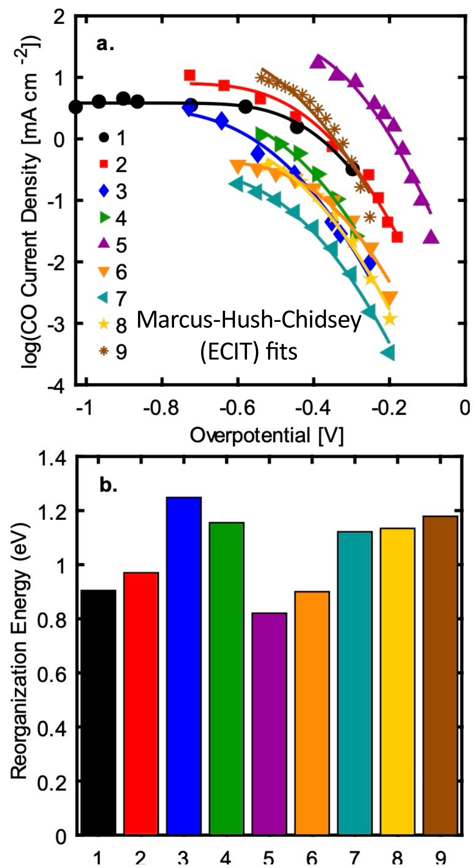
$$I_{0,HER} = \frac{eH_{DA}^2 \rho_e}{h} \frac{A}{A_s} \frac{e^{-\Delta \tilde{G}_\ddagger^{ICET}}}{\sin(\pi\alpha)\sqrt{\pi\tilde{\lambda}}} \frac{\tilde{c}_{H^+}^{1-\alpha}\,\tilde{c}_{H^\cdot}^{\alpha}}{\gamma_\ddagger^{IT}} \exp\left(\frac{-(1-\alpha)(\Delta\varepsilon_F - e\Delta\chi)}{k_B T}\right)$$

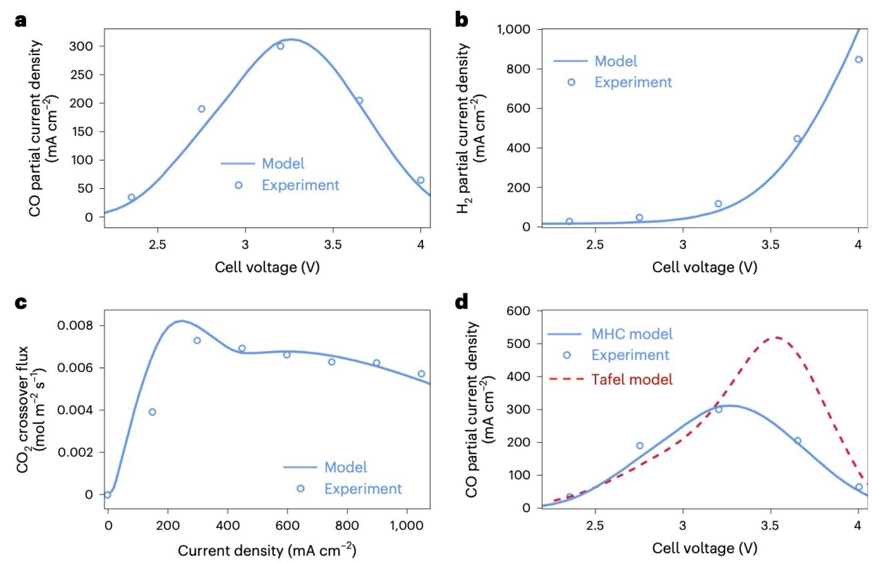
$$\log I_{0,HER} \propto \left(\frac{(1-\alpha)(\Delta\Phi + e\Delta\chi)}{k_B T}\right)$$

Marcus kinetics (ECIT) for CO_2RR



S. Brown, M. Orella… Y. Román-Leshkov, Y. Surendranath, MZB, F. Brushett, *ChemRxiv* (2020) [rejected]



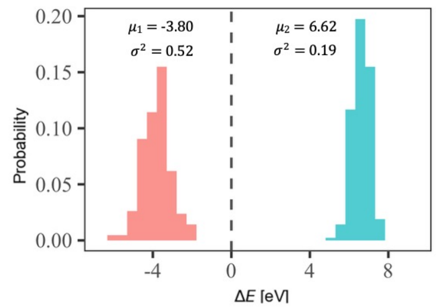


E. W. Lees, J. C. Bui, O. Romiluyi, A. T. Bell & A. Z. Weber, *Nature Chem. Eng*. (2024). [cited Brown (2020)]

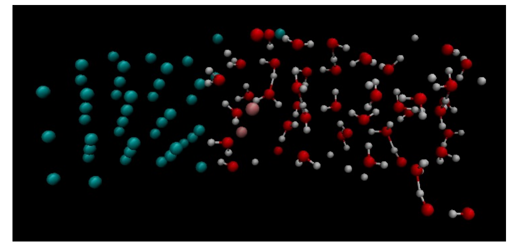
Ab initio prediction of CO_2RR Kinetics (ECIT)

E. Abraham, MZB & T. Van Voorhis, in preparation.

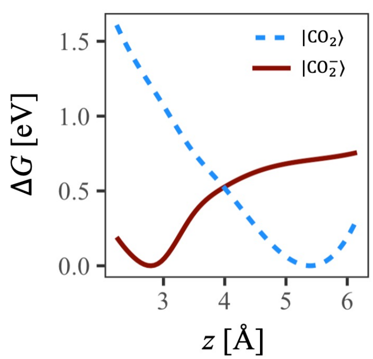
(1) Constrained density functional theory to sample over ET coordinate and construct Marcus parabolas

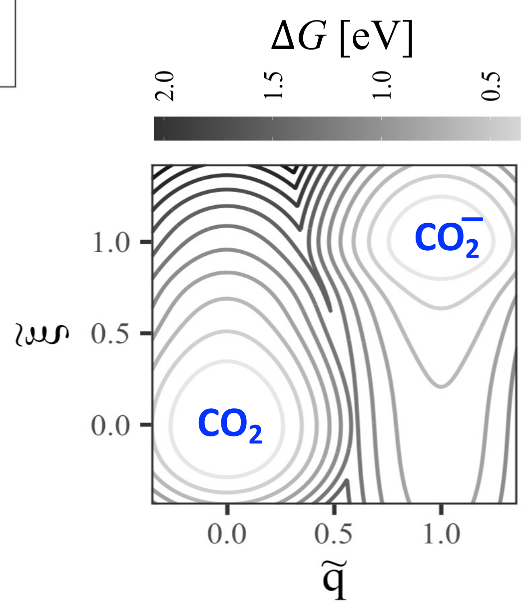


- Method adapted from Qin, Nat. Comm., (2023) 14:7607
- Dynamics propagated with CP2K electronic structure code



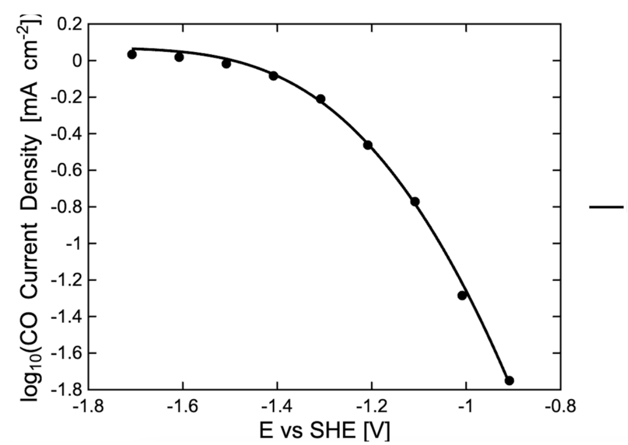
(2) Enhanced sampling / meta-dynamics to sample over IT coordinate





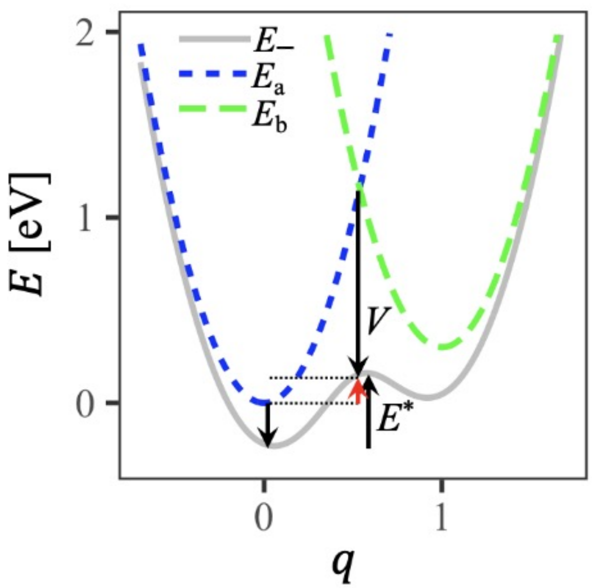
CIET free energy landscape

$$I \sim \left[\frac{\tilde{c}_O}{1+e^{\tilde{\eta}_f}} - \frac{\tilde{c}_R}{1+e^{-\tilde{\eta}_f}}\right] \mathrm{erfc}\left(\frac{\tilde{\lambda} - \sqrt{1+\sqrt{\bar{\tilde{\lambda}}}+\tilde{\eta}_f^2}}{2\sqrt{\bar{\tilde{\lambda}}}}\right)$$



Why does non-adiabatic Marcus/CIET theory work so well, even for strong electron coupling?

E. Abraham, J. Yoon, T. Van Voorhis & MZB, in prep.



Weakly adiabatic, constant shift

New strongly adiabatic correction

$$\lambda_{\text{eff}} \approx \lambda - 4V(q^*) + \frac{4V(q_r)^2}{\lambda}$$

$$E^* = \frac{(\lambda_{\text{eff}} + \Delta G^\circ)^2}{4\lambda_{\text{eff}}}$$

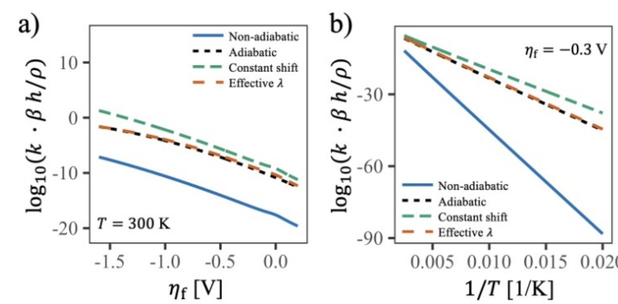
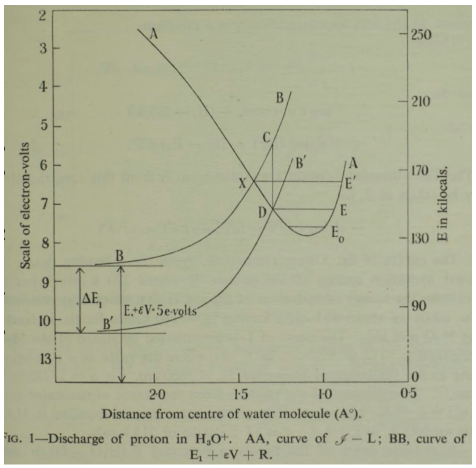


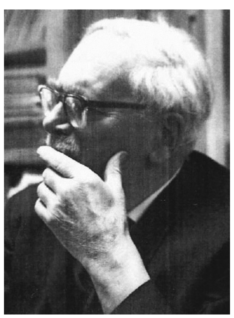
FIG. 4. (a) Tafel plot showing the (base-10) logarithm of the reaction rate k (nondimensionalized) plotted against the formal overpotential η_f at $T = 300$ K. (b) Arrhenius plot showing the dependence of the rate on the inverse temperature $1/T$ for fixed formal overpotential $\eta_f = -0.3$ V. In both panels the reorganization energy and coupling are set to $\lambda = 4.0$ eV and $V = 0.5$ eV respectively. In both

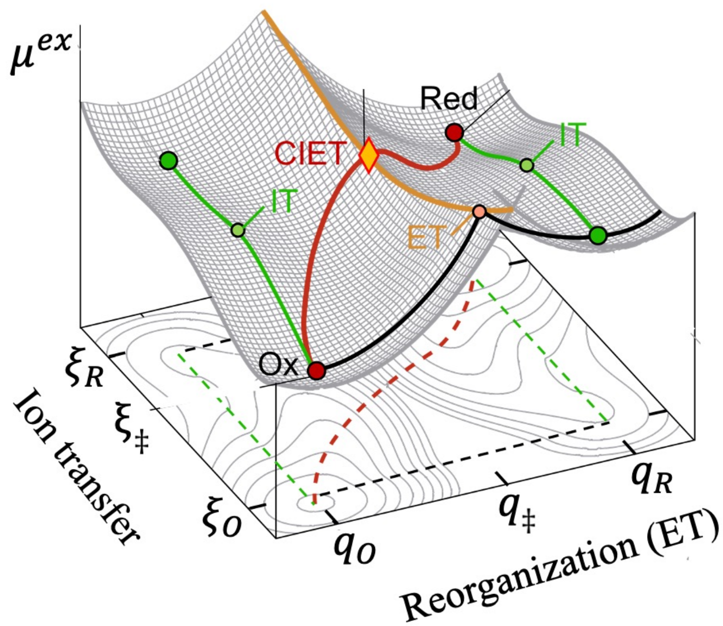
Resolves CO2RR paradox $\lambda_{MHC\ expt} = 0.75$ eV [Nocera], $\lambda_{ab\ initio} = 6.3$ eV [Qin], with $V = 2$ eV [this work]

Unified Quantum Theory of Electrochemical Kinetics by Coupled Ion-Electron Transfer

Gurney-Butler theory of ”ICET"

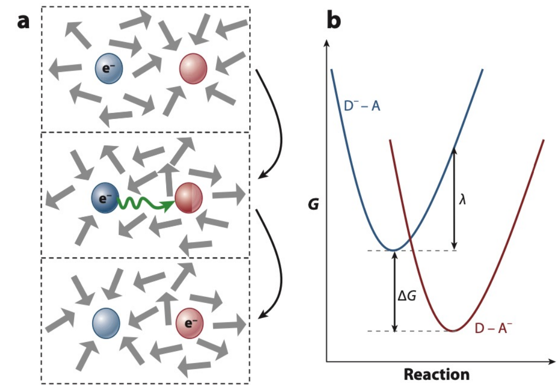






MZB, *Faraday Discussions* 246, 60-124 (2023).

Marcus theory of ET



Van Voorhis et al, Ann. Rev. Phys. Chem. (2010)