Improving the predictive accuracy of battery models using targeted experiments, advanced statistical analysis and first principles calculations

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[2]KBR Wyle Services, [3]NASA-Ames Research Center

New WVU / NASA-Ames collaboration

John Lawson (NASA-ARC)
Computational Materials Group

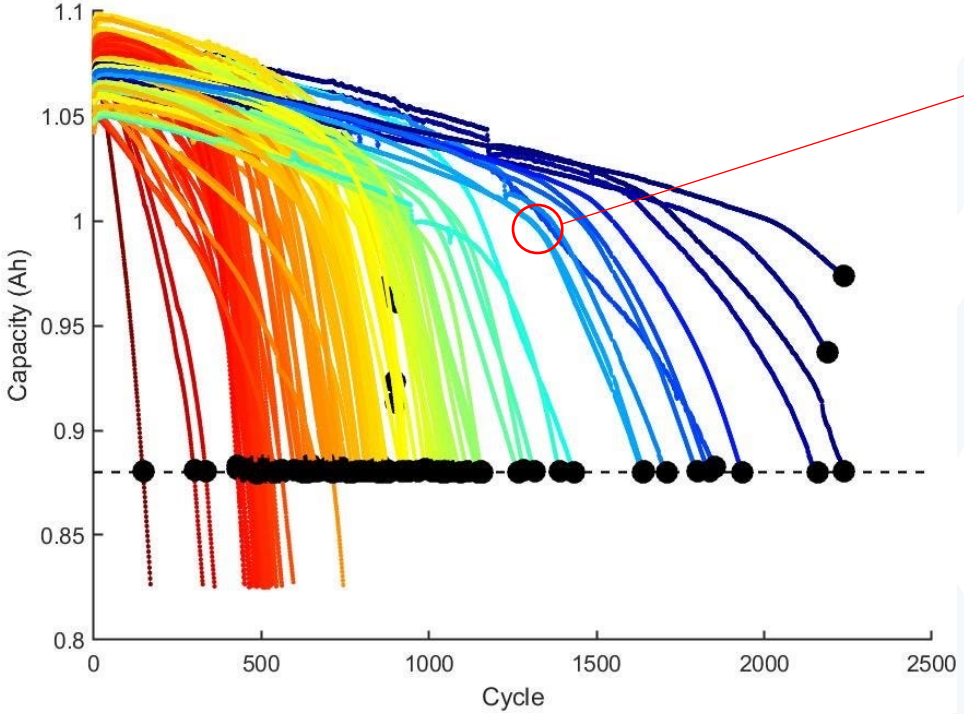
Joakim Halldin Stenlid (KBR/NASA-ARC)
Computational Catalysis / DFT

Mohit Mehta (KBR/NASA-ARC)
Continuum-Scale Battery Modeling

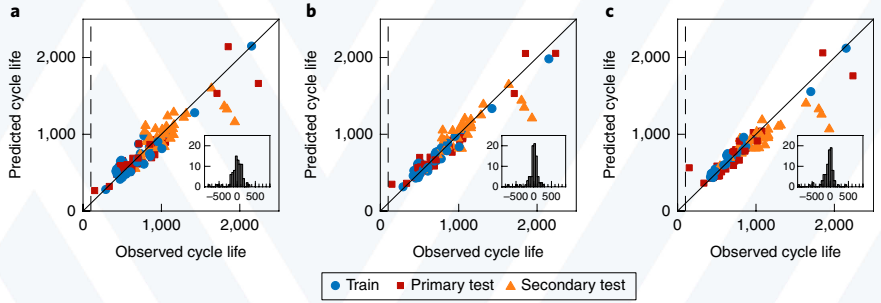
Junsoo Park (KBR/NASA-ARC)
DFT / Cluster Expansions

NASA's X-57 "Maxwell" all-electric aircraft

NASA partner Joby Aviation tests components at an Ames wind tunnel



the “knee”



data extract (left) and figure from K.A. Severson, *et al.*, *Nature Energy*, 2019

- **Physical models are better for making predictions about battery performance / health in variable operating conditions**
- **Physical models can get very complex**

Table VII. Parameter set for the Newman P2D model.

	Parameter	Unit	Positive electrode ($k = p$)	Separator ($k = s$)	Negative electrode ($k = n$)
	Active material		$LiNi_{1-x-y}Mn_xCo_yO_2$	Ceramic coated polyolefin[a)]	Graphite + silicon
Design specifications	Current collector thickness	m	$16{\cdot}10^{-6}$	—	$12{\cdot}10^{-6}$
	Electrode thickness (L_k)	m	$75.6{\cdot}10^{-6}$	$12{\cdot}10^{-6}$	$85.2{\cdot}10^{-6}$
	Electrode length	m	1.58		
	Electrode width	m	$6.5{\cdot}10^{-2}$		
	Mean particle radius (R_k)	m	$5.22{\cdot}10^{-6}$	—	$5.86{\cdot}10^{-6}$
	Electrolyte volume fraction (ε_k)	%	33.5	47	25
	Active material volume fraction ($\varepsilon_{act,k}$)	%	66.5	—	75
	Bruggeman exponent (b)	—	2.43	2.57	2.91
Electrode	Solid phase lithium diffusivity ($D_{s,k}$)	$m^2\ s^{-1}$	$1.48{\cdot}10^{-15}$	—	$1.74{\cdot}10^{-15}$
	Solid phase electronic conductivity ($\sigma_{s,k}$)	$S\ m^{-1}$	0.18	—	215
	Maximum concentration ($c_{s,k}^{max}$)	$mol\ m^{-3}$	51765	—	29583
	Stoichiometry at 0% SOC	—	0.9084	—	0.0279
	Stoichiometry at 100% SOC	—	0.2661	—	0.9014
Electrolyte	Electrolyte ionic diffusivity ($D_{e,k}$)	$m^2\ s^{-1}$		See 23	
	Electrolyte ionic conductivity ($\sigma_{e,k}$)	$S\ m^{-1}$		See 24	
	Transference number (t^+)	—		0.2594	
	Initial electrolyte concentration (c_{e0})	$mol\ m^{-3}$		1000	
Reaction	Open Circuit Voltages (U_k)	V	see Fig. 12 or 8	—	see Fig. 12 or 9
	Activation energy	$J\ mol^{-1}$	$17.8{\cdot}10^3$	—	$35.0{\cdot}10^3$
	Reaction rate (m_k)	$A\ m^{-2}\ (m^3\ mol^{-1})^{1.5}$	$3.42{\cdot}10^{-6}$	—	$6.48{\cdot}10^{-7}$

a) LGchem have been using a ceramic coated separator (SRS) since about 2006 which is a nanoceramic coating on polyolefin, they have licensed bhoemite coated separator from Optodot in 2016.

Journal of The Electrochemical Society, 2020 **167** 080534

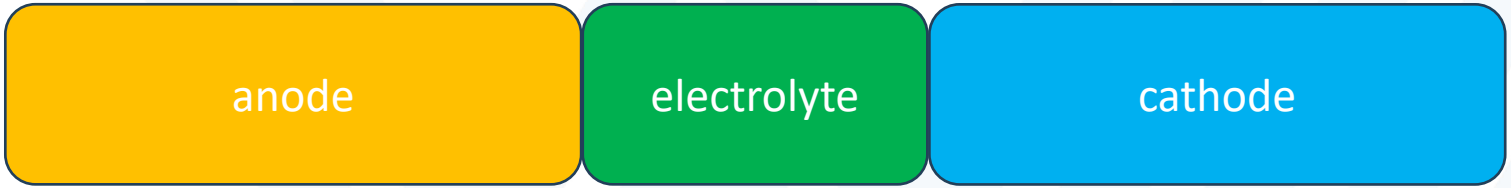
P2D model: 35 parameters, no cell degradation included

Cell operation parameters (no degradation)

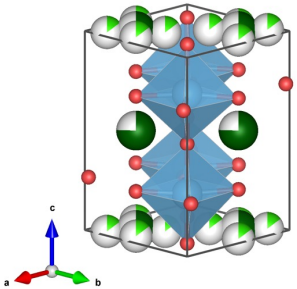
- Activity coefficients in cathode & anode
- Transport parameters in cathode & anode
- Cathode-electrolyte interfacial equilibrium, resistance & capacitance
- Anode-electrolyte interfacial equilibrium, resistance & capacitance
- Electrolyte transport parameters

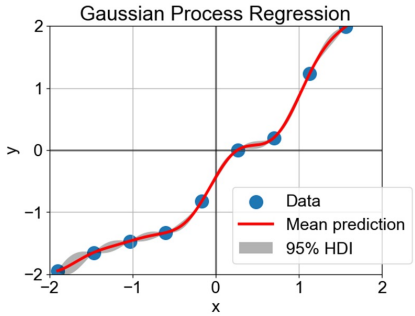
All are really *functions* of SOC / local concentrations / potentials

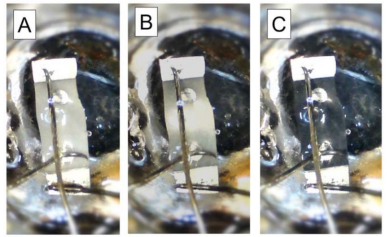
ASSB cell-level model



u_{transp} k_{chargtfr} r_{degrad}



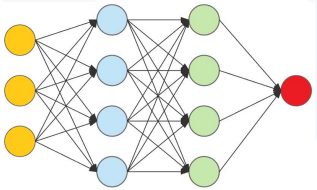


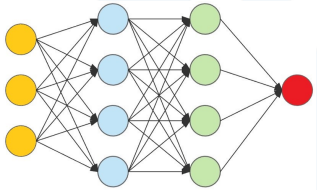


Journal of The Electrochemical Society, 2023 **170** 050530

paradigms for scientific machine learning

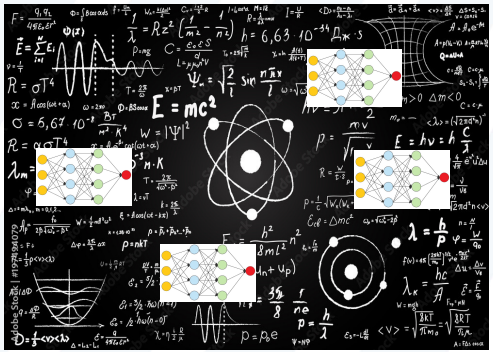
inputs → physical model → sometimes inaccurate outputs

inputs →  → uninterpretable outputs / bad extrapolation

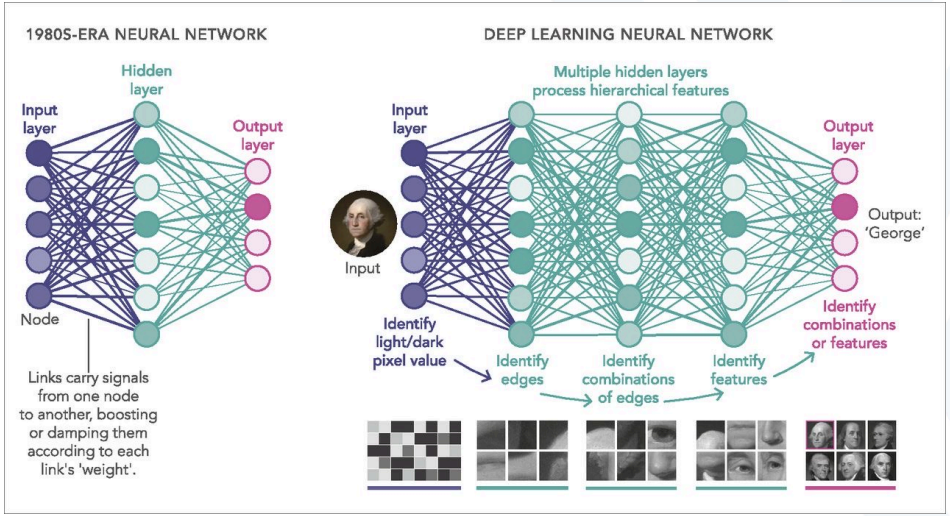
inputs → physical model →  → still can't extrapolate

embedded machine learning

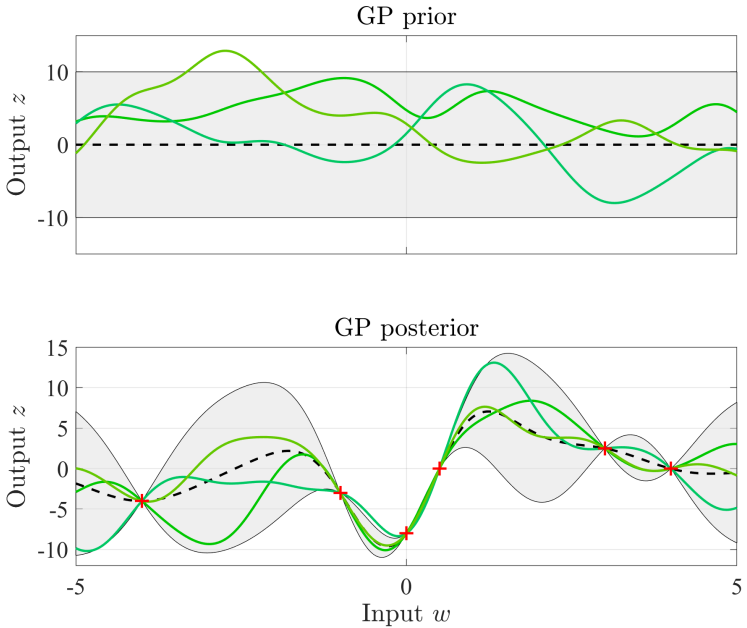
accurate, interpretable, extrapolable



Gaussian processes are great for large input spaces like images and physical functions



MM Waldrop, PNAS, 2019

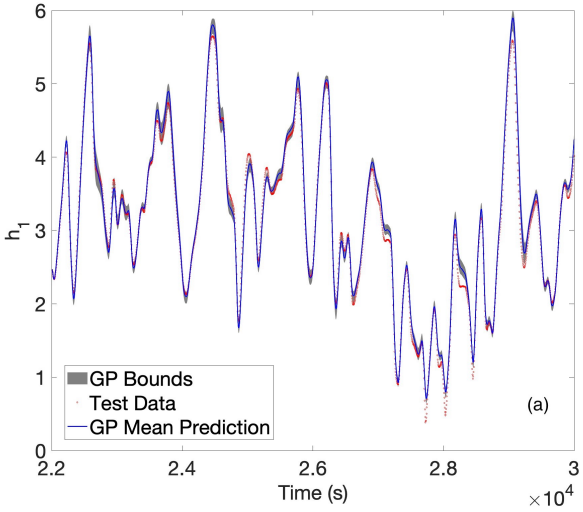


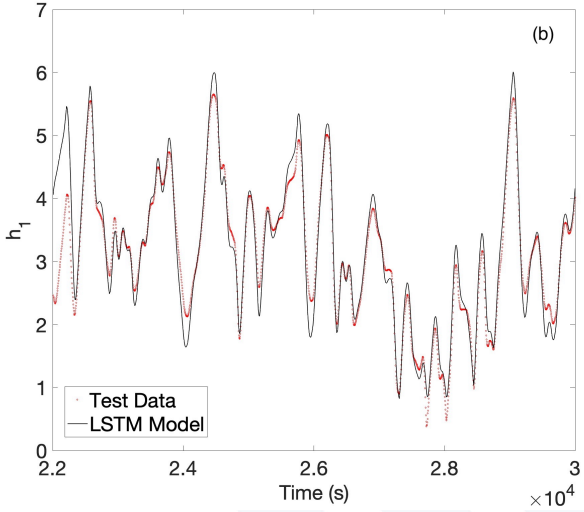
M. Maiworm, *et al.*, arXiv, 2019

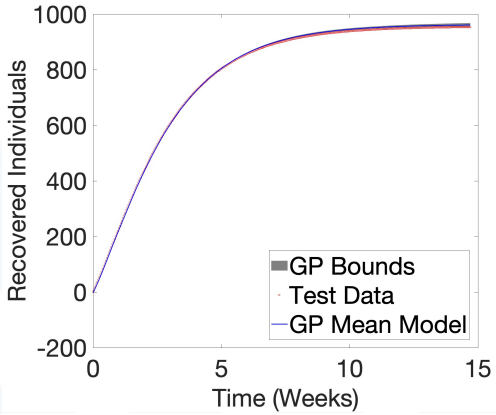
$$\dot{h}_1 = \delta_1(h_1, h_2, u_1)$$
$$\dot{h}_2 = \delta_2(h_1, h_2, u_2)$$

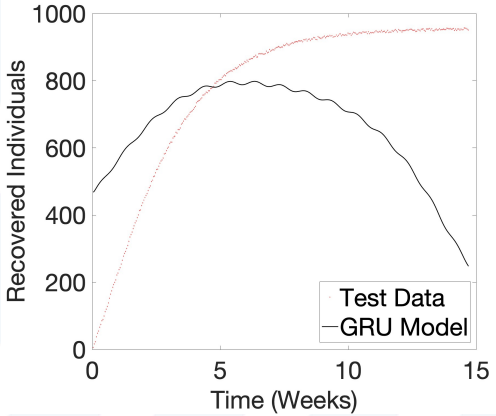
Table 1: Cascaded tanks 5-fold cross validated accuracies: derivatives

Method	$\dot{h}_1$ (MAE/10^{-4})	$\dot{h}_2$ (MAE/10^{-4})
OAK	17±4.7	36±2.4
BSS-ANOVA	18±6.5	39±3.6
ResNet	36±14	61±15
RF	30±9.4	49±4.9







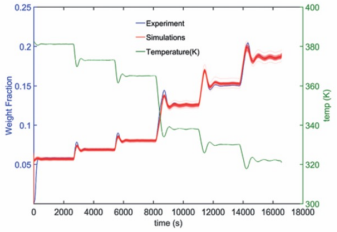


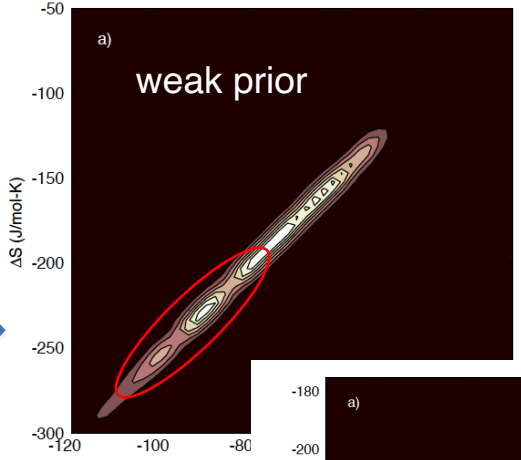
K. Hayes, *et al.*, *arXiv*, 2022

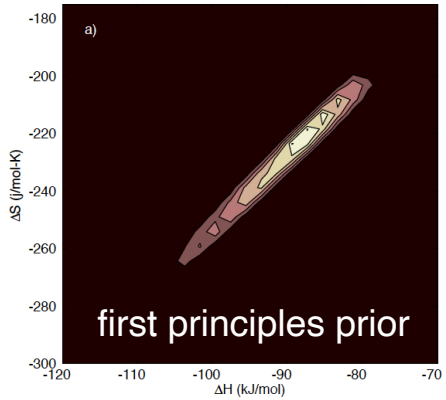
github.com/ESMS-Group-Public/FoKL-GPy
pip install FoKL

$$2R_2NH + CO_2 \leftrightharpoons R_2NCOO^- : R_2NH_2^+$$

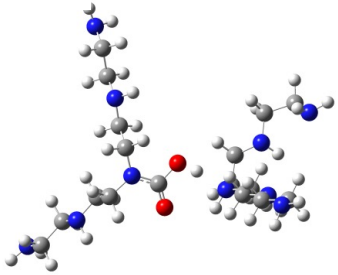
Bayesian model calibration uses prior knowledge on parameters when making estimates

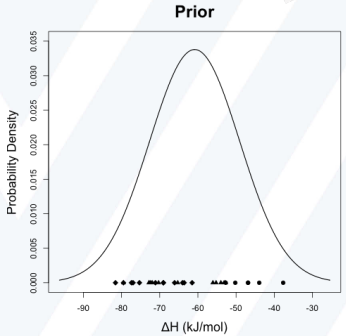




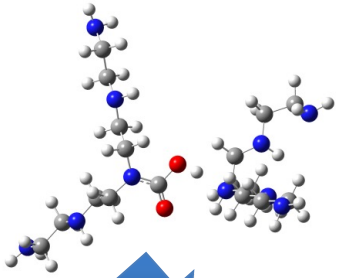


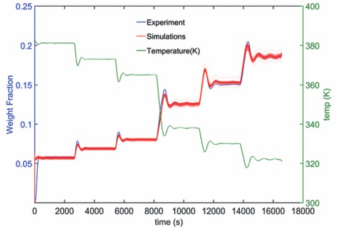
first principles priors reduce model uncertainty and ambiguity

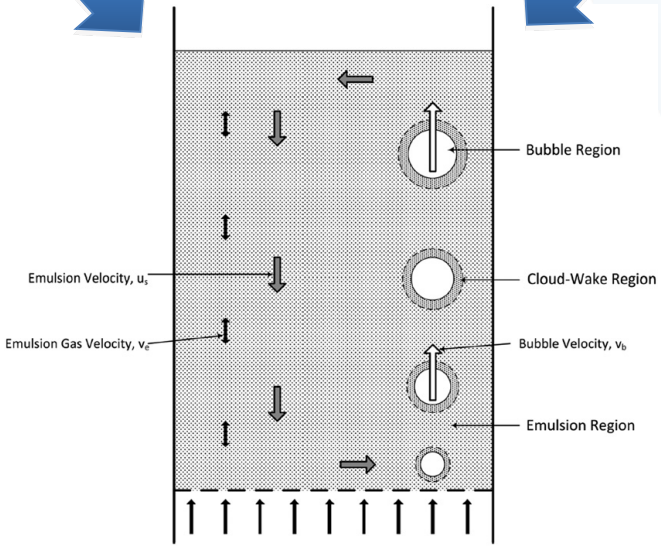


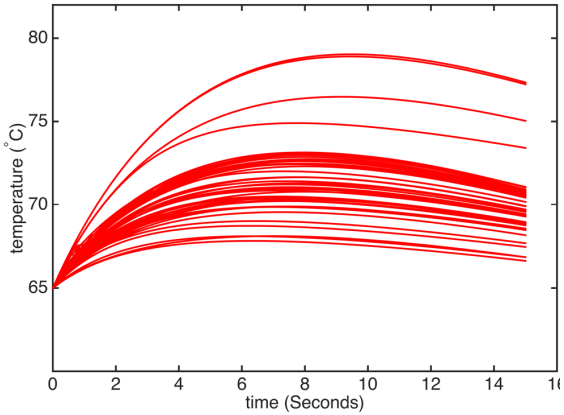


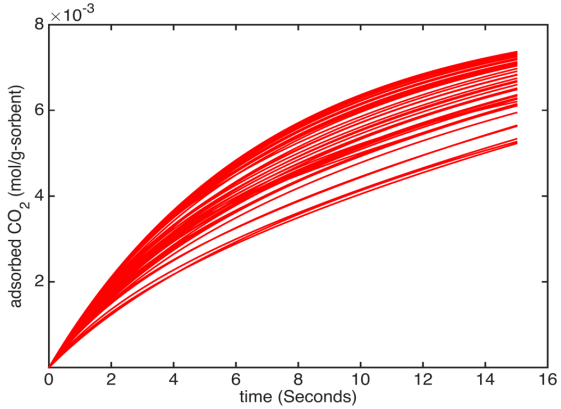
DS Mebane *et al.*, *PCCP*, 2013

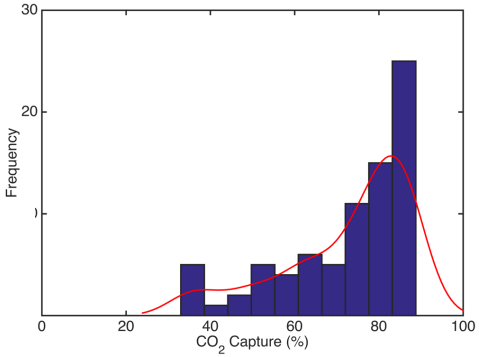






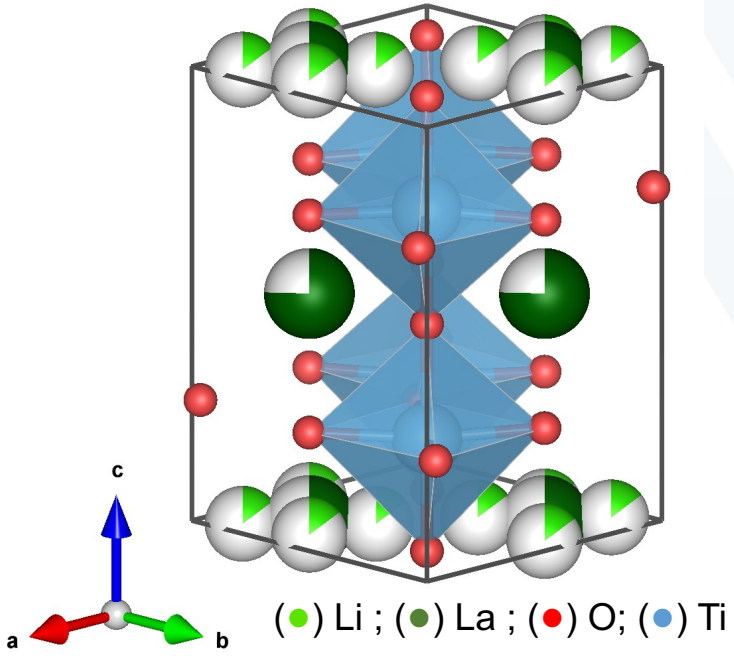




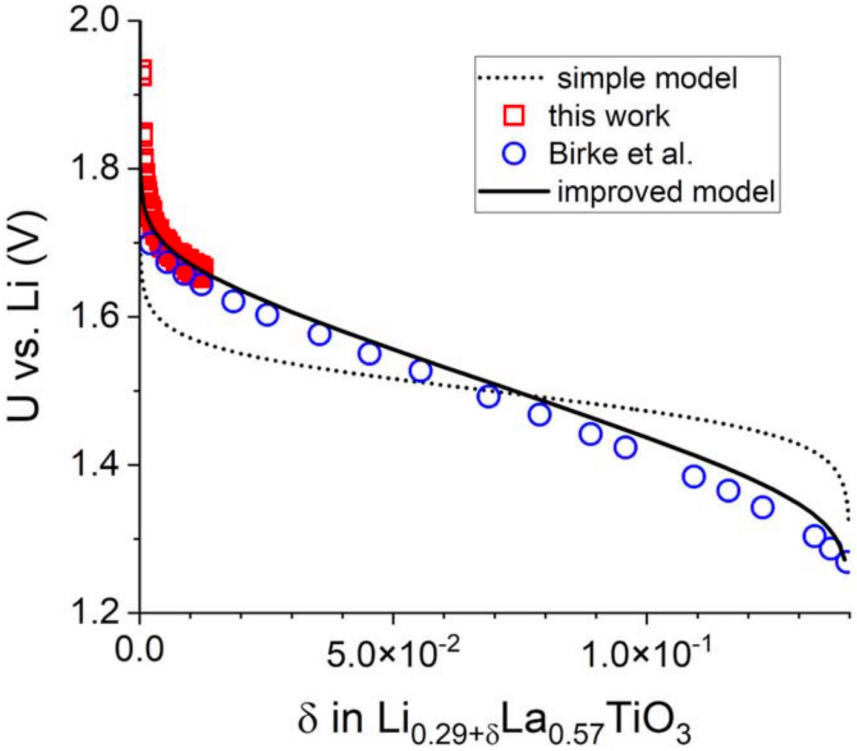


K Li, *et al.*, *Reaction Chemistry & Engineering*, 2017

LLTO as high-rate anode material

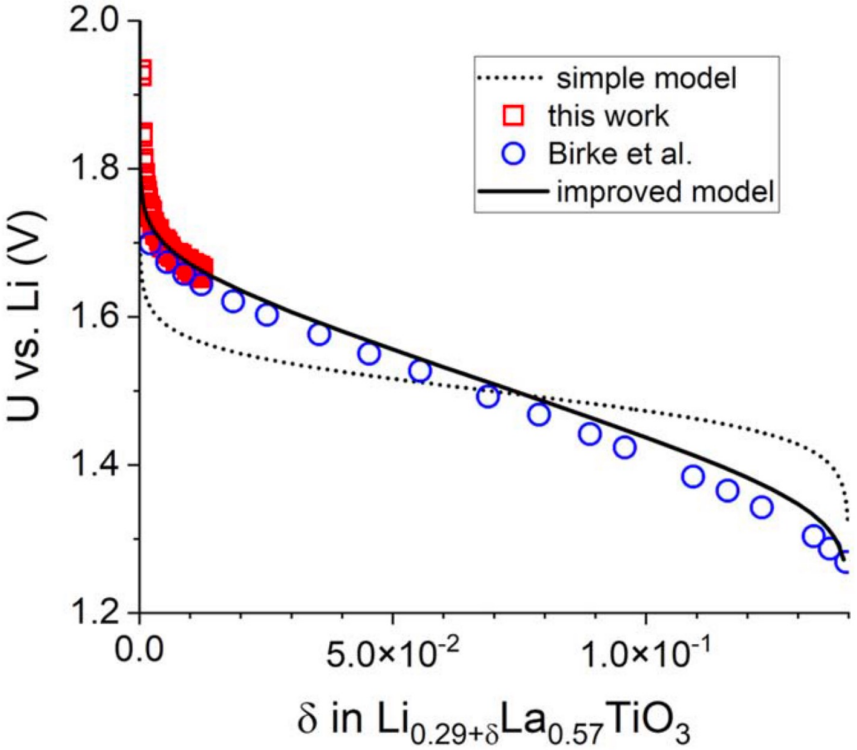


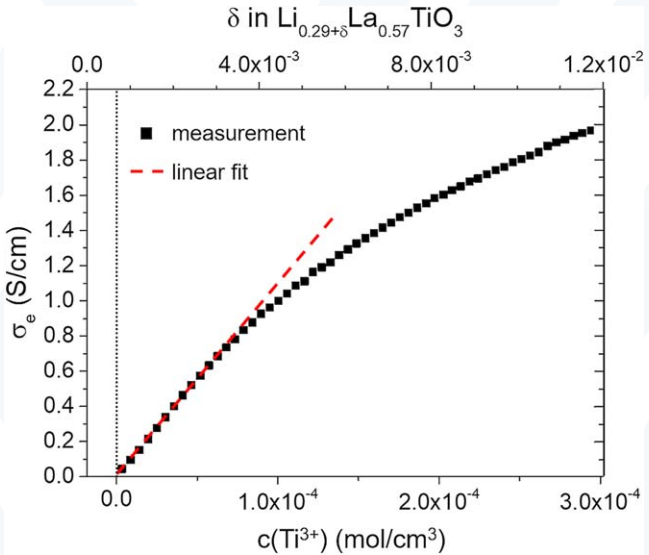
$Li_{0.3}La_{0.5667}TiO_3$



Ring, et. al., *JECS* 2023

LLTO as high-rate anode material





$$\mathrm{Li} + \mathrm{v}''_{\mathrm{A}} + \mathrm{Ti}^{\mathrm{x}}_{\mathrm{B}} \rightleftharpoons \mathrm{Li}'_{\mathrm{A}} + \mathrm{Ti}'_{\mathrm{B}}$$

Ring, et. al., *JECS* 2023

LLTO as high-rate anode material

ARTICLE

https://doi.org/10.1038/s41467-020-17233-1 OPEN

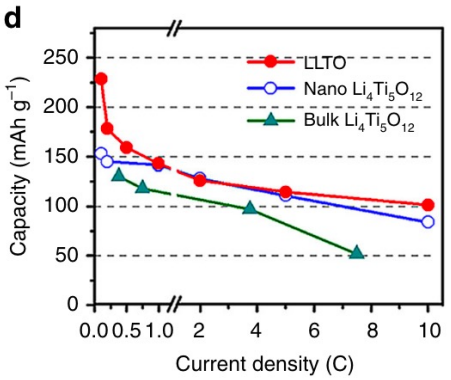
Check for updates

Lithium lanthanum titanate perovskite as an anode for lithium ion batteries

Lu Zhang[1,7], Xiaohua Zhang[2,7], Guiying Tian[3,4,7], Qinghua Zhang[5], Michael Knapp[4], Helmut Ehrenberg[4], Gang Chen[1], Zexiang Shen[1,6], Guochun Yang[2✉], Lin Gu[5✉] & Fei Du[1✉]

Conventional lithium-ion batteries embrace graphite anodes which operate at potential as low as metallic lithium, subjected to poor rate capability and safety issues. Among possible alternatives, oxides based on titanium redox couple, such as spinel $Li_4Ti_5O_{12}$, have received renewed attention. Here we further expand the horizon to include a perovskite structured titanate $La_{0.5}Li_{0.5}TiO_3$ into this promising family of anode materials. With average potential of around 1.0 V vs. Li^+/Li, this anode exhibits high specific capacity of 225 mA h g^{-1} and sustains 3000 cycles involving a reversible phase transition. Without decrease the particle size from micro to nano scale, its rate performance has exceeded the nanostructured $Li_4Ti_5O_{12}$.

- excellent rate capability
- >3000 cycle stability
- 1-1.7 V vs. Li/Li^+
- 225 mAh/g capacity



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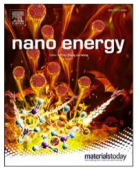


A microstructure engineered perovskite super anode with Li-storage life of exceeding 10,000 cycles

Junru Wang [1], Mengmeng Wang [1], Jingchao Xiao [1], Jiemin Dong, Yixuan Li, Liming Zhang, Juntao Si, Bi-cai Pan, Chu-sheng Chen, Chun-hua Chen [*]

CAS Key Laboratory of Materials for Energy Conversions, Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, Anhui, China

ARTICLE INFO

Keywords:
Lithium lanthanum titanium nickel oxide
Ultra-long cycle life
Storage mechanism
First-principles calculation
Lithium-ion battery

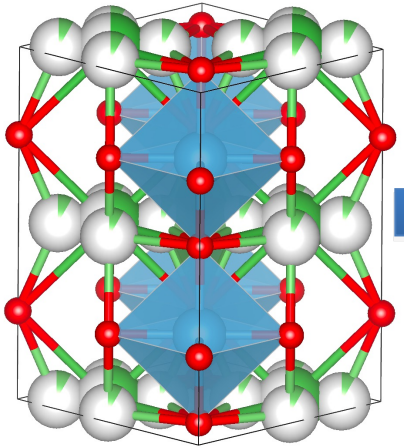
ABSTRACT

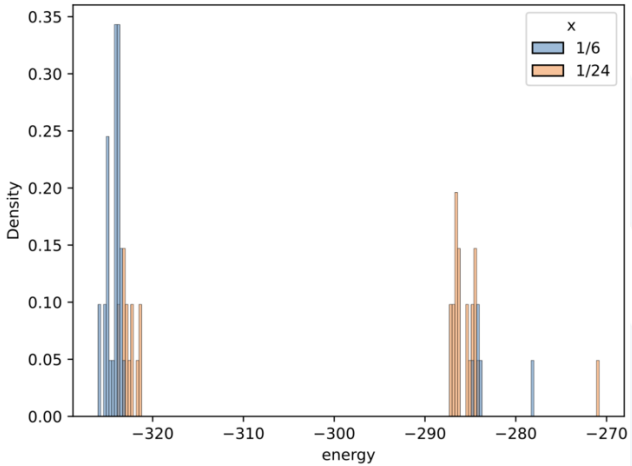
Rechargeable lithium-ion batteries have largely promoted our modern civilization in the past few decades. However, nowadays lithium ion technology is still dominated by the early invented materials which suffer from low volumetric capacity and limited cycle life. Herein, a Li-ion-conducting perovskite material $Li_{0.33}La_{0.56}Ti_{0.9}Ni_{0.1}O_{3-\delta}$ is synthesized as a new anode material. After carbon coating and in-situ Ni-exsolution, this novel engineered material emerges as a super anode (Super A©) with all-around outstanding characteristics compared with other counterparts including the state-of-the-art anode graphite. This new anode has a low working potential (1 V vs. Li^+/Li), high reversible capacity (352 or 457 mAh g^{-1} under different modes), ultra-long cycle life (over 10,000 cycles at 2 A g^{-1}), excellent fast-charge, low-temperature and anti-overcharge performances. Particularly, Super A© can achieve a rather high volumetric capacity up to 2267 Ah L^{-1} (vs. 608, 837 and 2062 Ah L^{-1} for $Li_4Ti_5O_{12}$, graphite and lithium, respectively). Based on quantumchemical calculations, we propose a new lithium storage mechanism in coupling vacancies existing in the perovskite structure. This work presents a promising next-generation anode material for commercial lithium-ion products. It also provides a new methodology to design ceramic-based electrode materials for the electrochemical rechargeable batteries.

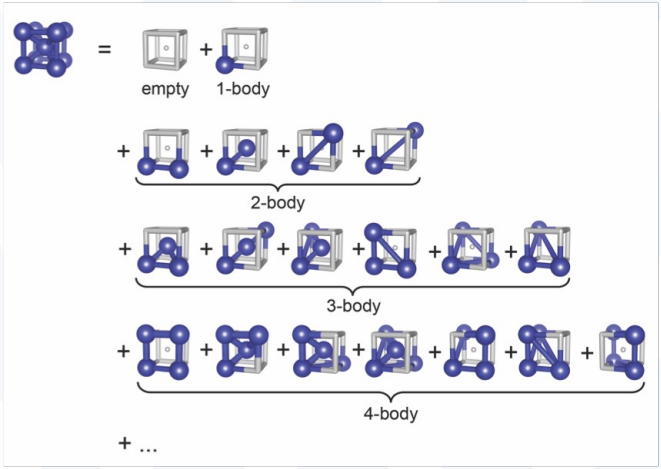
Ni-doping: 352 mAh/g and 10000 cycles?

There's probably space for optimization

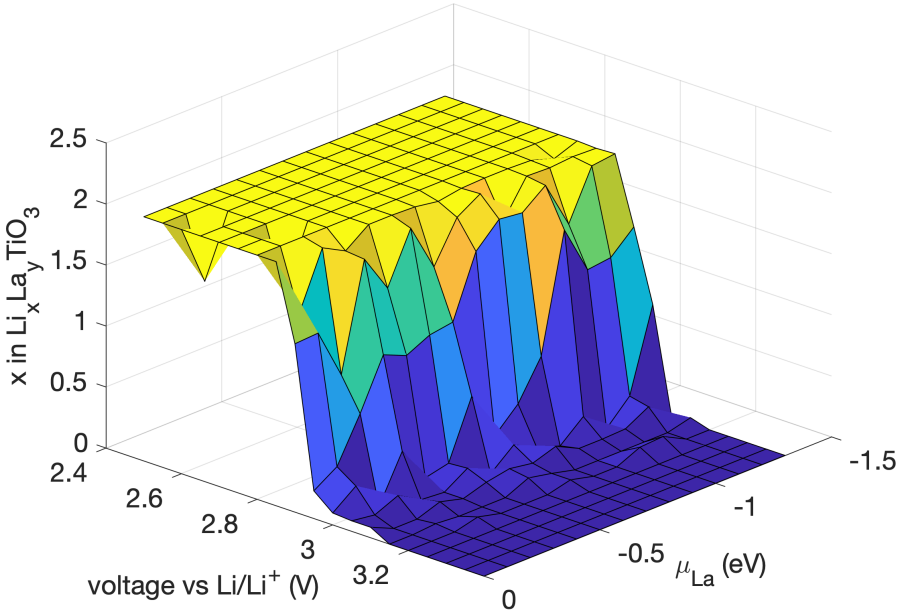
First principles modeling of cell potential

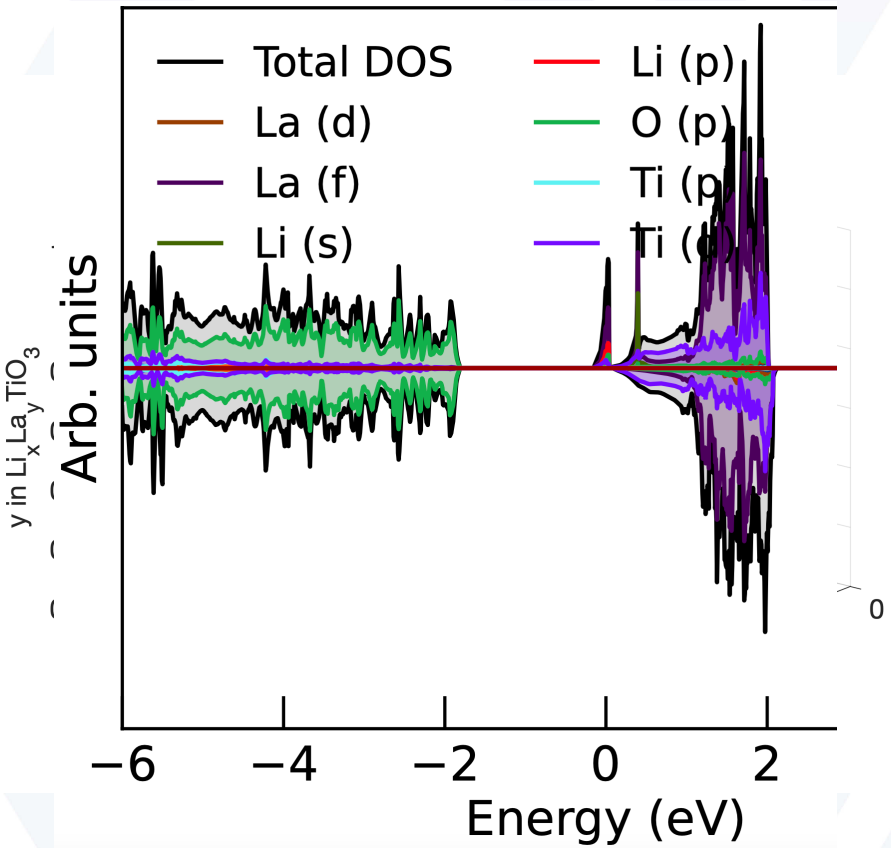




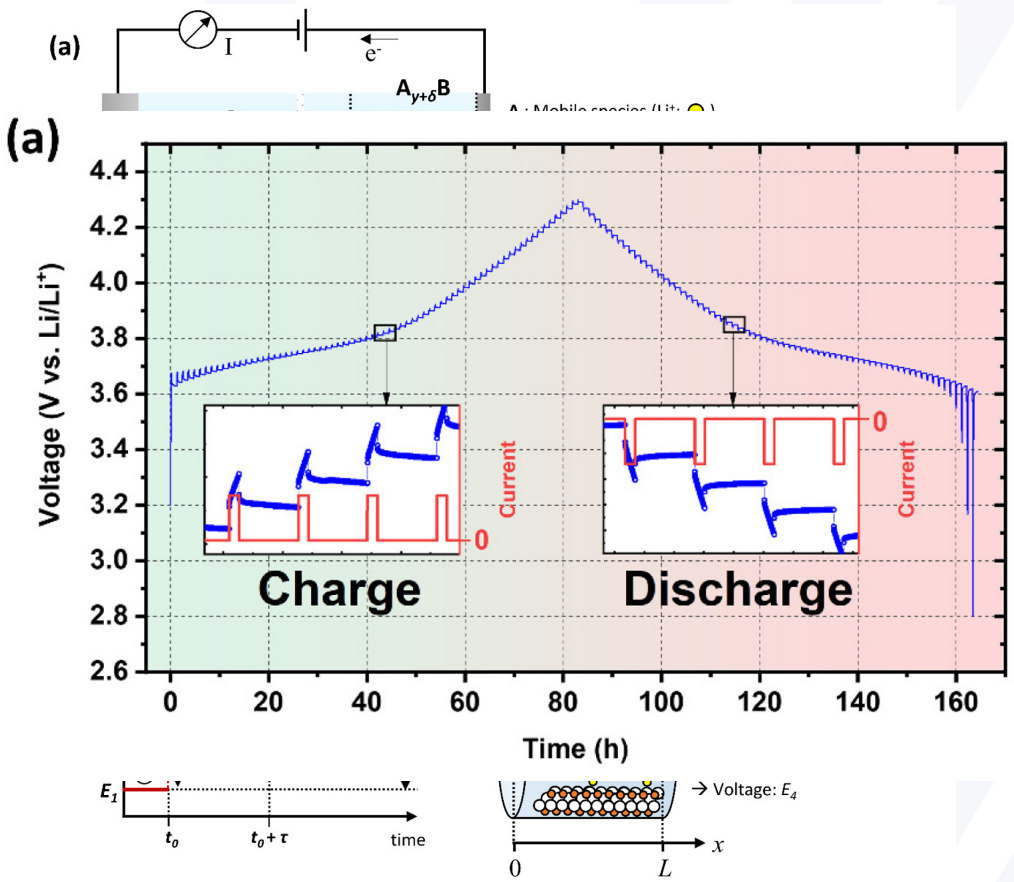


Monte Carlo simulations give μ_{Li} vs. c_{Li}


x in $Li_xLa_yTiO_3$
2.5
2
1.5
1
0.5
0
2.4
2.6
2.8
3
3.2
voltage vs Li/Li^+ (V)
0
-0.5
-1
-1.5
μ_{La} (eV)


Total DOS
La (d)
La (f)
Li (s)
Li (p)
O (p)
Ti (p)
Ti (d)
y in $Li_xLa_yTiO_3$
Arb. units
−6
−4
−2
0
2
Energy (eV)

Galvanostatic Intermittent Titration Technique (GITT) is designed to isolate electrode transport



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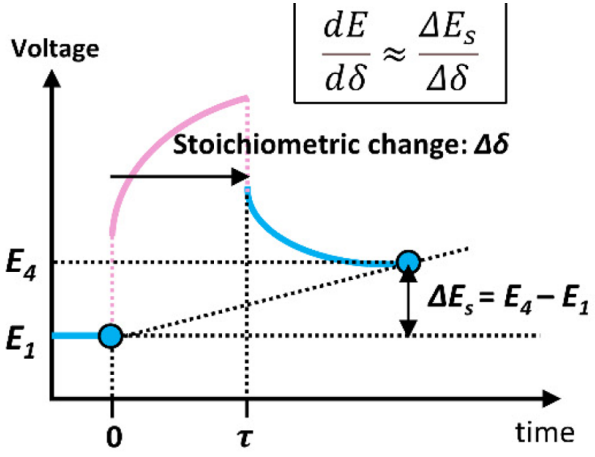
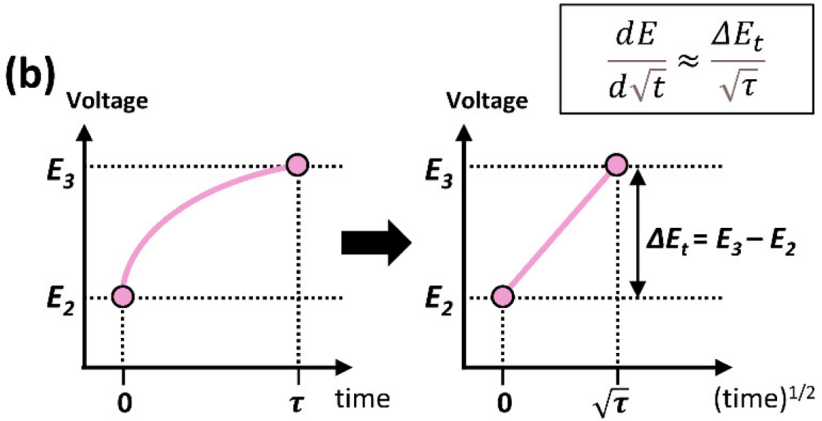
GITT: Weppner & Huggins, 1977

$$D = \frac{4}{\pi}\left(\frac{V_M I_0}{S F z_{Li}}\right)^2 \left[\left(\frac{dE}{d\delta}\right) \Big/ \left(\frac{dE}{d\sqrt{t}}\right)\right]^2$$





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GITT assumptions

- *D* is constant for each step
- partial derivative of *E* wrt concentration is constant
- *E*(*t*) is parabolic during the current step
- diffusion is rate-limiting during the current step
- diffusion geometry is semi-infinite
- parasitic currents are minimal
- charging currents are minimal

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Table 1. Comparison of experimental conditions for GITT experiment

Current rate (or current density)	Duration time of the current	Relaxation time	Ref
C/10	5 min	2 h	[13]
C/20	90 min	5 h	[16]
20 mA g^{-1}	30 min	4 h	[20]
C/10	10 min	40 min	[21]
C/10	20 min	2 h	[22]
C/20	60 min	4 h	[23]
C/5	10 min	40 min	[24]
C/20	15 min	45 min	[25]
0.31 μA cm^{-2}	30 min	10 h	[26]
C/10	10 min	2 h	[27]
C/10	20 min	1 h	[28]
C/10	5 min	1 h	[29]
C/10	30 min	2 h	[30]
C/20	20 min	2 h	[31]
0.4 C	5 min	3 h	[32]
C/25	90 min	10 h	[33]
20 mA g^{-1}	30 min	10 h	[34]
C/20	120 min	10 h	[35]

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Galvanostatic Intermittent Titration Technique Reinvented: Part I. A Critical Review

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The galvanostatic intermittent titration technique (GITT), introduced in 1977 by Weppner and Huggins, provided a readily accessible means to measuring the chemical diffusion coefficient of electrochemical electrode materials. The method continues to be widely used today, but the reported diffusivity values are highly inconsistent, ranging as much as four orders of magnitude for some Li layered oxide compositions. Even qualitative trends of diffusivity are inconsistent, suggesting significant flaws in the implementation of the method. Other variants of the GITT method also suffer from similar inconsistency problems. Here we identify numerous sources of significant error including composition-dependent reaction overpotentials, mathematical flaws in the relaxation analysis methods, finite-size and non-planar geometry effects, inter-particle inhomogeneity issues, early transient effects, and surface area uncertainties. We propose a simple relaxation analysis scheme using the time variable $\sqrt{t_{\text{relax}}+\tau}-\sqrt{t_{\text{relax}}}$, where t_{relax} is relaxation time and τ is the galvanostatic pulse duration. We also propose to use dense diffusion-limited samples to isolate the bulk-diffusion process in the time domain. Chemical diffusivity can be extracted much more reliably with this improved implementation of the GITT method.

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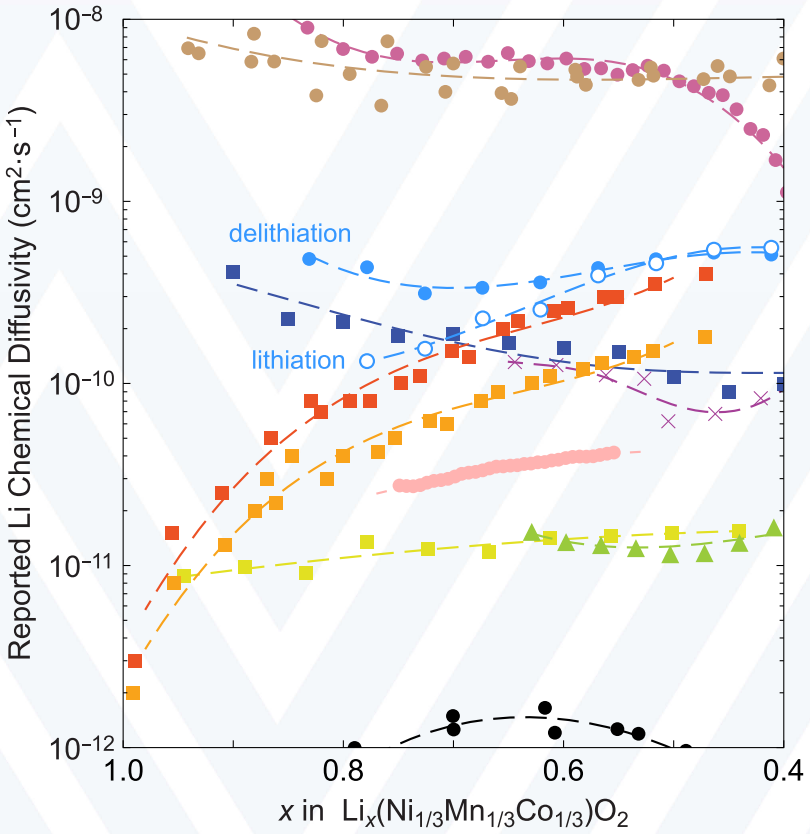


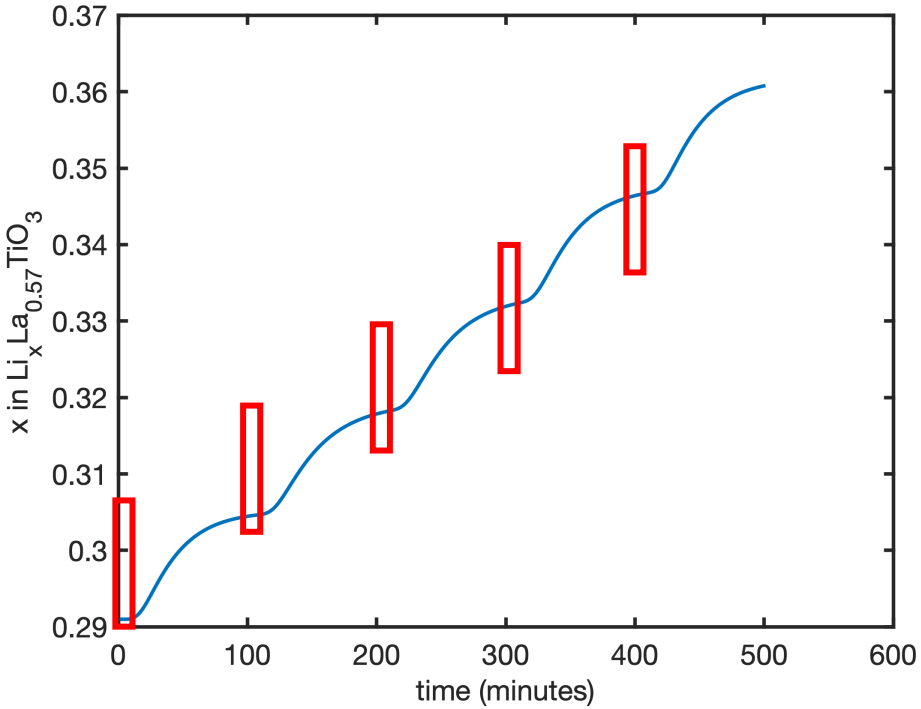
GITT via numerical & statistical analysis

known flux from $t = 0$ until $t = t_{\text{pulse}}$

during relaxation the contact directly monitors $c(x = L, t)$

two assumptions:

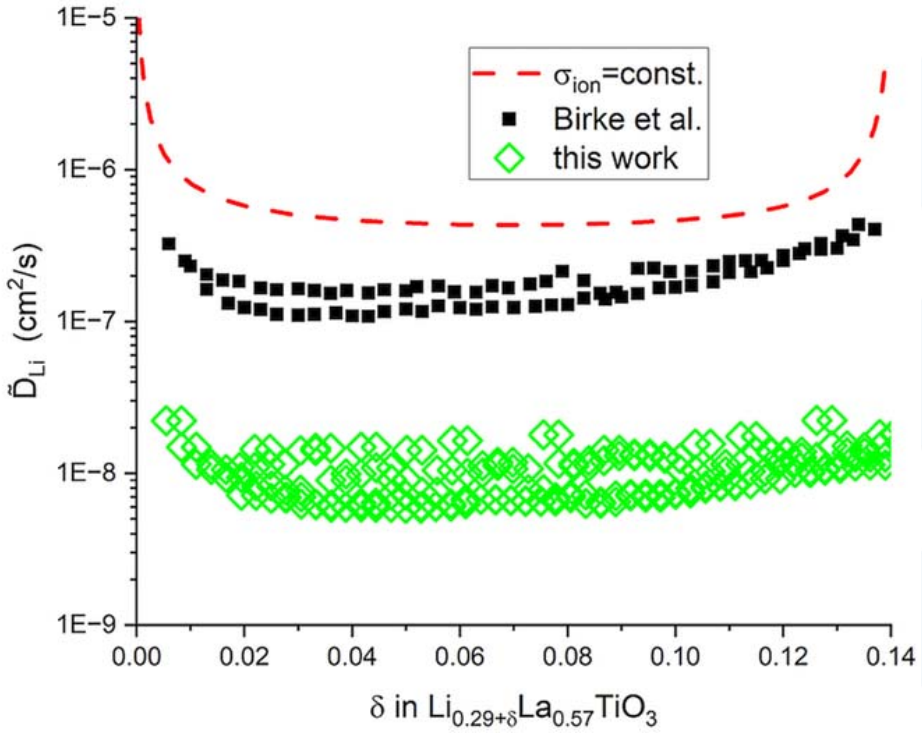
- **parasitic currents minimal**
- **charging currents minimal**

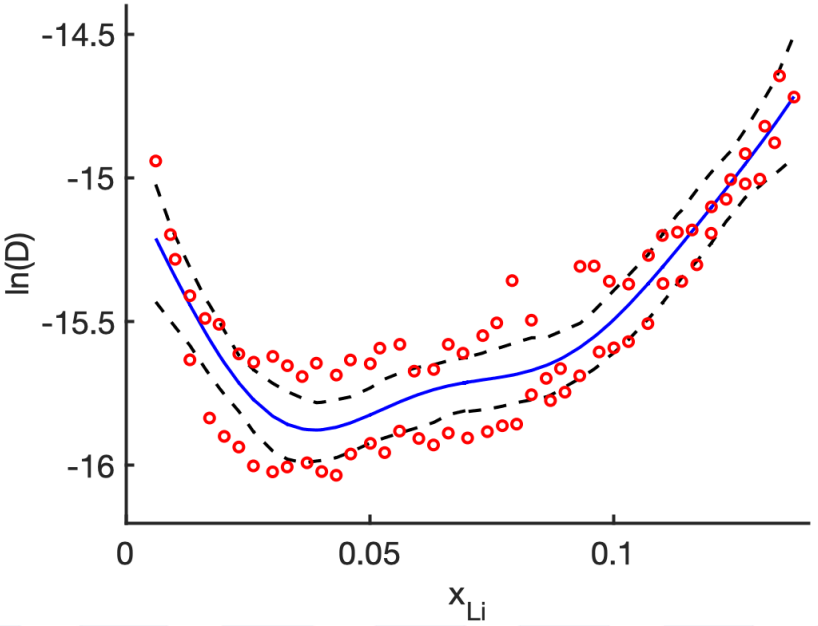


larger concentration steps possible (no need to equilibrate)

more accurate estimates of D as function of concentration

proof-of-concept coming soon





$$\frac{\partial \zeta}{\partial t} = \frac{\partial}{\partial x}\left\{ RTu\left[\frac{2-\zeta}{1-\zeta} + \frac{\partial \ln\left(\gamma_{\mathrm{Li}}\gamma_{\mathrm{e}}\right)}{\partial \ln \zeta}\right]\frac{\partial \zeta}{\partial x}\right\}$$

Questions ?

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