CHEMICAL ENGINEERING
UNIVERSITY of WASHINGTON

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Probing Nonlinear Dynamics to Unlock New Insights into Battery Systems

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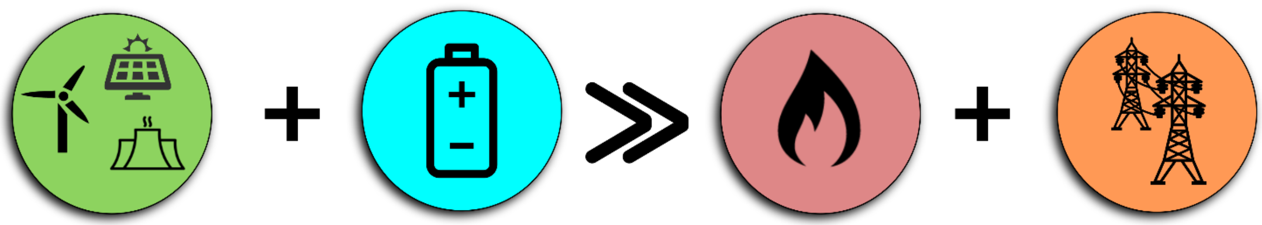
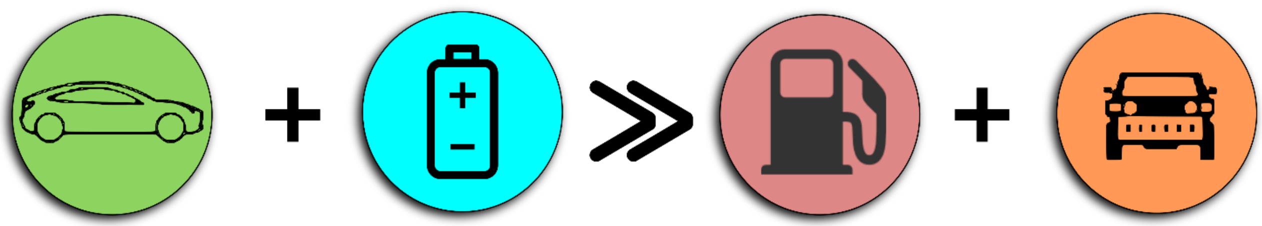
Vision for the future energy economy

Electric Power Grid:



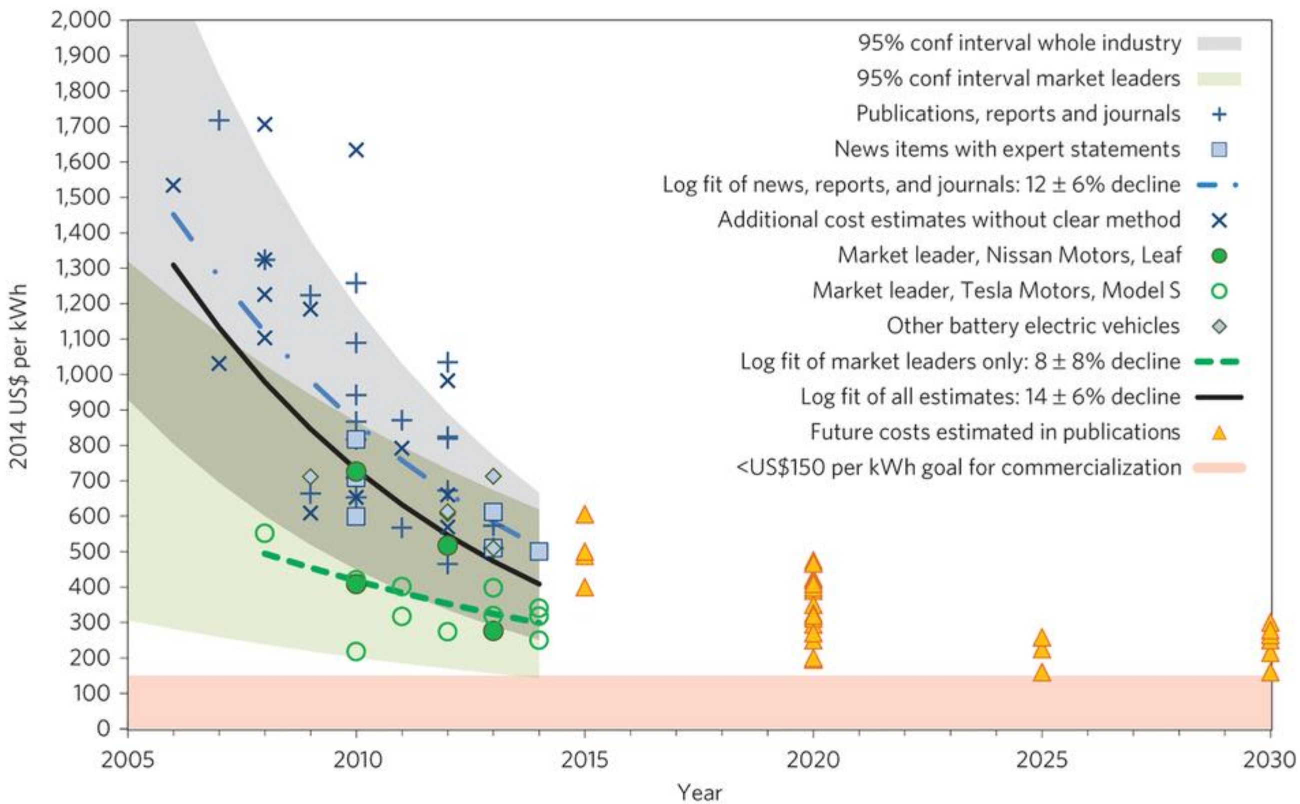
Transportation Industry:



Low cost, efficient, and fast charging batteries are key to continued advancement of the grid and electric vehicles.

Danielle Fong, TEDxDanubia (June 2015).

Li-ion battery prices are falling 14%/year!

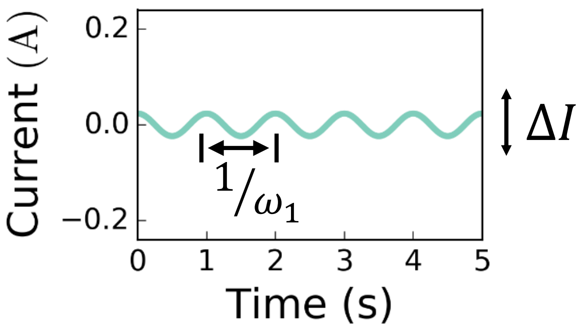


Advances in battery costs have been made primarily in manufacturing and materials.

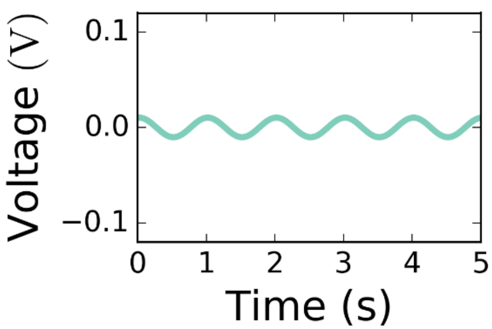
Nykvist, B. & Nilsson, M. *Nature Clim. Change* **5,** 329–332 (2015).

Today's Tool: Electrochemical Impedance Spectroscopy

Input:



Output:

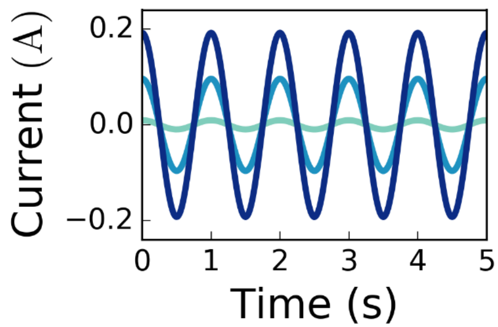


Small Perturbation
= **Linear** Response

EIS provides a *linearized* view into a nonlinear system.

Nonlinear Electrochemical Impedance Spectroscopy

Input:

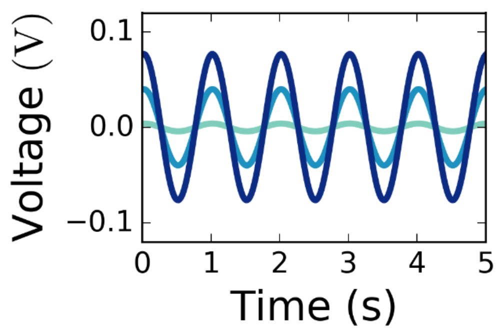


Increase
ΔI

Experimental Details:

750 mA-hr $LiCoO_2|C$
AUTOLAB PSTAT + FRA
Room Temperature

Output:



Moderate Perturbation
= **Harmonic** Response

Nonlinear EIS retains physics and information that are discarded in traditional EIS.

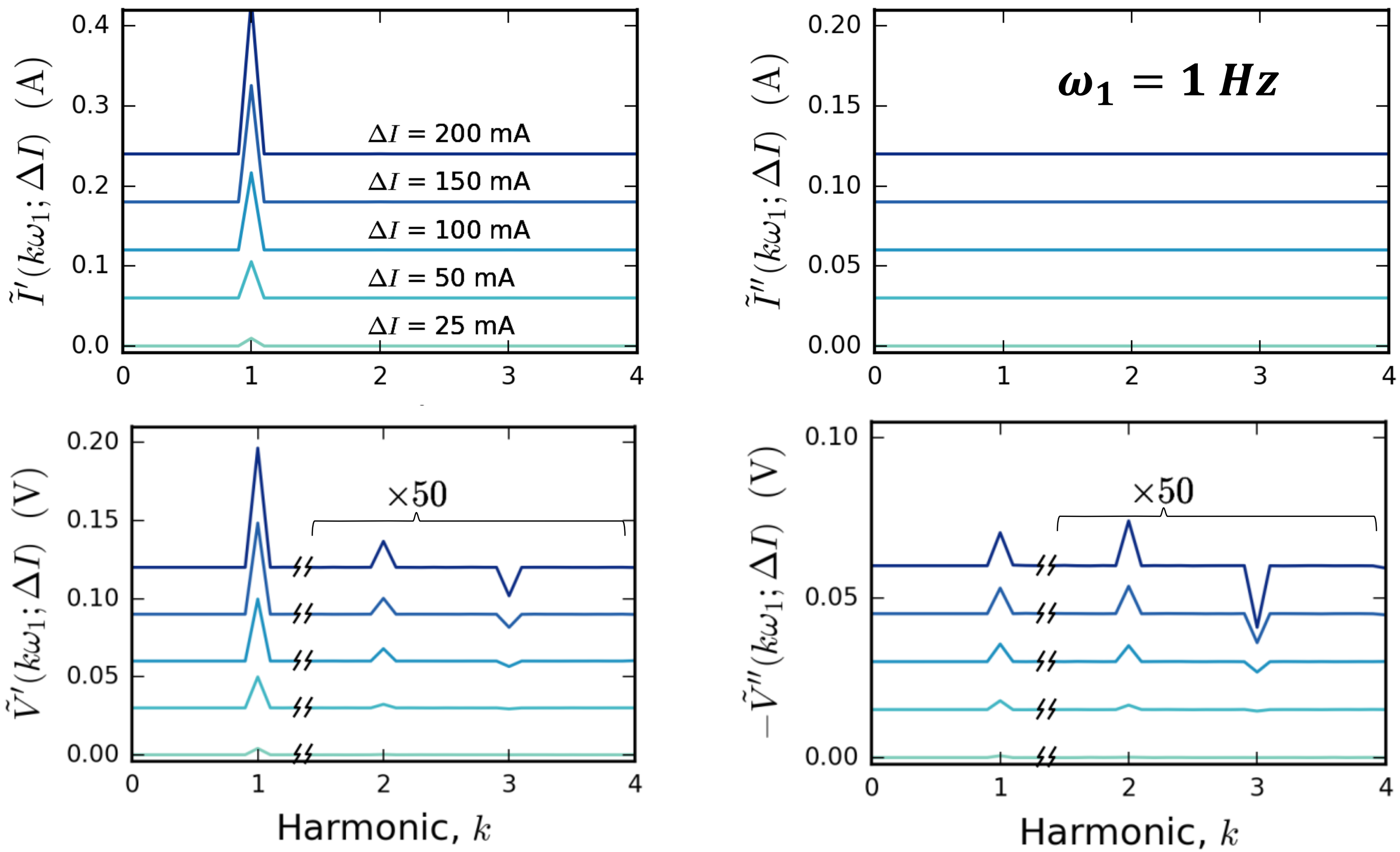
Darowicki, K. *Corrosion Science* **37,** 913–925 (1995)
Medina, J. A. & Schwartz, D. T. *Phys. Fluids* **8,** 2895–2905 (1996)
Wilson, J. R., Schwartz, D. T. & Adler, S. B. *Electrochimica Acta* **51,** 1389–1402 (2006)

Frequency domain analysis reveals harmonic structure

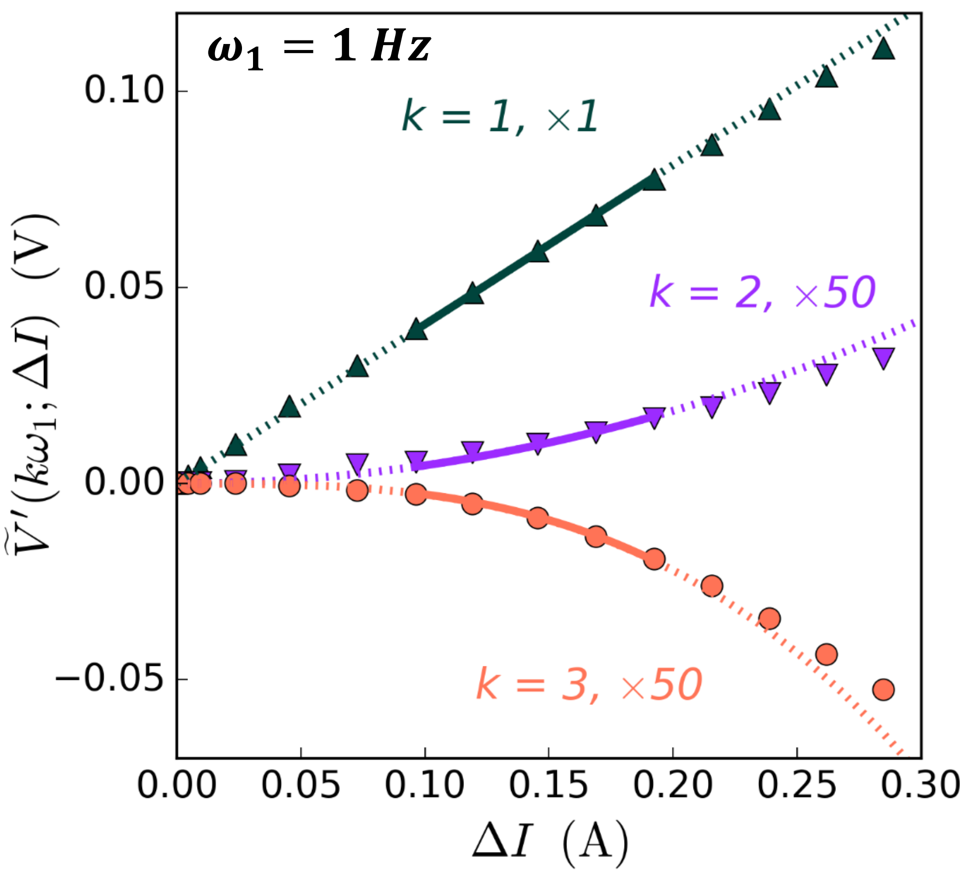
Real **Imaginary**

Current:

Voltage:



Harmonic signals depend nonlinearly on perturbation amplitude



Power law formulation allows us to extract **purely frequency dependent** impedance coefficients

$$\tilde{V}(k\omega_1, \Delta I) \approx \tilde{Z}_k(\omega_1)\Delta I^k$$

Darowicki, K. *Corrosion Science* **37,** 913–925 (1995)
Medina, J. A. & Schwartz, D. T. *Phys. Fluids* **8,** 2895–2905 (1996)
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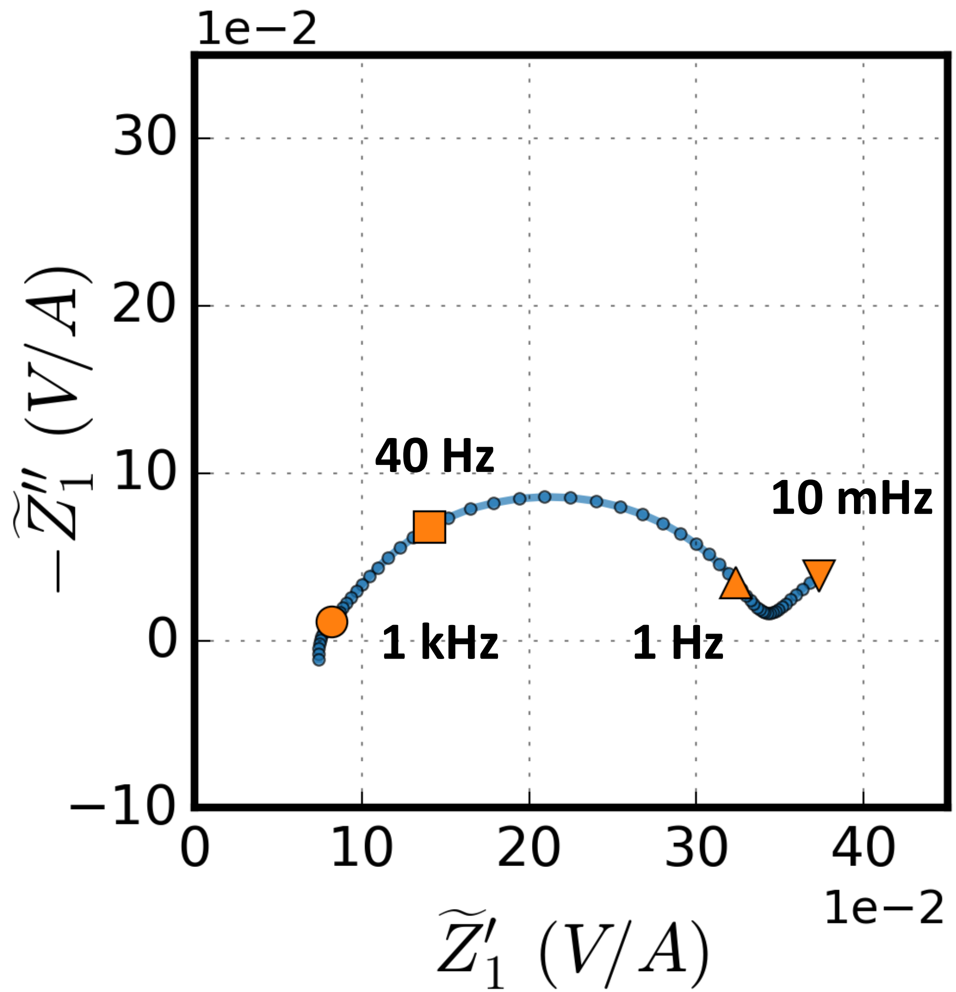
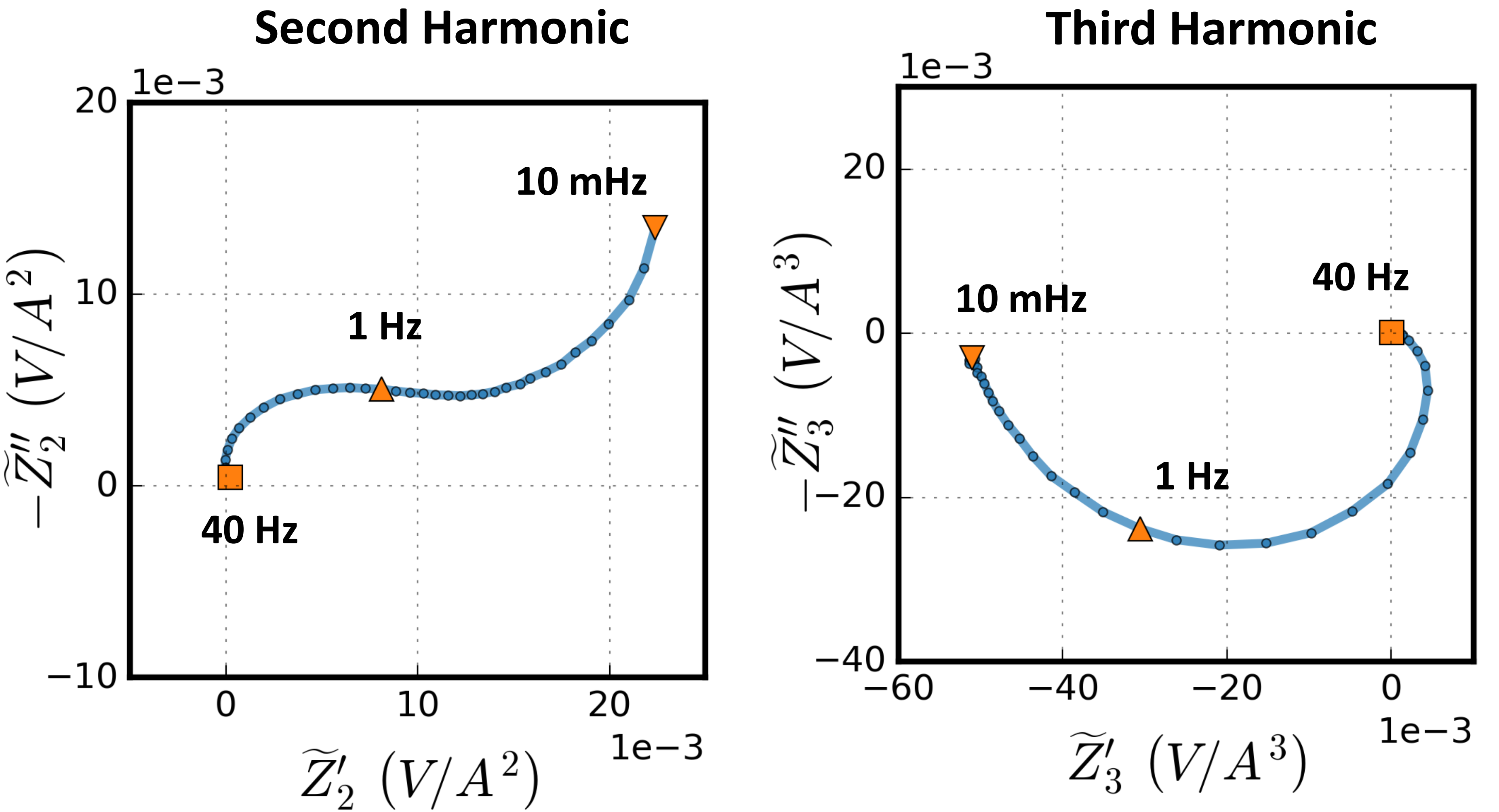
$\tilde{Z}_1(\omega_1), \tilde{Z}_2(\omega_1), \tilde{Z}_3(\omega_1)$ are frequency dispersion functions

- Dependent on the **fundamental physicochemical processes** of the battery not how the experiment is performed
- Hierarchical structure means we have some fundamental insight into the system:
  - Even harmonics are sensitive to symmetry

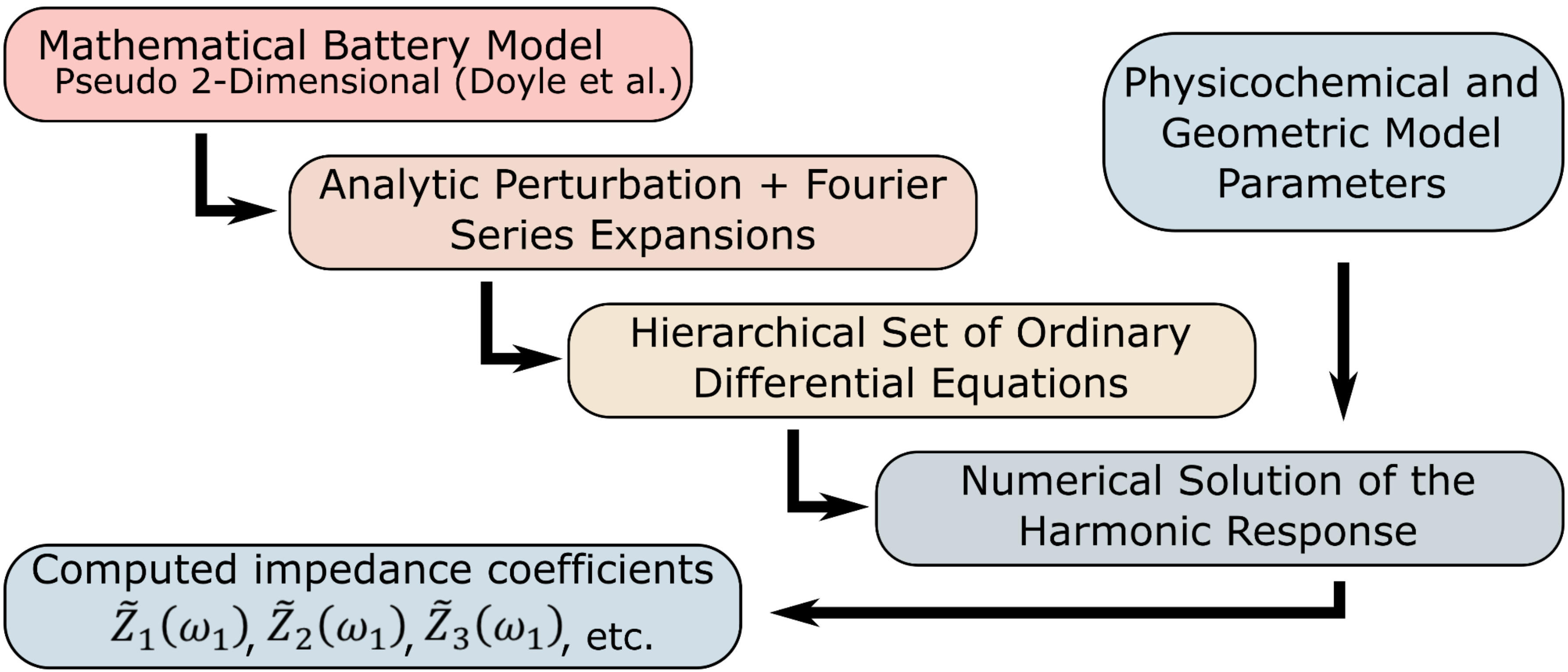
$\tilde{Z}_1(\omega_1)$ is the linear impedance response



First full NLEIS spectrum for a Li-ion battery



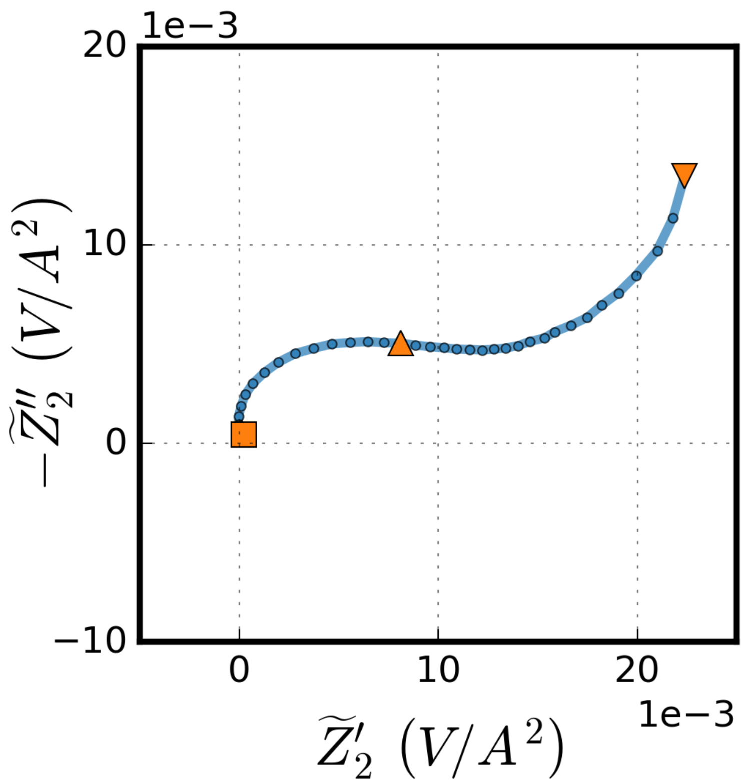
Full analysis: Mathematical modeling



Physics based models can unlock the informational power of nonlinear EIS measurements.

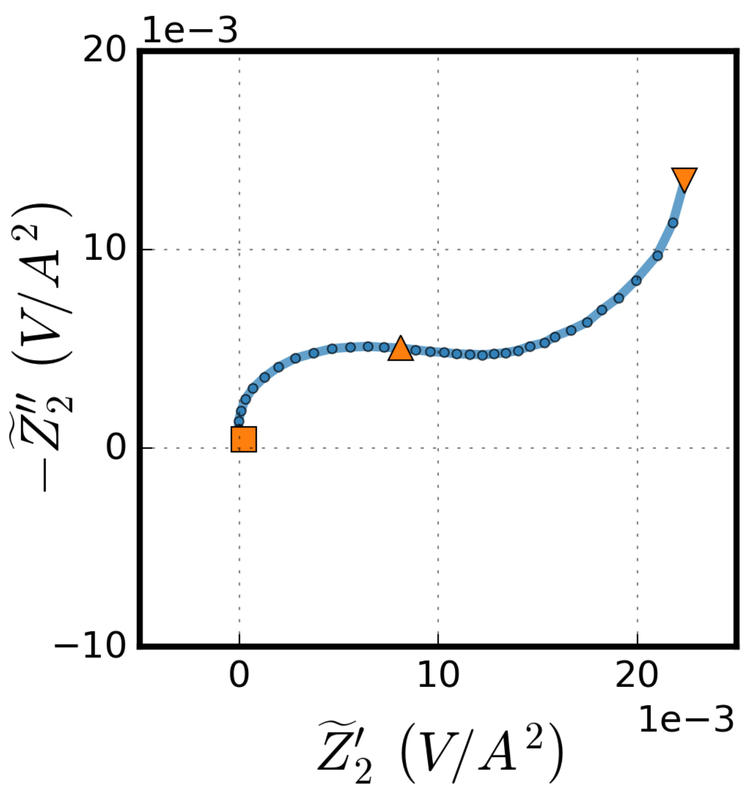
Standard literature parameters don't capture second harmonic physics

Experimental

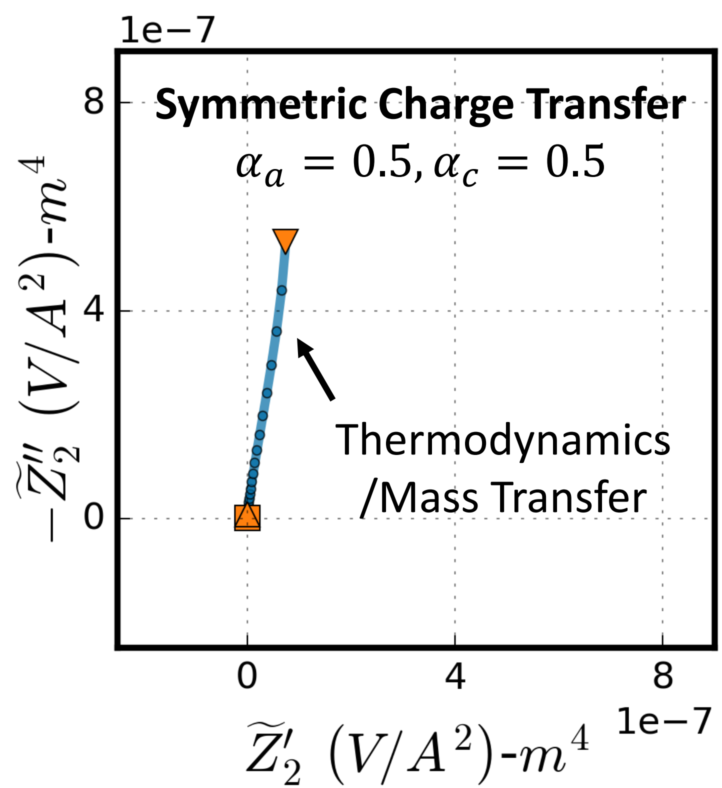


Standard literature parameters don’t capture second harmonic physics

Experimental

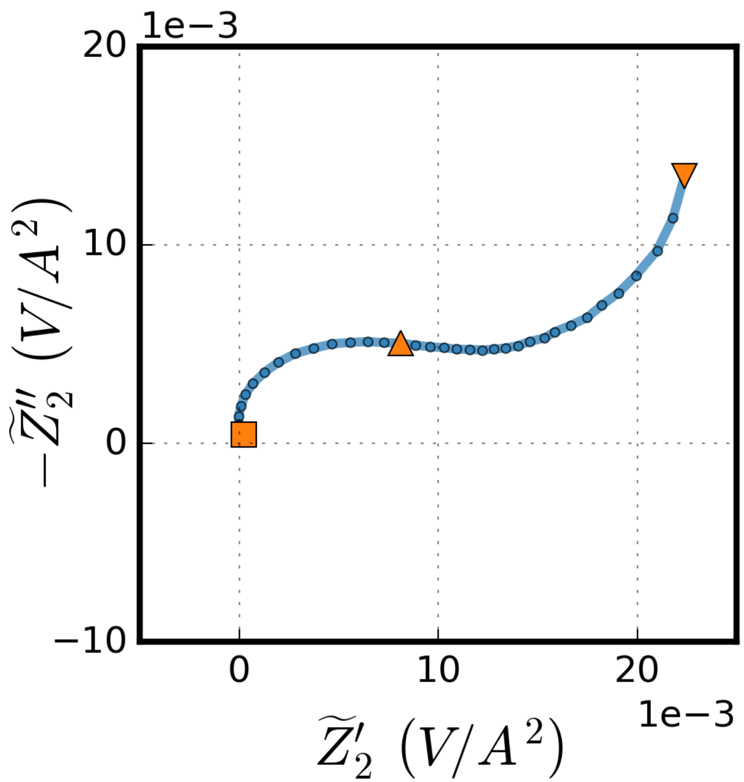


Computed

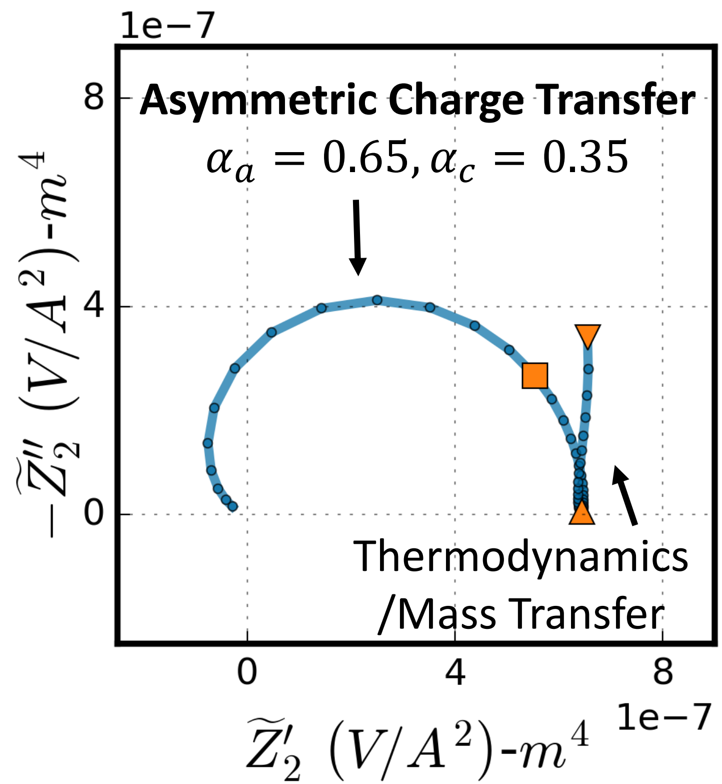


Changing single, symmetry parameter results in kinetic arc

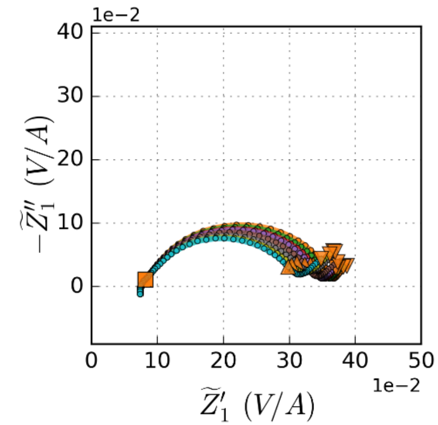
Experimental

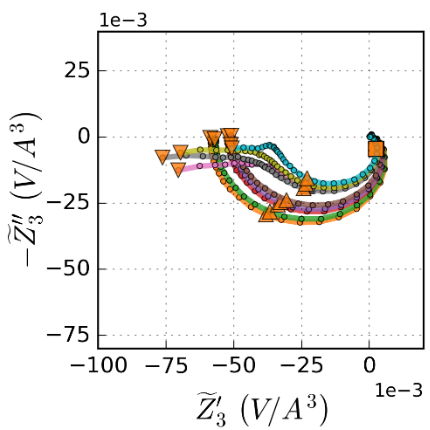


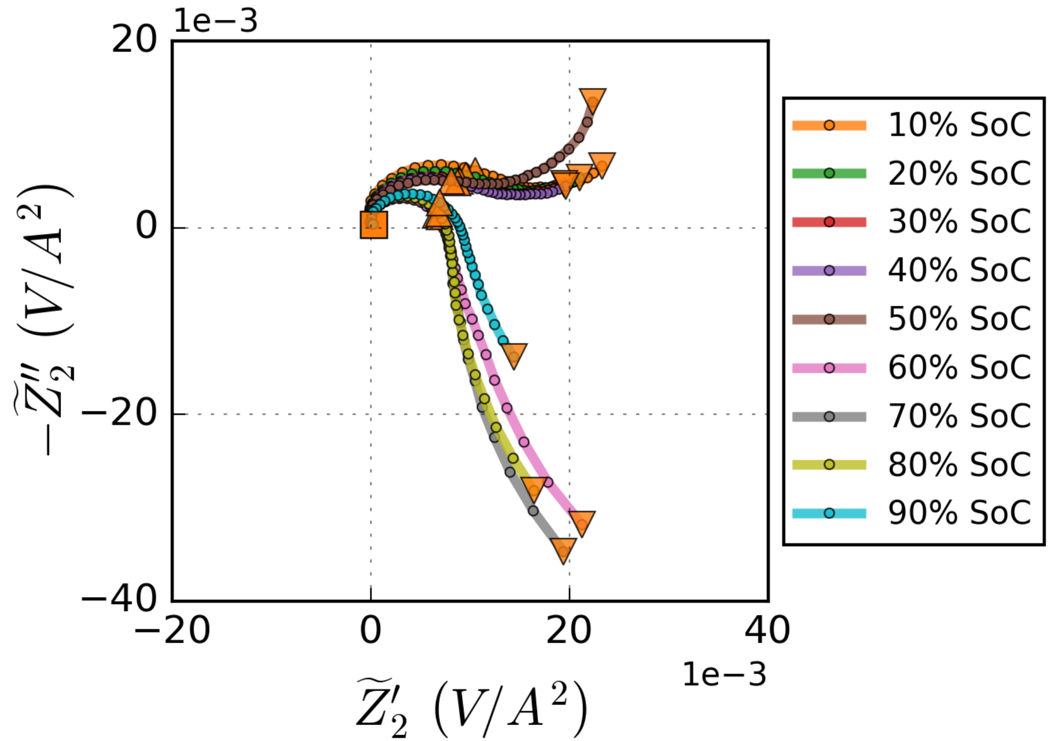
Computed



Nonlinear spectra are more sensitive to the battery's internal state







Nonlinear harmonics show sensitivity to varying internal states.

The next step: bringing together mathematical model and experiments

- Explore physics not captured in linear EIS

Second Harmonic Reaction Kinetics:

$$j_{f\,2,2}' = \frac{i_0(\alpha_a + \alpha_c)}{RT}\eta_{2,2}' + \frac{i_0\left({\alpha_a}^2 - {\alpha_c}^2\right)F}{4\,R^2T^2}\left({\eta_{1,1}'}^2 - {\eta_{1,1}''}^2\right)$$

- Insight into interactions between processes

Second Harmonic Overpotential:

$$\underbrace{\eta_{2,2}'}_{\text{Kinetics}} = \varphi_{2,2}^{s\prime} - \varphi_{2,2}' - \frac{dU}{dc^s}c_{2,2}^{s\prime} - \underbrace{\frac{1}{4}\frac{d^2U}{d{c^s}^2}}_{\text{Thermodynamics}}\underbrace{\left({c_{1,1}^{s\prime}}^2 - {c_{1,1}^{s\prime\prime}}^2\right)}_{\text{Mass transport}}$$

Sensitivity analysis will give insight into information content and inform experimental design.

Conclusion

- Nonlinear EIS has been useful in characterizing many other complex electrochemical systems. We are exploiting this for batteries!

- Bringing together harmonics simulations and experimental NLEIS measurements can enable:
  - More discrimination in physical models
  - Improved parameter estimation
  - Deeper insight into nonlinear processes like degradation

Acknowledgements

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