# Probing Model Sensitivity in Discharge Characteristics for a Li-$O_2$ Battery using Uncertainty Quantification

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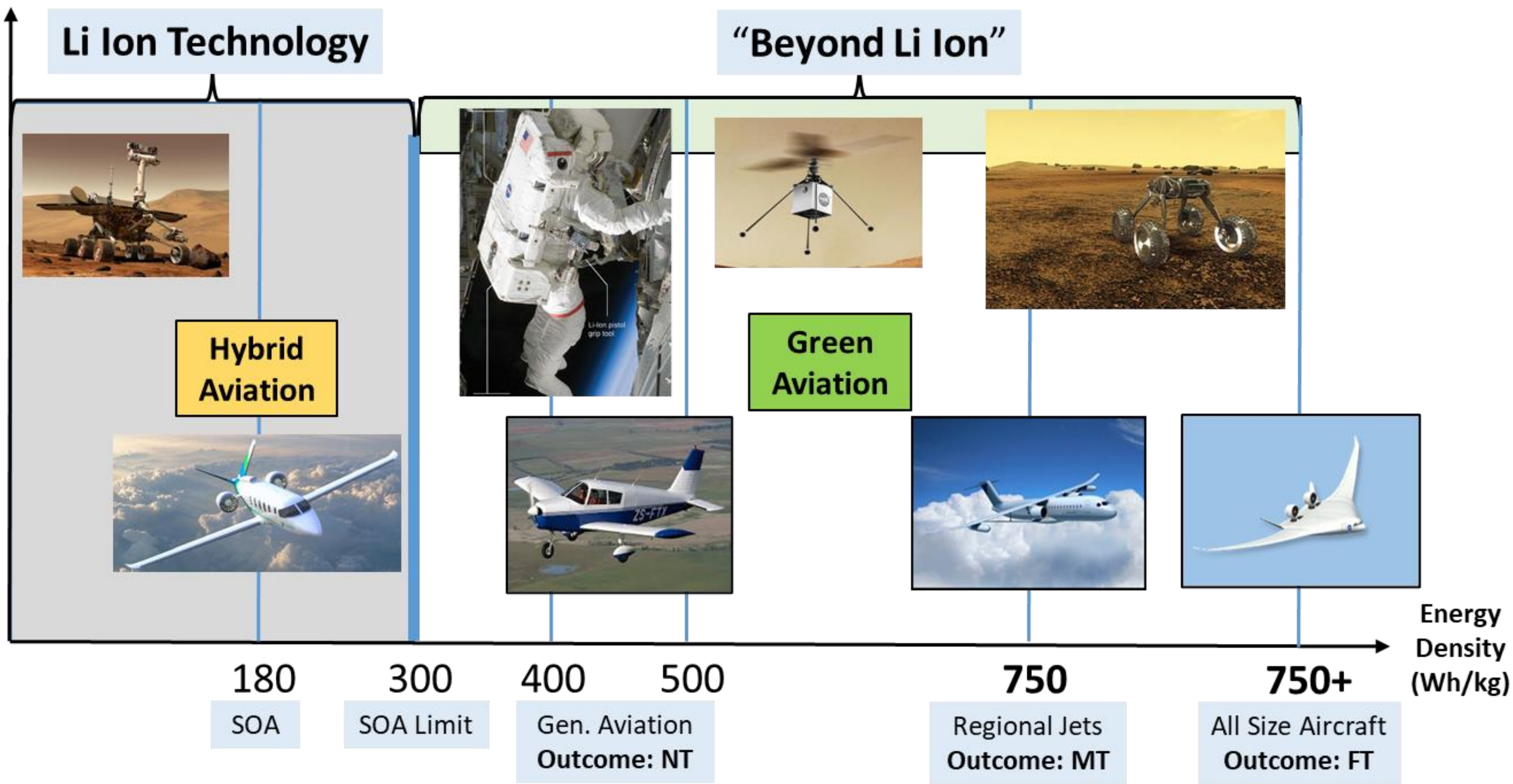
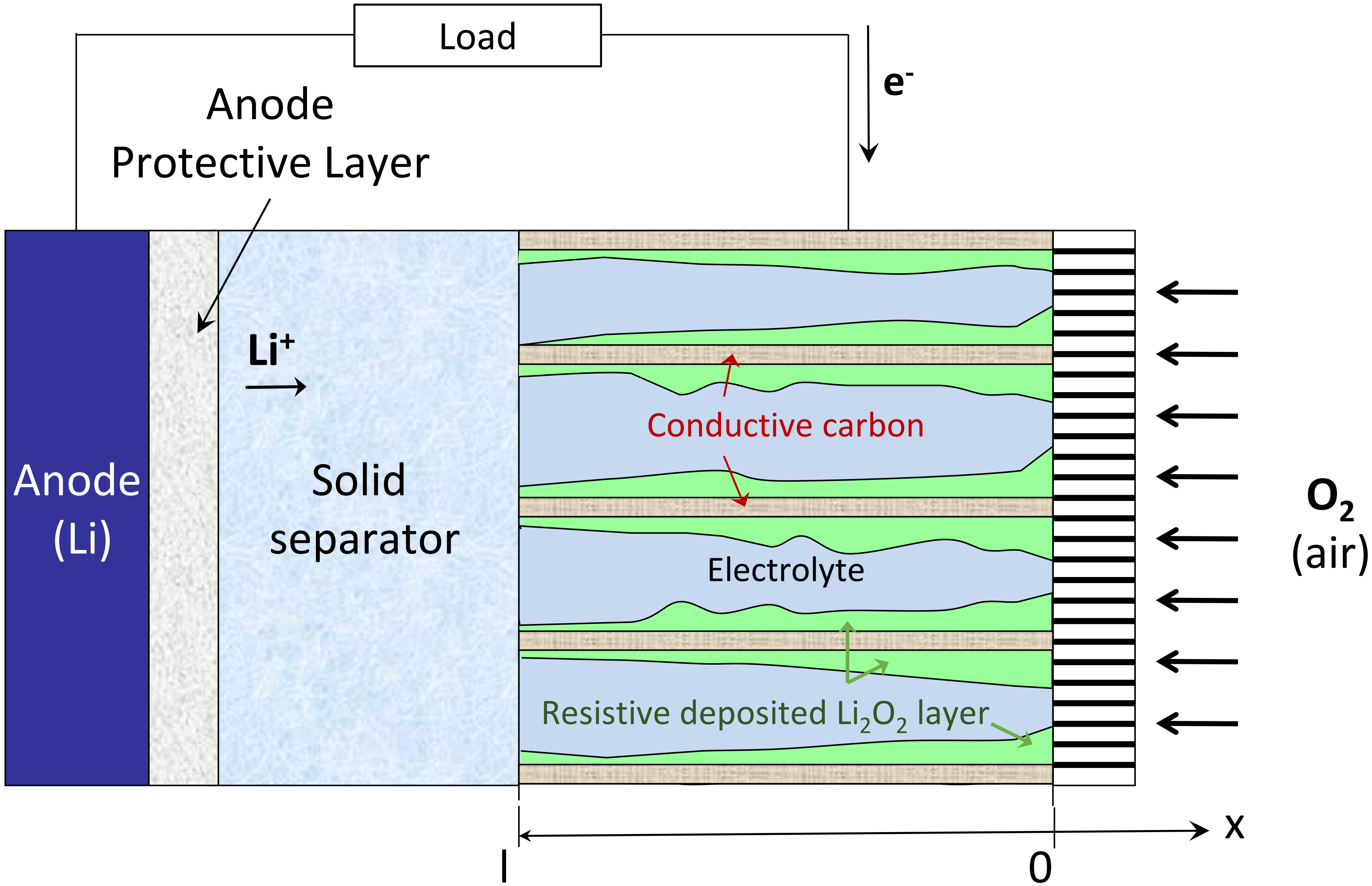
# Why Li-$O_2$?

## Major requirement is: High Energy Density

Other requirements are **rechargeable**, **safety**, power, recharge time, cost, etc.



# Introduction to Li-$O_2$ Battery




| | | |
|---|---|---|
| Discharge: | $\mathrm{Li} \rightarrow \mathrm{Li}^+ + e^-$ | $2\mathrm{Li}^+ + \mathrm{O}_2 + 2e^- \rightarrow \mathrm{Li}_2\mathrm{O}_{2(s)} \downarrow$ |
| Charge: | $\mathrm{Li}^+ + e^- \rightarrow \mathrm{Li} \downarrow$ | $\mathrm{Li}_2\mathrm{O}_{2(s)} \rightarrow 2\mathrm{Li}^+ + 2e^- + \mathrm{O}_2 \uparrow$ |

Mehta, M. & Andrei, P., 2014. *ECS Transactions*, 61(15), pp.39–55

# Computing Cell Potential (0D Model)

Total cell voltage:

$$\boldsymbol{V_{cell}(t) = E_{eq} - \eta_a - \eta_c(t) - \eta_{Li_2O_2}(t) - \eta_{other}}$$

$$\boldsymbol{\eta_{other} = 0}$$

Anodic overpotential:

$$\eta_a = 2V_T \sinh^{-1}\left(\frac{j_{\text{dis}}}{2j_{a0}}\right)$$

Cathodic overpotential:

$$\eta_c(t) = 2V_T \sinh^{-1}\left(\frac{\epsilon(t)}{a(t)}\frac{D_{O2}}{2\lambda(t)^2 k_c}\right)$$

$$\tanh\left(\frac{L_c}{\lambda}\right) = \frac{\lambda j_{\text{dis}}}{nFc_{O_2}\,\epsilon(t)D_{O2}}$$

Potential drop across $Li_2O_2$:

$$\eta_{\text{Li}_2\text{O}_2}(t) = R_{\text{Li}_2\text{O}_2}(t) j_{\text{dis}} \epsilon_{\text{Li}_2\text{O}_2}(t)$$

$$R_{\text{Li}_2\text{O}_2}(t) = \rho_{Li_2O_2} r_{p,0}\left[\left(\frac{\epsilon_{Li2O2}(\tau) + 1}{1 - \frac{2}{3}\epsilon_{Li2O2}(\tau)}\right)^{\frac{1}{3}} - 1\right]$$

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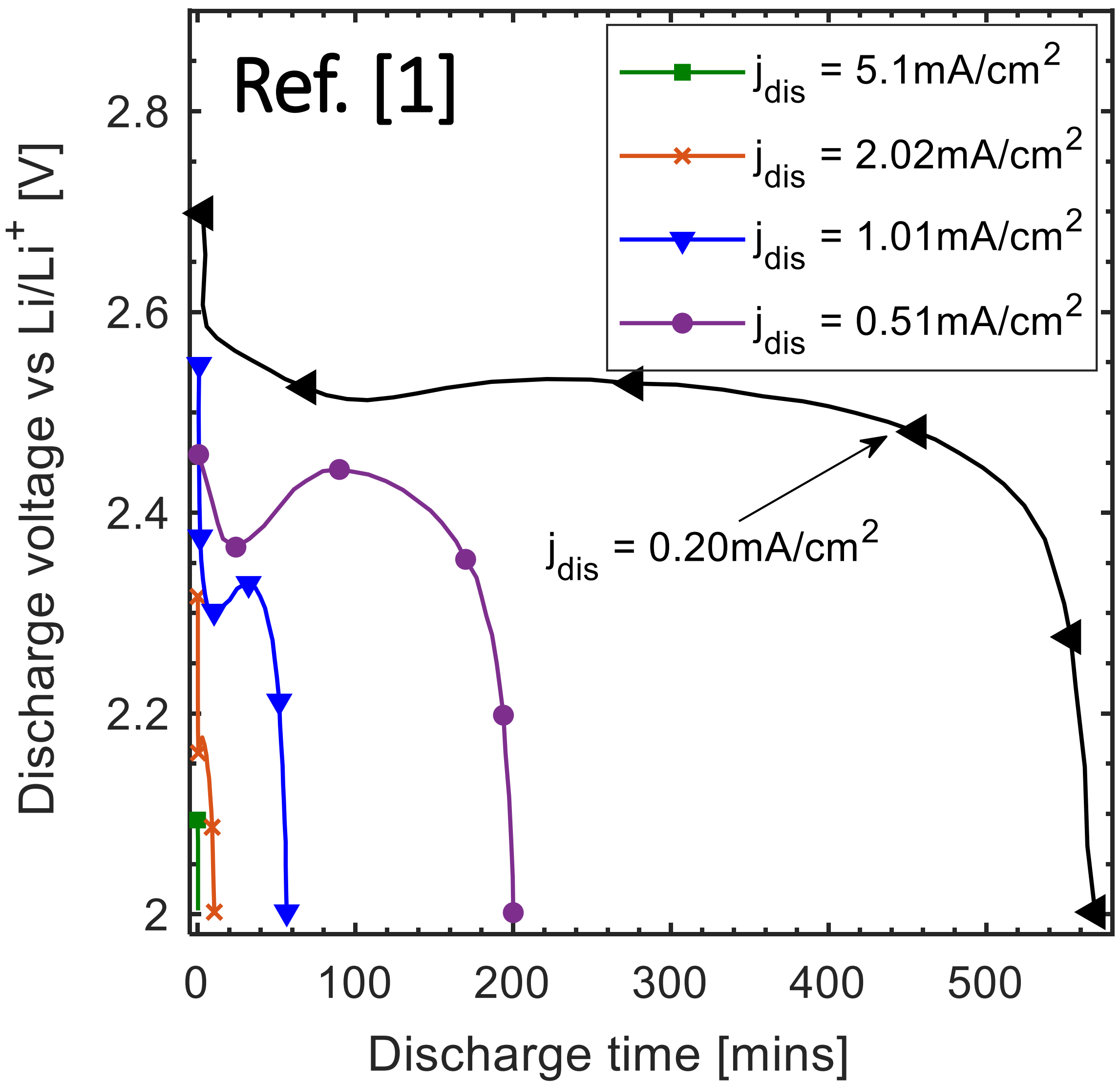
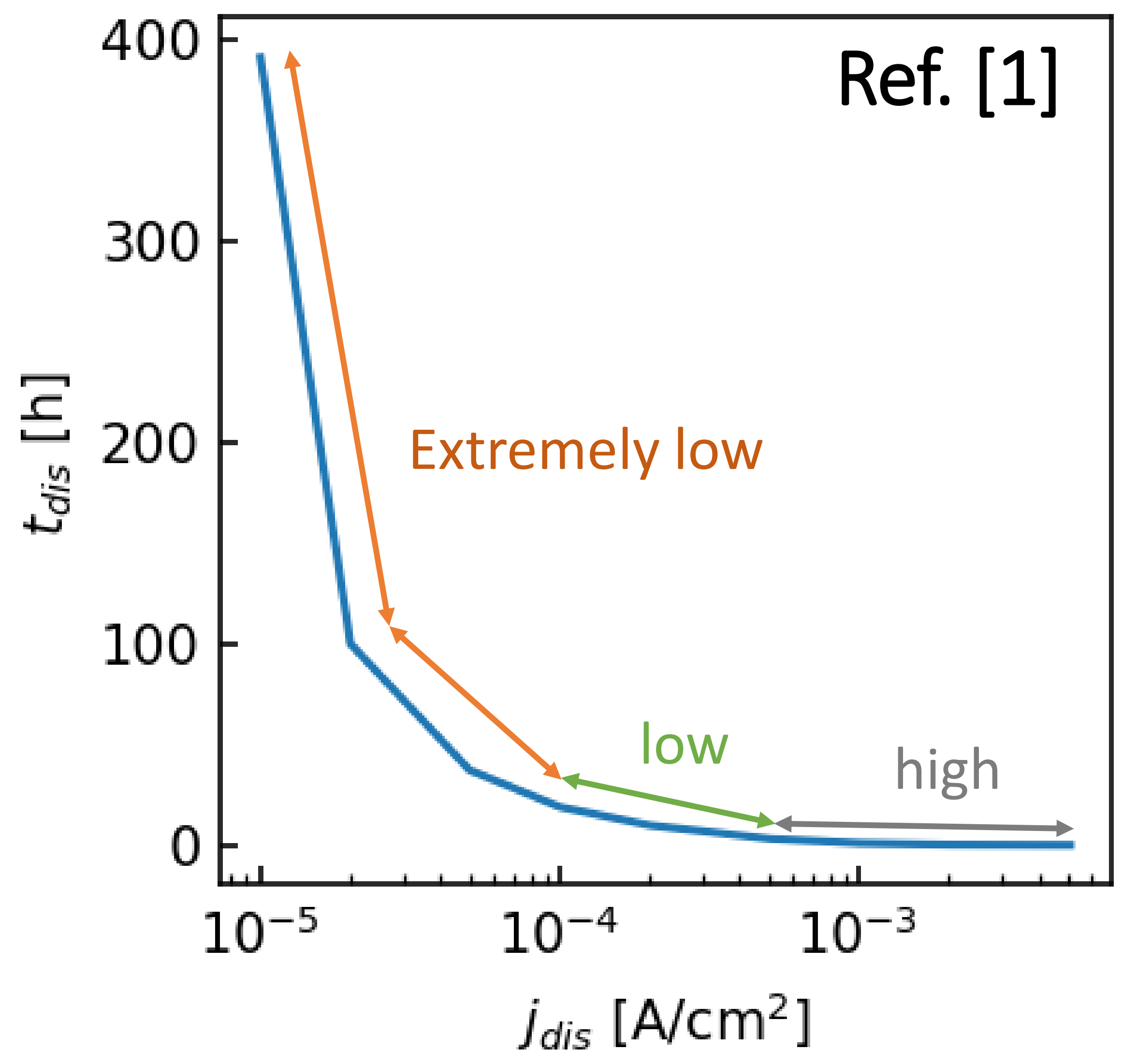
# Data used for Model Testing and UQ

## Different current densities lead to different deposition mechanism

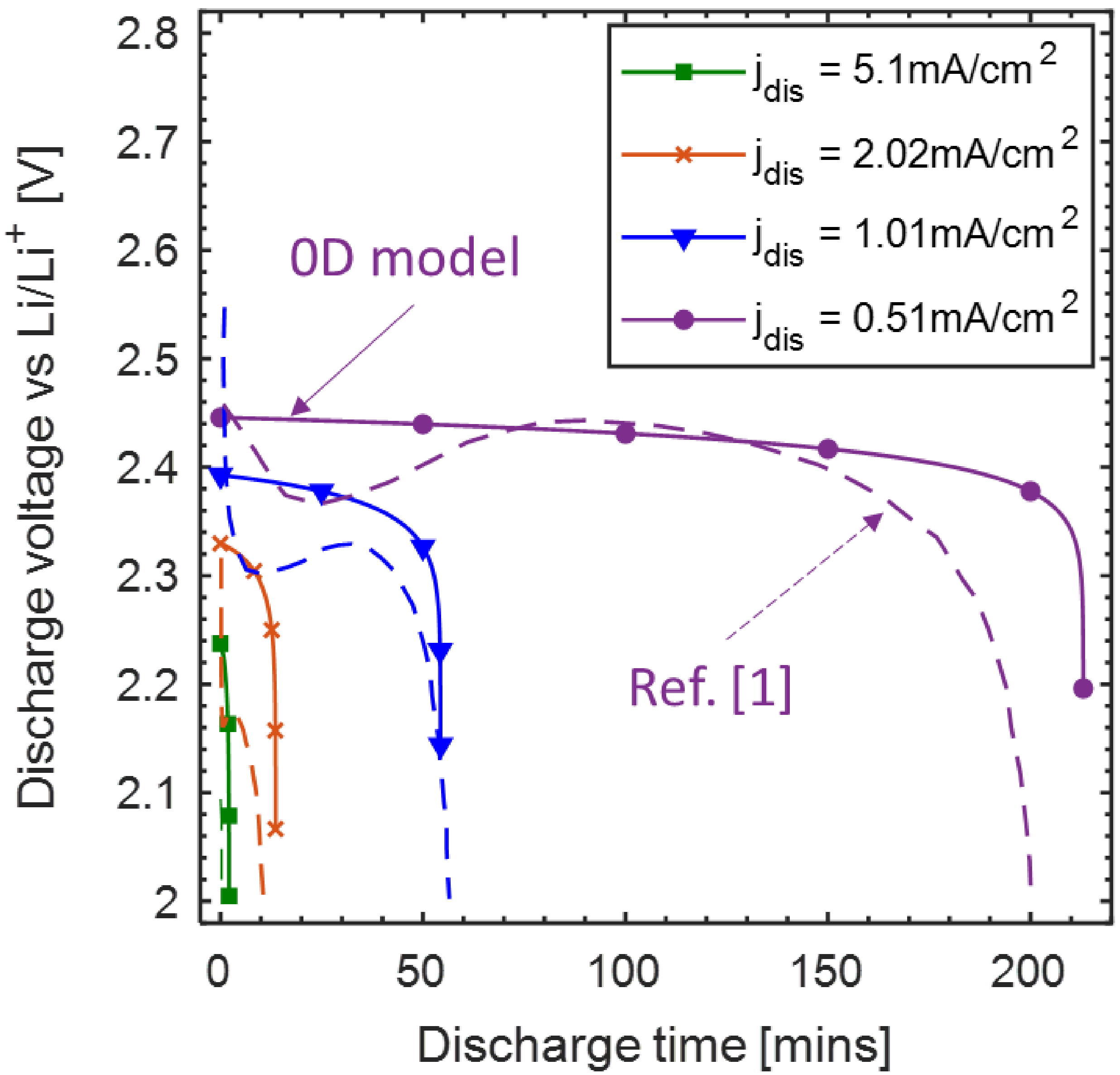


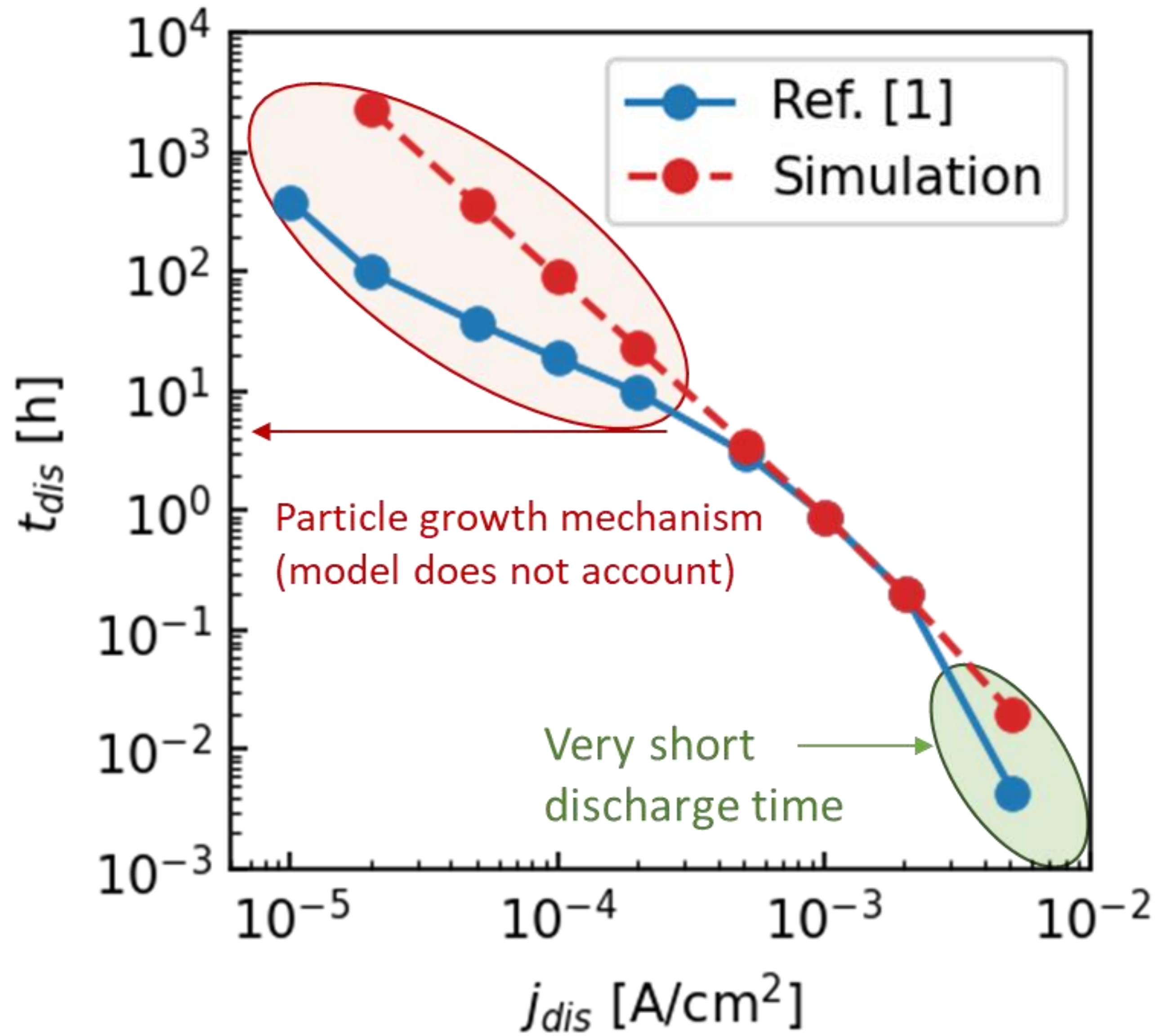




**A film deposition of lithium peroxide is often observed at high current densities**


[1] Gittleson, Forrest S., Reese E. Jones, Donald K. Ward, and Michael E. Foster. “Oxygen Solubility and Transport in Li–Air Battery Electrolytes: Establishing Criteria and Strategies for Electrolyte Design.” Energy & Environmental Science 10, no. 5 (2017): 1167–1179. DOI: 10.1039/c6ee02915a.

# Comparing the 0D Model with Experiments





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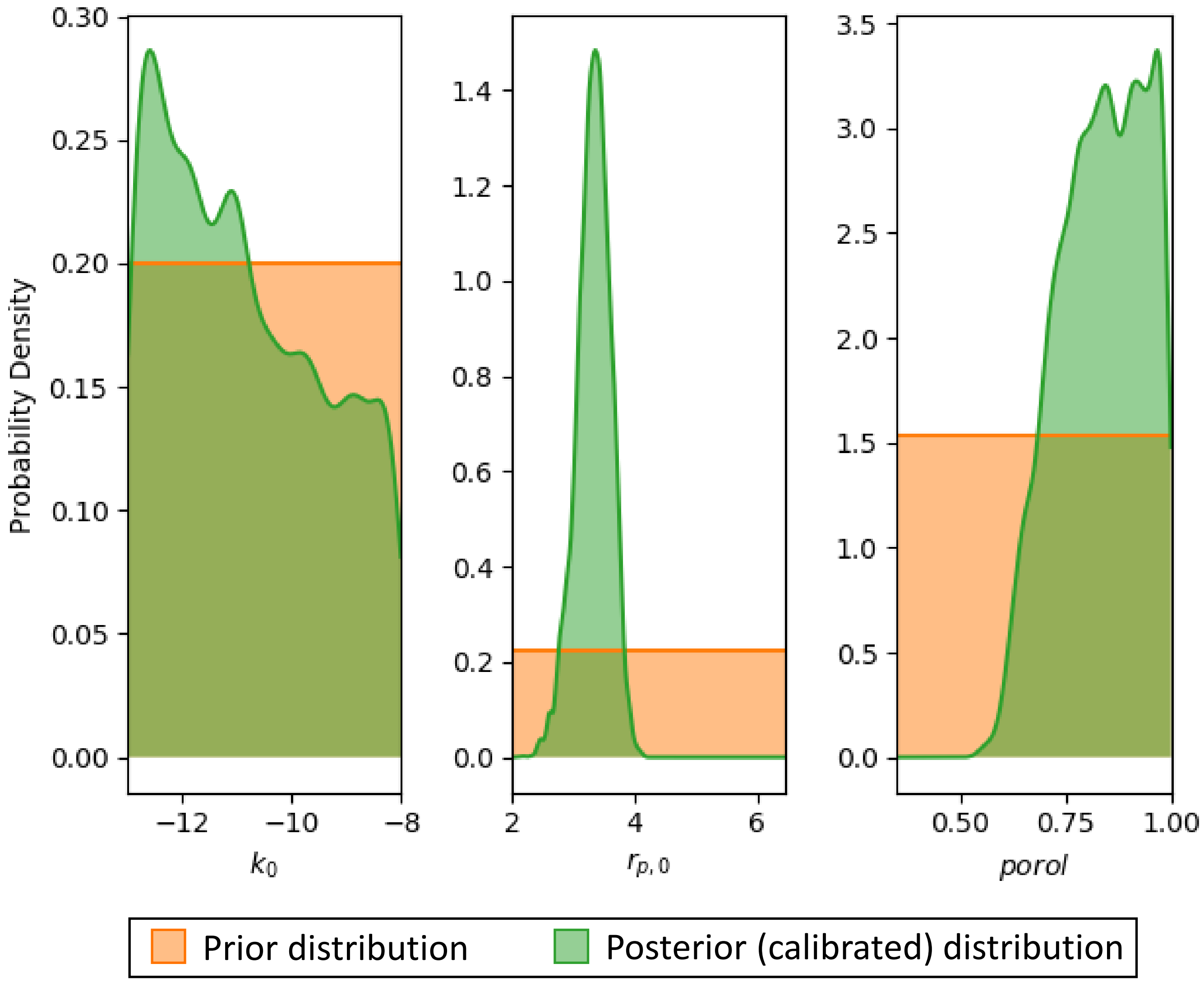
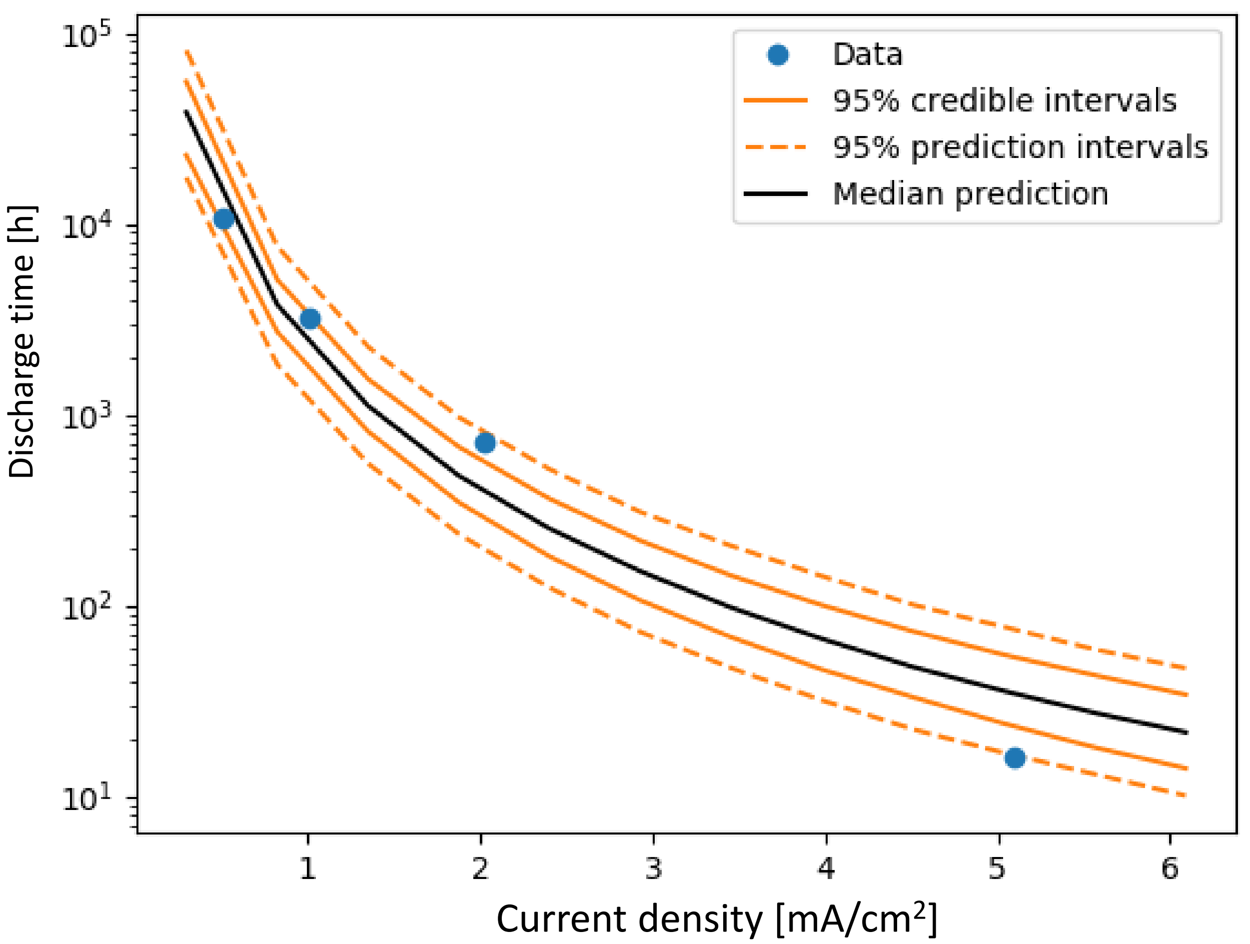
# Uncertainty Quantification

## Probabilistic calibration of model parameters



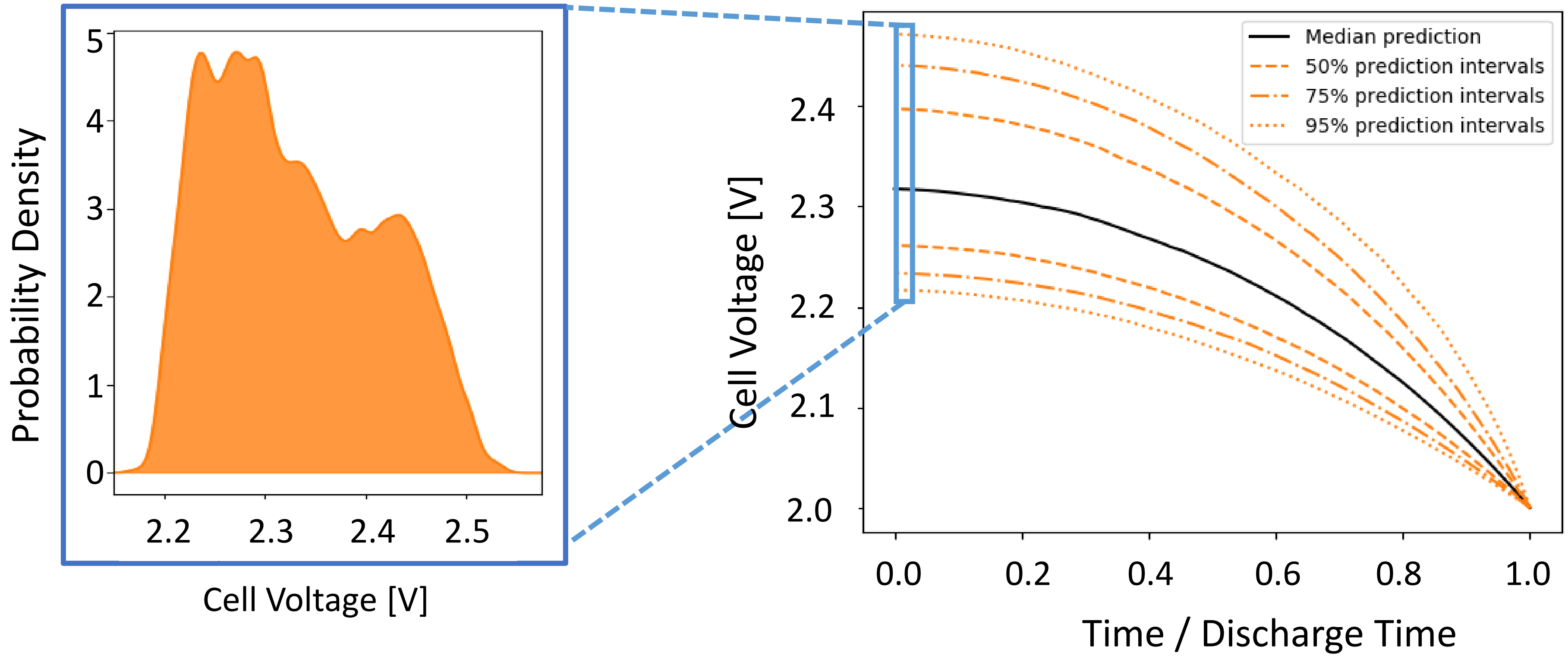

## Probabilistic prediction of discharge time



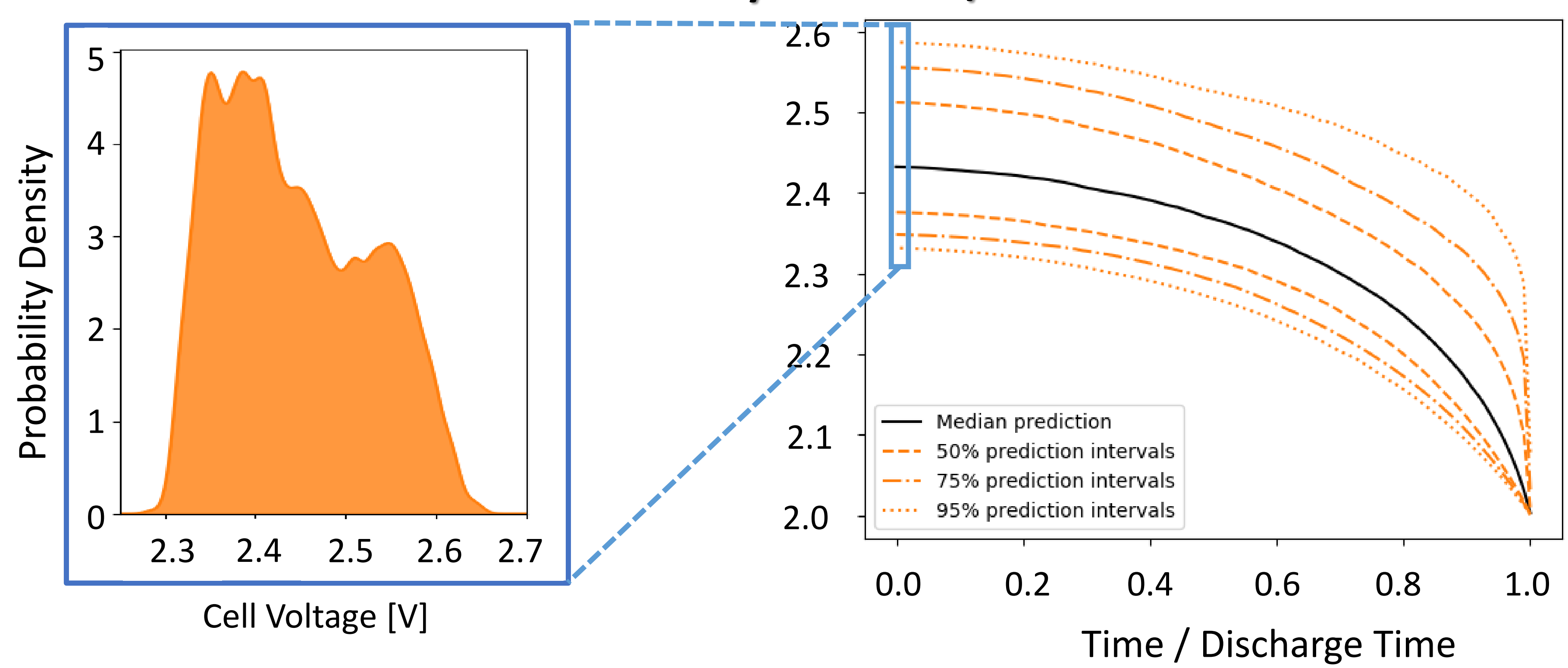

- Credible intervals contain the discharge time, with 95% probability
- Prediction intervals contain the value of a future data point (i.e., include effect of noise), with 95% probability

# Uncertainty in Voltage

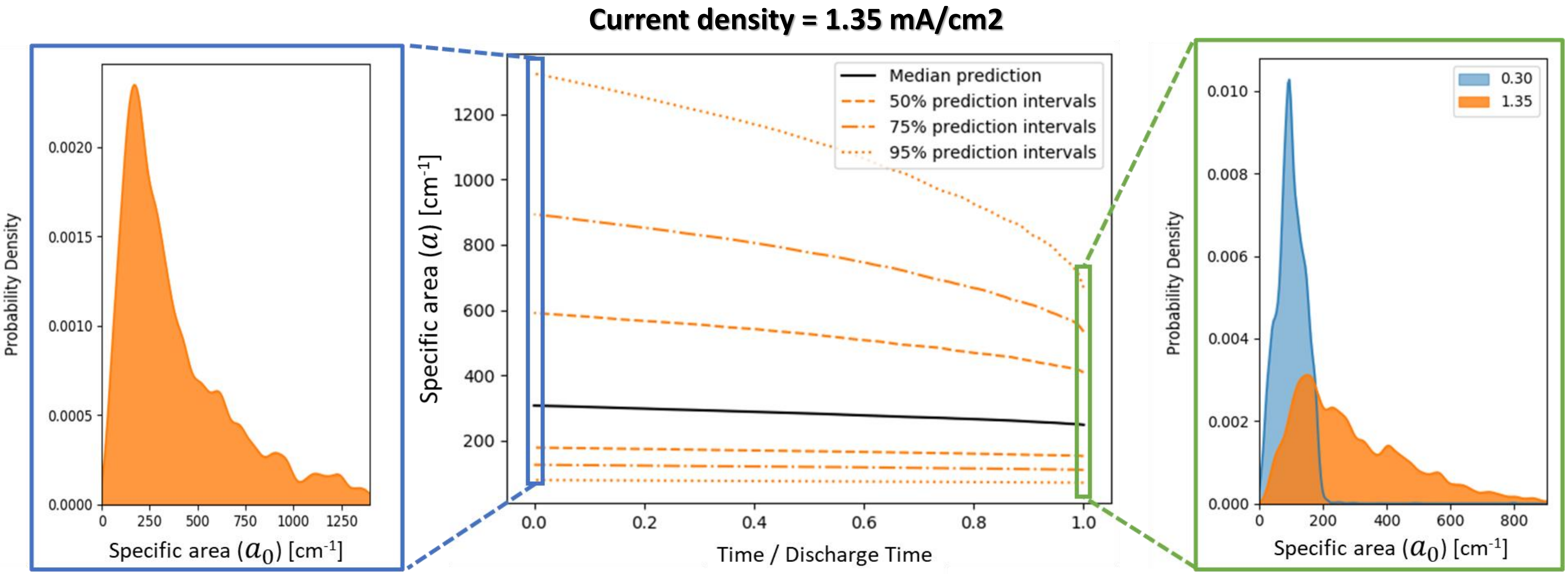
**Current density = 1.35 mA/cm2**




**Current density = 0.30 mA/cm2**



# Uncertainty in Specific Area



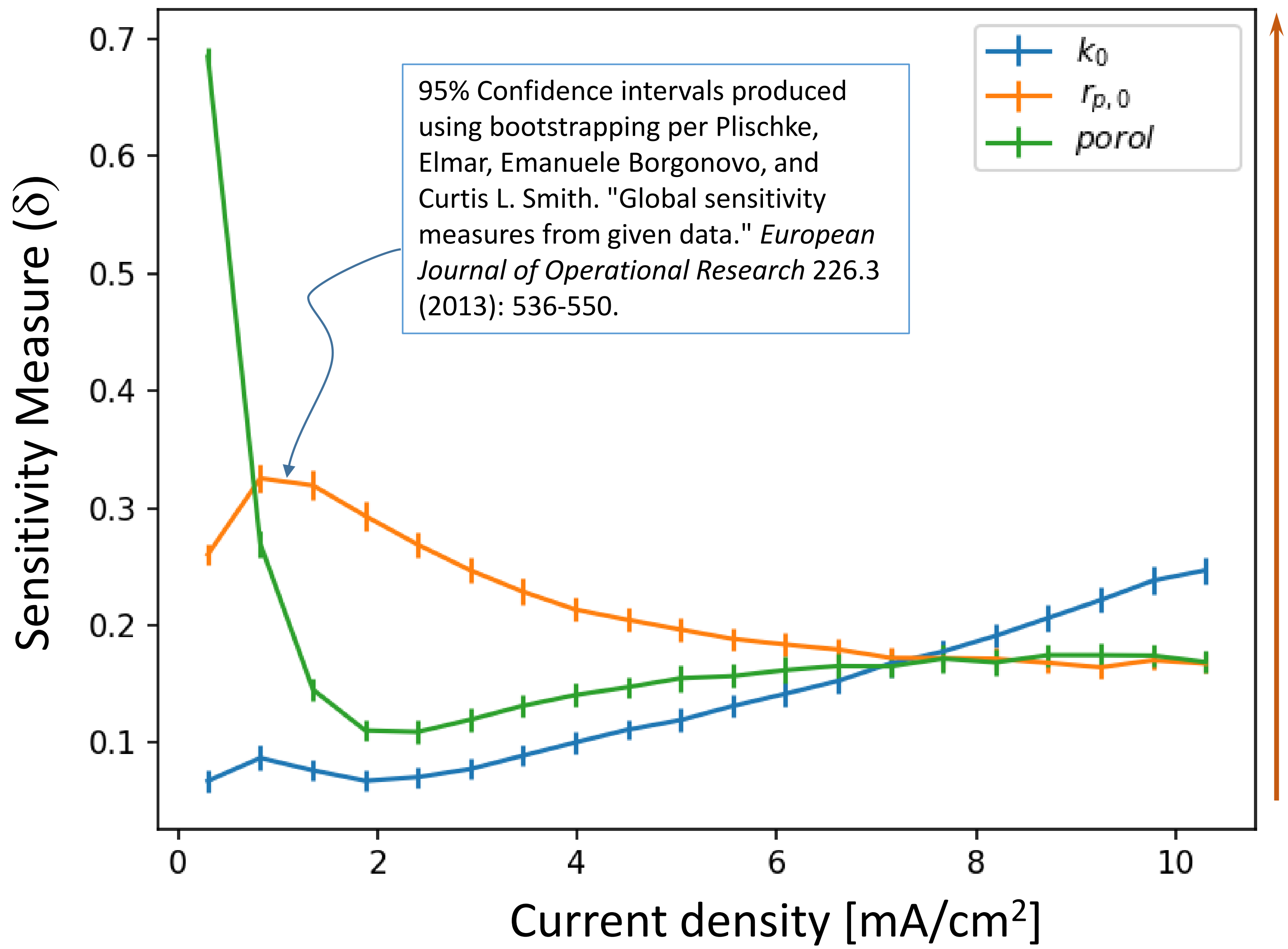

**Initial distribution**

**Final distribution**

UQ provides probability distributions of a random variable as it propagates through a model

# Global Sensitivity Analysis

## How does uncertainty in input parameters affect discharge time?



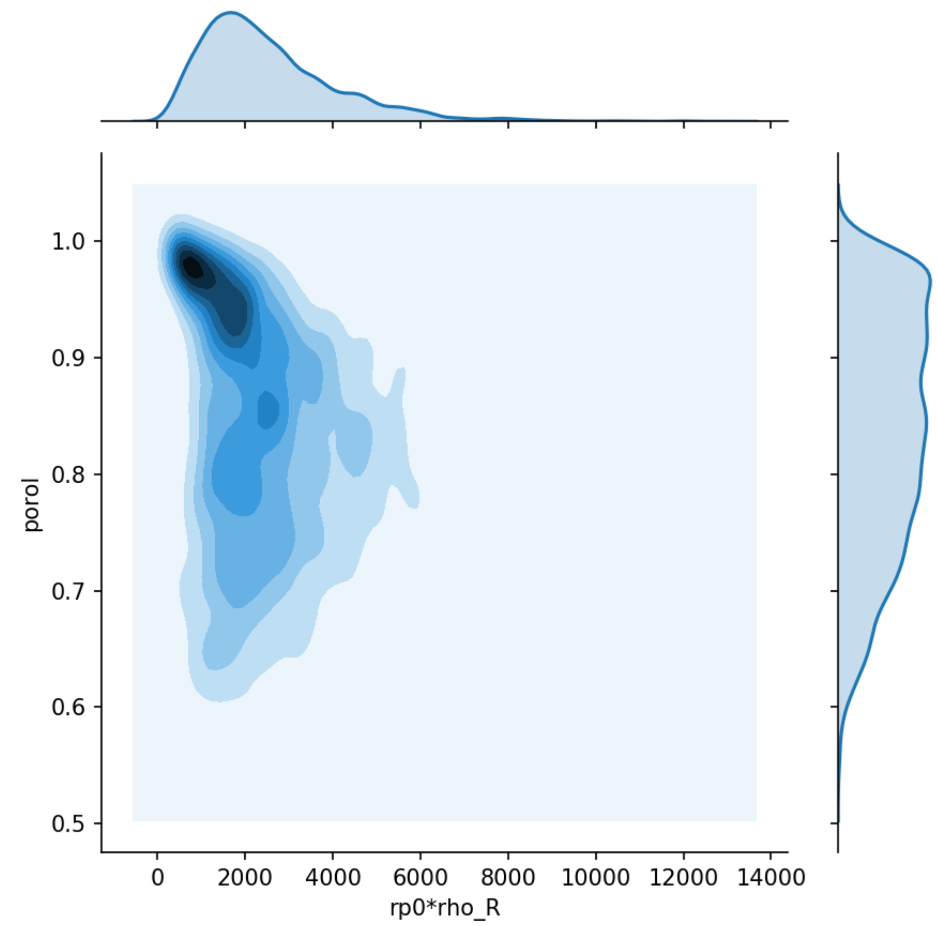

**The model is highly sensitive to porosity at low discharge currents, while it is sensitive to reaction rate at high currents**

Generated using the Python package SALib: Herman, Jon, and Will Usher. "SALib: an open-source Python library for sensitivity analysis." Journal of Open Source Software 2.9 (2017): 97. Specifically, the sensitivity measure used is the delta moment independent measure.

# Summary

## 1. Preliminary Work

- A 0D model is developed to simulate voltage response of a Li-$O_2$
- The uncertainty quantification framework is combined with a battery model to understand model biases
- UQ provides insights into the evolution in probability distributions (Bayesian framework)




## 2. Future Work

- Apply the UQ framework to other papers with more experimental data and other electrolytes
- Compare uncertainties between different microstructural, and lithium peroxide growth and resistivity models

# Backup Slides

# Parameters being Simulated

| Parameter | Value | Unit | Reference |
|---|---|---|---|
| **Constants** | | | |
| Open Circuit Voltage | 2.959 | V | Theoretical |
| Temperature | 298.15 | Kelvin | Experimental |
| $O_2$ diffusion coefficient (1M LiTFSI in TEGDME) | $0.814 \times 10^{-6}$ | $cm^2/s$ | Fitted |
| Area (areal) | 1.767 | $cm^2$ | Experimental |
| $O_2$ concentration (1M LiTFSI in TEGDME) | 1.016 | mM | Assuming $p_{O2} = 0.21$ |
| Cathode thickness | 235 | mm | Experimental |
| Anode current density | 0.617 | $A/cm^2$ | |
| **Variables** | | | |
| Specific area | 1998 | $cm^{-1}$ | Calculated |
| Porosity | 0.8 | - | Experimental |
| Electrical resistivity | 1.9 | MΩ/cm | Assumed |
| Cathodic reaction rate constant | $2 \times 10^{-12}$ | cm/s | Assumed |
| **Bounds** | | | |
| Specific area | $10^3 - 10^6$ | $cm^{-1}$ | |
| Porosity | $0.35 - 0.8$ | - | |
| Electrical resistivity | $10^6 - 10^{11}$ | Ω/cm | |
| Cathodic reaction rate constant | $10^{-8} - 10^{-13}$ | cm/s | |