Modelling Degradation in Lithium-Sulfur Batteries

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Anode Surface Reactions

Lithium Sulfur (Li-S) batteries currently deliver around **350 Wh/kg** instead of the theoretical 2700 Wh/kg due to various degradation processes [1]. Figure 1 shows the series of cascading reactions in the cathode that lead to the reduction/oxidation of sulfur species. Due to the presence of sulfur in different reduced states within the electrolyte, these species can diffuse through the separator and interact with the anode surface. These lead to two phenomena which cause degradation: **Polysulfide Shuttling** and **Solid Electrolyte Interphase (SEI) formation.**
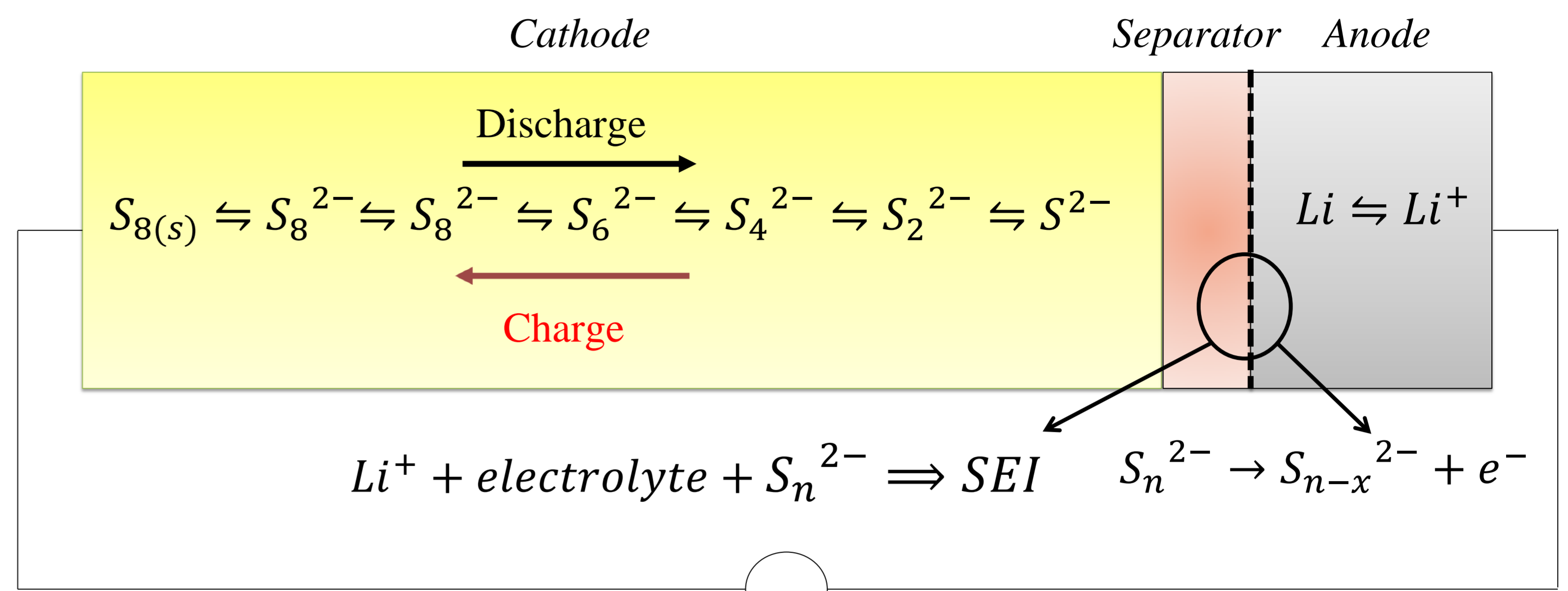

Figure 1. Li-S battery and anode surface reactions

SEI growth and Capacity fade

- Lithium metal anode reacts with the electrolyte and polysulfide species to form a Solid Electrolyte Interphase (SEI).
- If the SEI is not stable, the charge transfer resistance at the anode interface keeps increasing, causing a drop in potential.
- We extend a previously developed model [2] to include a metal anode, with an SEI at the surface. This modifies the overpotential in the Butler-Volmer equation at the interface to the following.
- $\eta = \Phi_s - \Phi_l - \Delta\Phi_{s,SEI} - E_{eq}$ where Φ_s is the anode surface potential, Φ_l is the electrolyte potential, E_{eq} is the equilibrium potential and $\Delta\Phi_{s,SEI}$ is the resistance due to the SEI.
- The modified potential curves are shown in Figure 2, where an increase in $\Delta\Phi_{s,SEI}$ causes a consistent drop in potential.
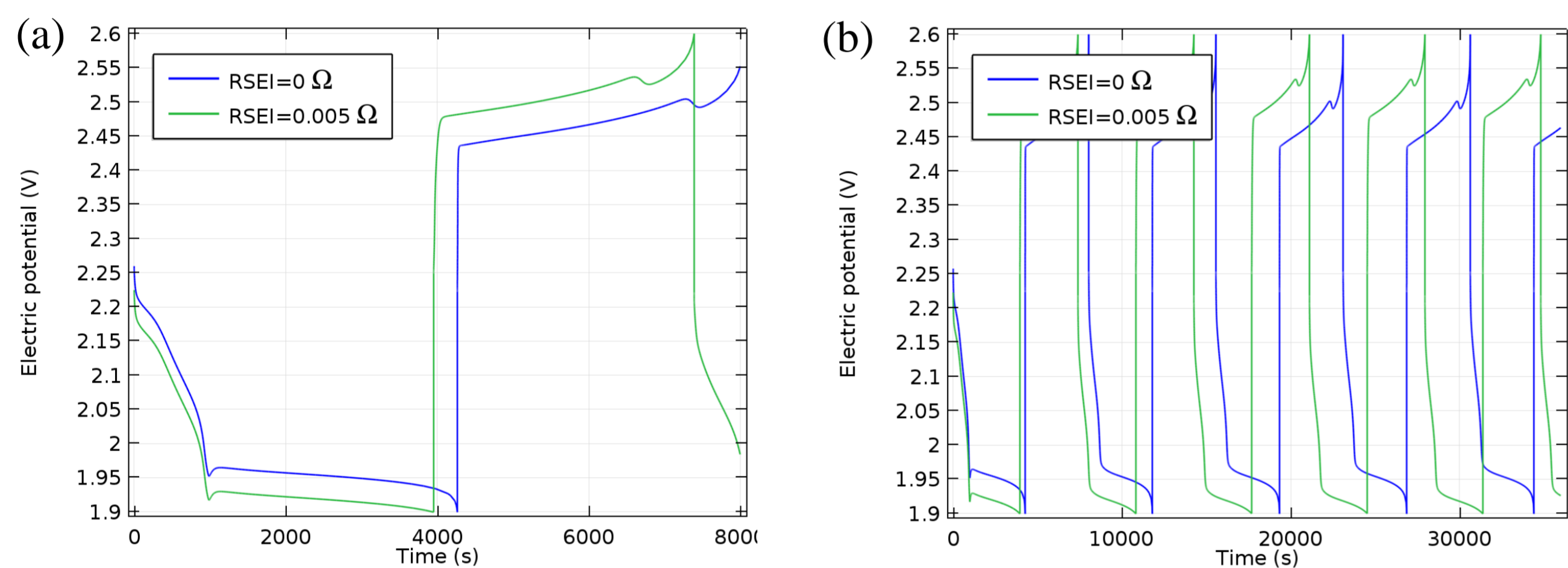

Figure 2. Voltage profile at different values of SEI resistance (a), and voltage profile over charge and discharge at constant SEI (b).

- However, in a real battery the SEI grows over time. Hence, it is more accurate to have the resistance due to the SEI modelled as a function of time $\Delta\Phi_{s,SEI} \equiv f(t)$
- The addition of a time dependent SEI leads to a gradual decrease in the capacity which is reflected in the voltage profile on cycling
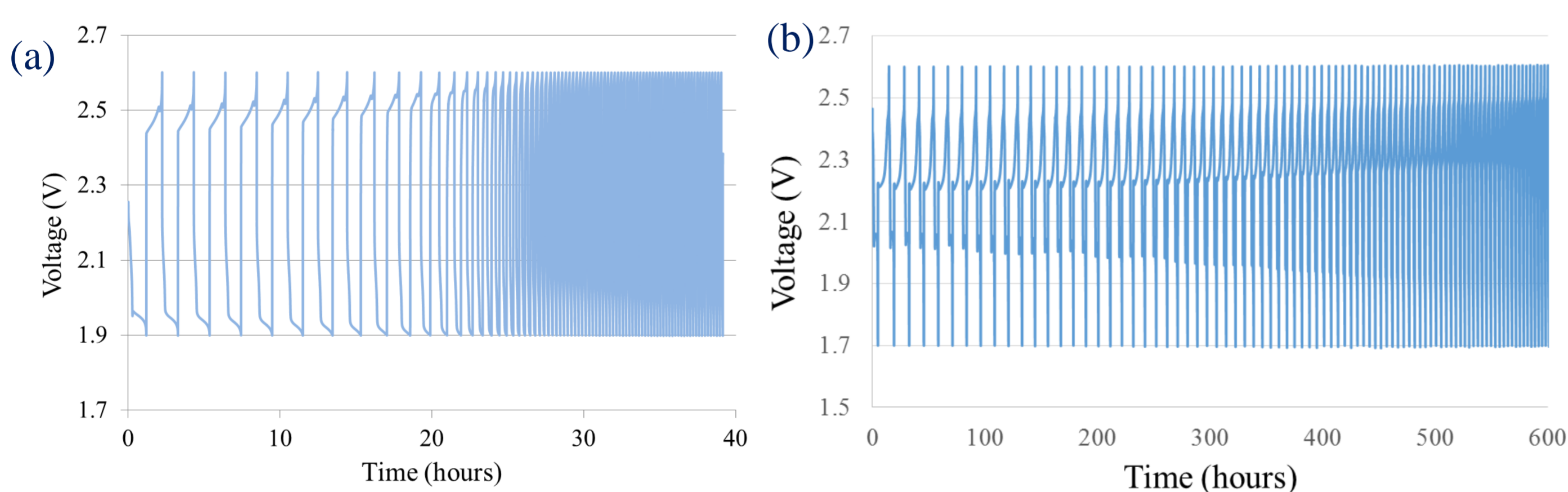

Figure 3. Voltage profile from model (a) compared to experimental results (b).

References:
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2. K. Kumaresan, Y. Mikhaylik, R.E. White, 'A Mathematical Model for a Lithium-Sulfur Cell', (2008), Journal of the Electrochemical Society, 155(8), A576-A582
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Polysulfide Shuttle and Heat generation

- During charging, higher order sulfur species diffuse to the anode surface and get reduced to lower order species, counter to the charging current.
- This parasitic **'shuttle current'** prevents complete charging by continuously flowing, which leads to **rapid heat generation** and also thermal runaway, even after current is removed.
- Following [3], we use the equation of rate of production of polysulfide species $[c_{ps}]$, where k_s is the shuttle constant, which estimates the fraction of polysulfide species which is part of the total charge current, i_{ch}.
- $\frac{\partial[c_{ps}]}{\partial t} = i_{ch} - k_s[c_{ps}] \quad [c_{ps}] = [c_{ps}]_0 e^{-k_s t}$
- The rate of heat generation is modelled as $\dot{q} = Bk_s[c_{ps}]$, where B is a fitting parameter. The battery pack is modelled using the standard heat equation with convective boundary conditions.
- First the model is run without current, in order to fit the shuttle constant and the convective coefficient to match experimental results.
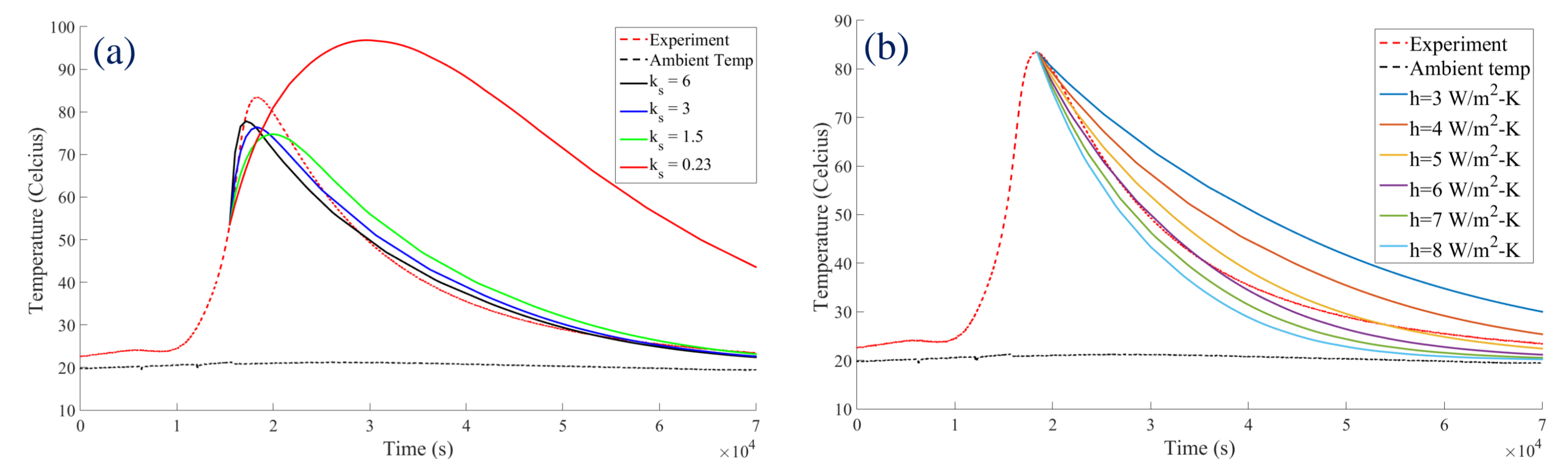

Figure 4. Fit of shuttle constant (a) and convection coefficient (b).

- The temperature profile of the battery pack indicates a small temperature gradient exists.
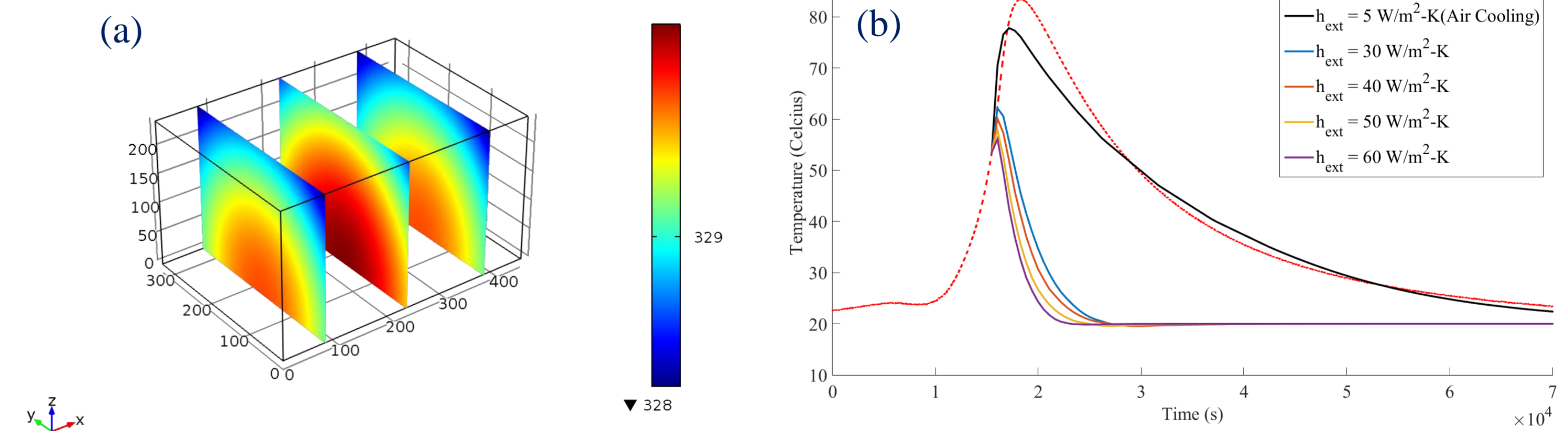

Figure 5. Battery pack temperature profile (a) and effect of forced convective cooling (b).

- Finally we simulate use forced convective coefficients, which shows that **active cooling can help mitigate the effect of shuttle current.**

- The fully fitted model, with charging current present (Figure 6). Active cooling has a greater effect since it is effective from the start of charge.
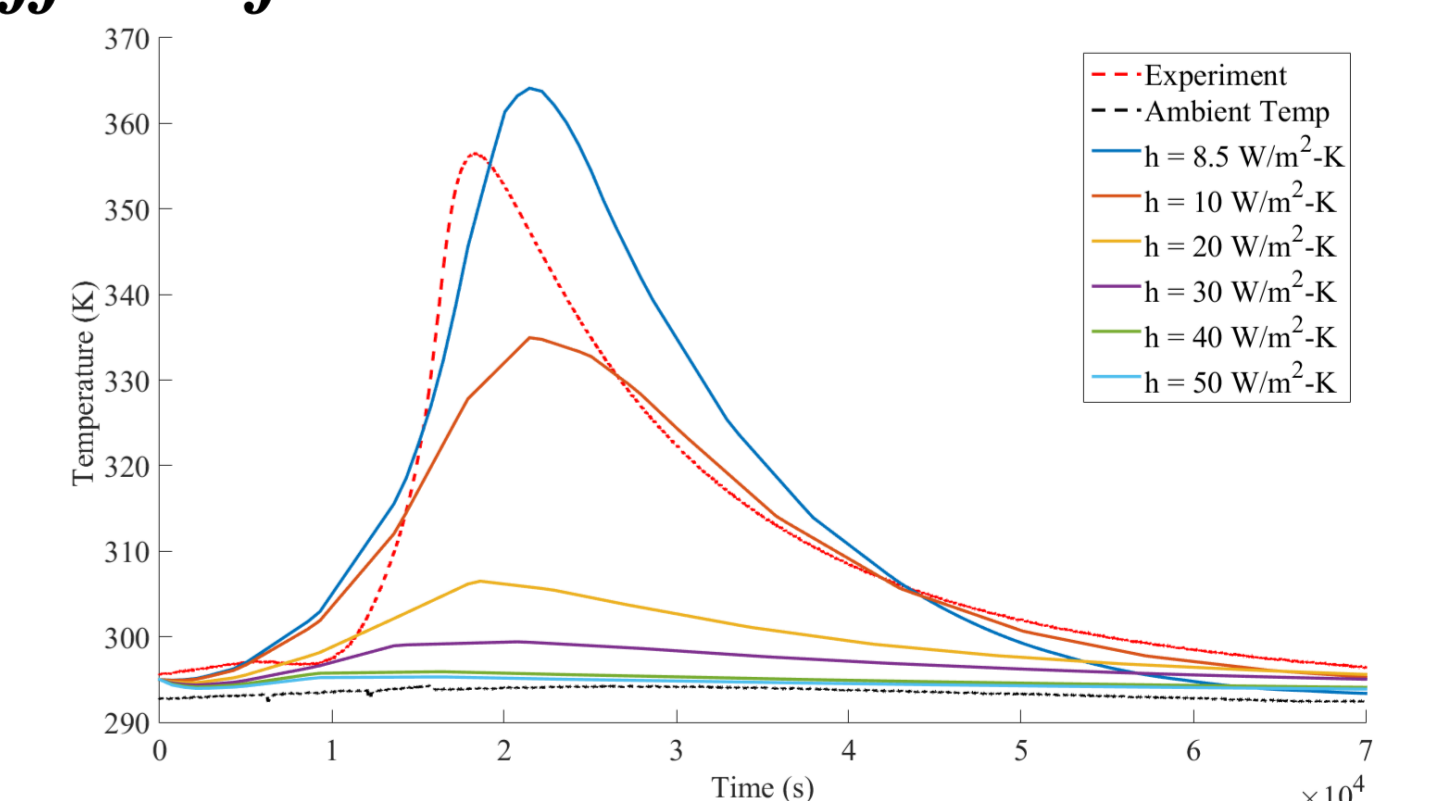

Figure 6. Complete model with charging current.