Abstract

• Constructing reaction networks for the thermal runaway of Li-ion batteries is time-consuming and potentially misses reaction pathways. Automating the simulation process allows for quick analysis of each electrolyte environment.

• NetGen was used to generate reaction networks for DMC, EC and a DMC/EC mix undergoing oxidation. Literature values were used to solve the system of rate equations under standard runaway conditions at 300 °C.

• The network was verified against the major combustion products of each system. CO₂, H₂O, and H₂ were generated but CO was missing. This indicates a deficit of reaction classes in the network generator.

• The concentration profile at 300 °C showed concentrations of all products near zero. This matches experimental conditions showing uncatalysed combustion begins at 700 °C.

• Further work on building reaction classes and computationally calculating kinetic parameters is recommended to develop automated reaction networks as a method of predicting temperature rates and gas emissions.

Generating Reaction Network

• The DMC network generated 91 species and 162 reactions. The major combustion products of H₂O, H₂, dimethyl ether, ethene and CO₂ were generated. CO was still absent.

• The EC network generated 247 species and 434 reactions. The major combustion products of H₂O, H₂, dimethyl ether, ethene and CO₂ were generated. CO was still absent.

• The EC/DMC network generated 505 species and 912 reactions. Most of these reactions were recombinations of EC and DMC radicals. The major combustion products of H₂O, H₂, dimethyl ether, ethene and CO₂ were generated but not CO or acetylene.

• Cross referencing with PubChem, 46 of the DMC network species have been characterised, 72 EC species and 266 in the DMC/EC network.

• The DMC/EC network generated CO₂ but only included one of the four pathways present in combustion.

Motivation

• Thermal runaway (overheating) is a major safety concern for Li-ion batteries.

• During thermal runaway, the components of the battery break down in a large reaction network, releasing noxious gases and propagating fire.

• Experimental research struggles to identify all gases produced, necessitating computational modelling.

• Computational modelling allows prediction of thermal runaway rates, and segregation of which components are responsible for each step and any modification of simulated reaction conditions.

Kinetic Modelling

• The kinetic parameters for the reactions were obtained from a mix of computational and experimental papers. All were calculated for the gas phase at 300 °C and 1 atm.

• The percentage of reactions in the networks with existing literature ranged from 5-20%. For the remaining reactions, an average activation and pre-exponential factor was used for the reactions of that reaction class.

• The concentration profiles at 300 °C generated using Parest had no products with a concentration higher than 10⁻²⁶ mol dm⁻³ at 700 s. Some concentrations were negative (< 10⁻⁵⁸ mol dm⁻³) indicating a concentration of 0 with a slight margin of error in the Double-Precision Differential or Algebraic Sensitivity Analysis (ddasac) algorithm.

• Oxidation only has oxygen initiation (carbonate+ O₂ → carbonate + HO₂) as the preliminary step, missing homolysis and decarboxylation, rationalising the low concentrations.

• The low concentrations is consistent with the experimental data showing combustion begins at ≈ 900 °C.

Impact / Next steps

• Build a network generator with the correct reaction classes for electrolyte decomposition.

• Use DFT and molecular dynamics to calculate the kinetic parameters for the reactions under battery conditions.

• Test the concentration profile against experimental conditions at multiple temperatures and concentrations.

References


Charles James is studying Chemistry with Maths at St Andrews. Interested in Physical Chemistry, specifically computational modelling of solid-state materials using DFT and physical modelling. Aspiring to study towards a PhD in Physical Chemistry leading into an academic career in Chemistry.

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CJ0 Motivation:
Once network rules are generated, new electrolyte compositions can be immediately analysed. Much safer, can spot dangerous cells before experimental research is conducted.
High accuracy: site accuracy
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