Reaction Networks for Li-Ion Electrolytes: A Step Beyond Experimental Research

Electrolyte Decomposition Reaction Networks & Kinetic Modelling using DFT/Experimental Data

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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. CO_2, H_2O and H_2 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 H_2O, H_2 and ethane were detected, but CO_2 and CO were missing.
- The EC network generated 247 species and 434 reactions. The major combustion products of H_2O, H_2, dimethyl ether, ethene and CO_2 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 H_2O, H_2, dimethyl ether, ethene, ethane and CO_2 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 CO_2 but only included one of the four pathways present in combustion.

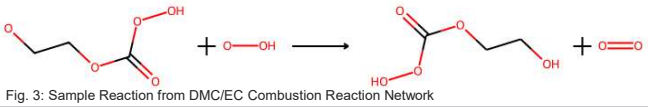

Fig. 3: Sample Reaction from DMC/EC Combustion Reaction Network

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^{-23} mol dm^{-3} at 700 s. Some concentrations were negative (< -10^{-59} 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.c only has oxygen initiation (carbonate+ O_2 → carbonate· + HO_2) 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.

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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 easy modification of simulated reaction conditions.

Fig. 1: Li-Ion Battery under Thermal Runaway

Methods

NetGen used an oxidation network generator with 19 reaction classes to simulate decomposition of ethylene carbonate (EC), dimethyl carbonate (DMC) and an EC/DMC mix in the presence of oxygen. Kinetic parameters were extracted from literature for each reaction in the network and used to build a kinetic model from the system of rate equations. The network was simulated at 300 °C, 1 atm. using Parest. The networks were visualised with Cytoscape.

Fig. 2: Kinetic Modelling Process

Conclusions

- Multiple automation programs were created to enhance research productivity. This would allow future researchers more time to focus on calibrating the network generator and computational calculation of kinetic parameters.
- The reaction network was able to identify some of the major combustion products (CO_2, H_2O, H_2) with simple bonding, but was unable to identify the products with triple bonds or zwitterions (CO). NetGen also did not simulate homolytic cleavage or ionisation reactions.
- The concentration profile showed all products with a near-zero concentration after 700 s at 300 °C. This is expected because experimental combustion studies of carbonate electrolytes show decomposition begins at 700 °C. The activation energies in a battery would be lower because of adsorption to the electrodes but there was no literature values under these conditions for most reaction classes.

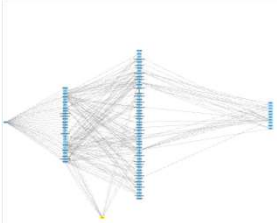

Fig. 4: DMC Combustion Reaction Network

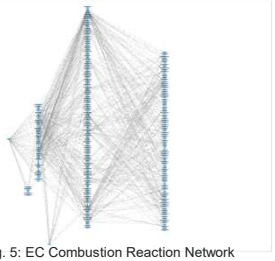

Fig. 5: EC Combustion Reaction Network

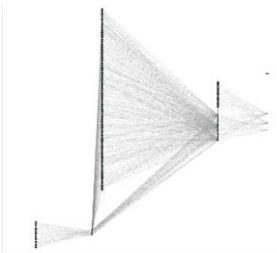

Fig. 6: DMC/EC Combustion Reaction Network

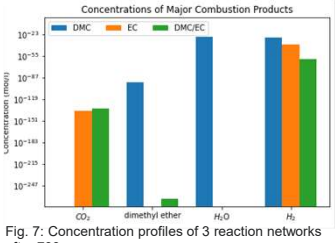

Fig. 7: Concentration profiles of 3 reaction networks after 700 s

References

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- E. Koninckx, J. G. Colin, L. J. Broadbelt and S. Vernuccio, *ACS Engineering Au*, 2022, **2**, 257–271. graph

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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Slide 1

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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