Building better batteries through electrochemical modelling.

Modelling Electrochemical Cell Reactions

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Abstract

By developing scalable electrochemical modelling software, I have been able to assess and evaluate the efficiency of a wide collection of cells under a range of criteria, highlighting a select group to which I can now recommend for further, more-specialised research. From my results, I have not only demonstrated the scope of efficient alternatives to Lithium-Ion battery variations but have also documented the general behaviour of electrochemical cells along with details for hundreds of other specific configurations. Although there are many factors which cannot be practically considered when modelling such a large pool of data, my results have shown clearly that certain configurations show greater potential in terms of capacity, efficiency and energy density than others, streamlining the research and development process and ultimately aiding in the necessary advancement of battery technology.

Data Generation

Beginning as a simple script which modelled a single cell under pre-defined conditions, the Data Generation software has grown to become an incredibly comprehensive and useful tool. Named ECMS (Electrochemical Cell Modelling System), it generates a comprehensive index of redox models under various conditions with the aim of highlighting the most efficient and practical battery types for specific situations. Its flexible architecture allows the database to easily scale as more electrode data is inputted, enabling the software to create even larger catalogues in the future with no code modifications.

The python-based program is structured as five primary modules; an executable response module (ECMS), an initialisation module (INIT), an environment configuration module (SEC), a data generation module (DGS), and a chemical syntax decoder module (ECMS_DECODER). The raw data which is produced is stored in a MySQL Database which is hosted on a local server by default (this, among other values, can be easily edited via the application.xml file). Data such as the atomic mass of elements and standard state reduction potentials are vital for many of the calculations and so are stored locally via XML documents.

The Nernst equation, seen below, can be used to find a cell's open-circuit voltage under a given operating temperature and state of charge.

$$E = E^0 - (RT/nF)\ ln\ Q$$

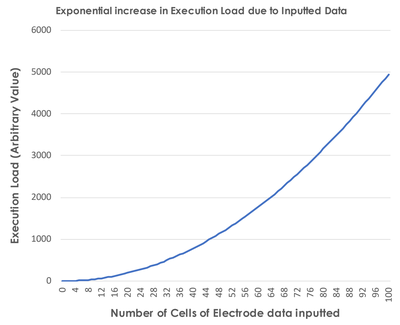
By appropriately alternating certain values for each cell configuration, a discharge curve can be modelled at a range of operating temperatures. While the values R and F remain constant, the variables E^0, Q and n are defined by specific calculations regarding the unique properties of each cell; essentially these are what distinguish between efficient and inefficient cells. As ECMS executes, most of the processing load is due to the various algorithms designed to calculate these values.

$$C = nF/m\ X\ 5/18$$

Furthermore, I have integrated algorithms to calculate other key cell characteristics, including capacity and energy density. Determined using Faraday's law, these properties are arguably just as important as the open-circuit voltage and discharge curvature of a given cell configuration.

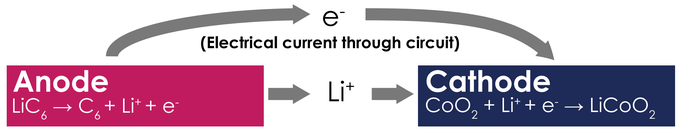
The general equation to find the capacity in Milliamp Hours per gram of an electrochemical cell can be noted above. To find the energy density in Watthours per gram, the software simply multiplies this value by the mean voltage of the modelled cell.

Throughout the development of this project, over 300 unique cell configurations have been successfully modelled. Although I developed the software to automatically scale with more electrode data, it is still signifigantly CPU intensive and thus takes an extensive amount of time to model each individual cell. Furthermore, the rate at which the execution load increases is an quadratic function, meaning a small increase in input data can at times result in weeks of additional processing time (see figure to the right). Ultimately, this means that ECMS can model any cell as long as some basic information for each involved electrode is inputted.



Theory

An electrochemical cell, commonly reffered to as a battery cell, is a device which facilitates electrochemical processes in which electrons flow from an oxidising negative electrode (anode) to a reducing positive electrode (cathode). This is a known as a Redox reaction although it is frequently described as two half-reactions. An illustration of the electrochemistry in a Lithium Cobalt Oxide cell can be seen below.



$$CoO_2 + LiC_6 \rightarrow LiCoO_2 + C_6$$

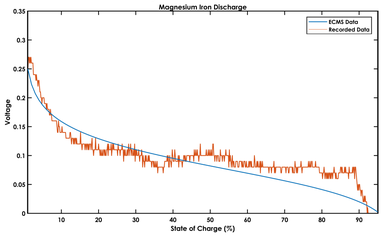
As the Lithiated Graphite anode oxidises, electrons and positive Lithium Ions are produced. As the positive ions flow to the Cathode, the electrons are forced through through an electrical circuit before reducing to Lithium Cobalt Oxide.

Whenever the reaction is spontaneous, the cell is referred to as Galvanic. In contrast, an Electrolytic cell is one which uses electrical energy to essentially reverse the Galvanic reaction. To summarise, a typical battery is Galvanic while it discharges and Electrolytic whenever it recharges.

To model these processes in order to predict various properties of an electrochemical cell, the standard reduction potentials of each electrode must be known. However, these values can only be obtained through physical measurements so I had to gather them from various trusted sources. This along with the atomic mass of each involved element, is all that needs inputted into the system to generate theoretical models of a given cell. By inputting a relatively large repository of electrode data, the software can model every stable cell configuration, allowing for a thorough comparison of cell types.

Experimental Verification

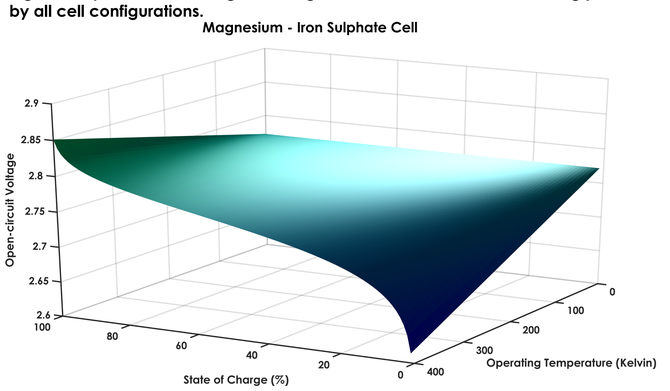
Due to the nature of this project, it would defeat the purpose to manufacture a cell under lab conditions for every modelled configuration and record how it behaves under every operating temperature. However, it would also be bad scientific practice to simply accept the computer-generated results as being accurate without further experimentation. To allow a fair evaluation of the ECMS data, I synthesised a select group of cells, recorded their behaviour and contrasted the results to that generated by the software. Although this did not necessarily prove the accuracy of the computer-generated data, it certainly added credibility.



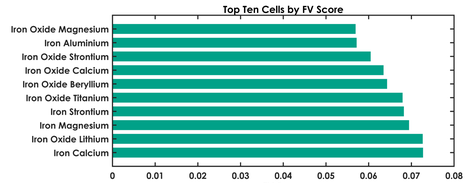
Upon contrasting the appropriately formatted results to the predicted information, I found that generally, the experimental data supported the models (note the above-left figure). That being said, only specific variables such as voltage were able to be recorded under fixed standard state conditions due to technical limitations. Ideally, this and other cell characteristics would be tested under a range of operating temperatures as to validate all aspects of the modelling system, adding further credibility to the generated data. All things considered, the experimental data gathered is certainly substantial enough to ensure the level of validity needed for the software to function well and realise its ultimate purpose.

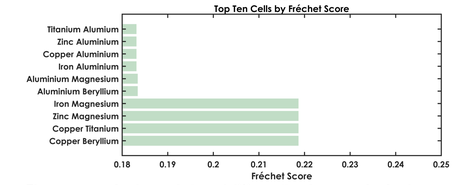
Results

Through electrochemical modelling, I have illustrated the effect of operating temperature on a cells efficiency and discharge curvature (see below figure). My results have shown that in terms of overall performance, all cells change with temperature in a nearly uniform fashion, indicating that the most efficient cells at one temperature will be more or less the same at another. It is also important to note how the generated models have shown that at lower operating temperatures, the open-circuit voltage is more consistent throughout the discharge cycle than at higher temperatures. Although the magnitude differs, this trend is seemingly shared by all cell configurations.

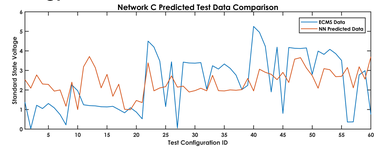


Furthermore, using machine learning through applied artificial neural networks, I was able to prove the lack of correlation between molecular mass and standard state voltage (see figure to the right). Although the idea is rarely disputed within the scientific community, there is seemingly little/no substantial evidence disproving a relationship between these two pivotal sets of values. After configuring and testing a number of intelligent neural networks, I can confidently conclude that there is absolutely no correlation between voltage and molecular mass (note the lack of correlation in the figure to the right). Collectively, the models were again able to provide new insight into electrochemical cell technology in ways that would not have otherwise been possible.





The generated models additionally demonstrated how the number of moles of transferred electrons in a cells balanced reaction have a linear correlation with capacity (note the parallel curves on the right figure), allowing more-massive electrodes such as Ferrate and Magnesium Sulphate to outperform lighter ones in terms of capacity per gram. After much thought, I credited this trend to increased internal resistance as a result of heavier ions drawing more energy to flow between the cell's electrodes.



The digital models have also highlighted Aluminium electrodes as being best-suited in terms of discharge consistency (bottom left diagram). However, this only considers the Fréchet distance, a measure of discharge consistency. For the fairest comparison, I created my own ranking system involving a value named the FV Score which acknowledges voltage as well as discharge curvature. Based on my findings (see top left figure), Iron and Iron Oxide electrodes are most efficient, performing with a high yet consistent voltage. However, when examining both measures, one cell stands out; Iron Aluminium. With a consistent power output, high median voltage (3.143V), a high capacity (267.84mAh/g) and a reasonable energy density (841.82Wh/g), it certainly shows a lot of potential in terms of large-scale energy storage.