Surface electrochemistry methods for a safer Li-ion battery: understanding and preventing short circuits

Developing methodology to observe and quantify metal plating in complex 3-electrode systems, using copper as a benchmark

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ABSTRACT

Dendritic growth of electroplated metal on anodes in LIBs leads to **short circuits** due to separator penetration, and an alternate flow of current through the cell. This raises **serious safety concerns** as well as **degrading the functional integrity of the cell**, including its:

- **Cycle Life**
- **Energy Density**
- **Capacity Retention**

If we seek to mitigate dendrite formation, we must first learn more about them – and how we can monitor (and then quantify) them.

One new technique proposed applies the **Sauerbrey principle**, which relates resonance frequency to mass. In practice, this principle can be used to calculate the mass of thin layers added to a **Quartz Crystal Microbalance** (QCM) crystal surface. This internship realised the use of electrochemical QCM (or **eQCM**) apparatus, a potentiostat, Q-Sense and EC Lab software, to closely monitor and then precisely quantify metal electroplating character.

Cu was chosen as a benchmark metal for this project because of its simpler electroplating profile relative to Li (Cu is non-SEI forming). Cu plating character is fairly well published and documented in the literature.

MOTIVATION

Efforts aimed at mitigating dendrite formation, whether through direct or indirect means, are pivotal to enhancing the **safety**, **cost efficiency**, and **sustainability** of LIBs. Successful mitigation strategies offer the prospect of **improved capacity retention** and **extended cycle life**, thereby fostering safer and more economically viable LIBs. The future expansion of Li-based battery applications within the Energy Storage Sector hinges significantly on advancements in this critical research domain.

SAUERBREY IN ACTION

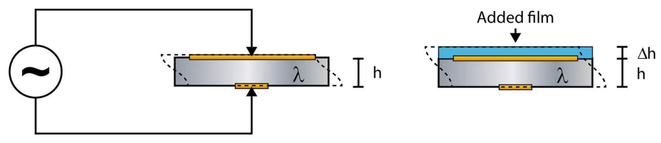
The relation between resonance frequency and mass was discovered by Günter Sauerbrey in 1959, and is practically used to calculate the mass of thin layers.

In QCM technology, this relationship succinctly encapsulates **a linear equation correlating the acoustic oscillation frequency of a quartz crystal with surface mass alterations**.

$$\Delta m = -C \cdot \frac{\Delta f}{n}$$

m = mass
f = resonance frequency
n = harmonic number
C = quartz crystal mass-sensitivity constant

This enables measurement of **extremely low mass changes** per unit area with **high levels of precision.**



eQCM METHODS

Adapted from a simple 3-electrode system to a more complex eQCM setup

The eQCM module [bottom right] saw use of a quartz crystal thin film Au working electrode (**WE**)[above]; Pt plate counter electrode (**CE**); Q-sense WPI Dri-REF™ Ag/AgCl reference electrode (**RE**); varying concentrations of $CuSO_4 \cdot 5H_2O$ in 0.1 M H_2SO_4 acting as the **electrolyte**, which was siphoned through the system using solvent pump apparatus so that the ion concentration in solution remained constant despite plating/stripping; a thin rubber O-ring was used as a **separator**, holding the WE and CE apart.

In crystal resonators, **the resonance frequency is inversely proportional to the mass**, so adding mass lowers the resonance frequency. Upon **Reduction** (at lower potentials), **plating occurs** at the WE, the resonance **frequency is decreased** (additional mass of the plated Cu on the crystal); upon **Oxidation** (at higher potentials), the **Cu is stripped** and the resonance **frequency returns to its original value**.

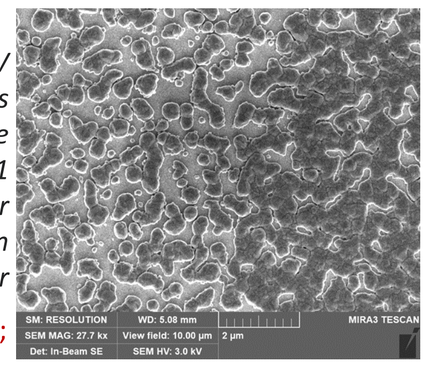
Many batches of CVs using different lower cut-off potential were performed, as well as varying scan rates; potential window; electrolyte concentration 0.01 to 0.001 M CuSO4·5H2O in 0.1 M H2SO4.

USE OF SEM IMAGING TECHNIQUES

After establishing an efficient Cu plating technique with eQCM, our investigation aimed to illuminate the **morphological characteristics** of the metal deposition on the thin-film Au-coated quartz crystal WEs. The ensuing image illustrates an exemplary plated crystal.

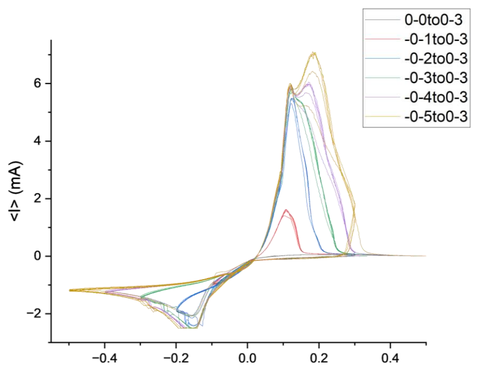
Here, we ran a forwards LSV sweep to ensure the WE was entirely stripped. Then we galvanostatically plated at 1 mA (0.9 mA/cm²) and held for 10mins. Electrodes were then transported and prepared for SEM.

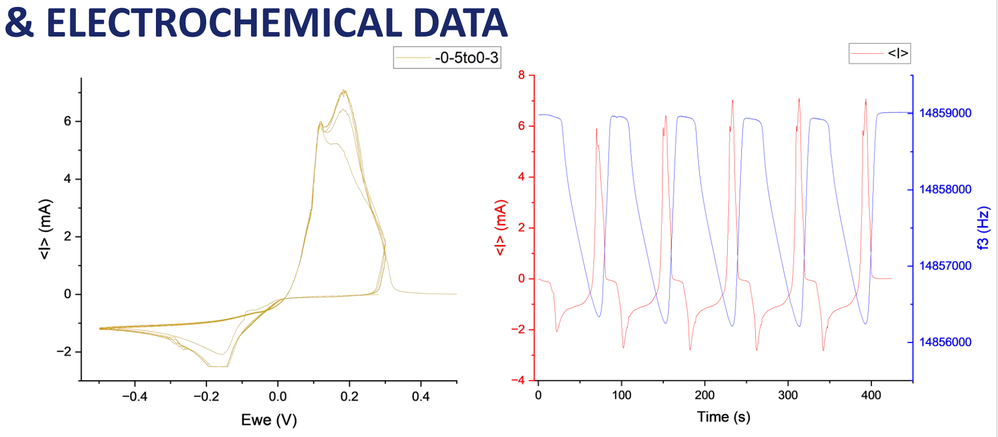
[Cu = darker regions; Au = lighter regions]



eQCM & ELECTROCHEMICAL DATA

The plot below portrays a group of six **5-cycle CVs** that were run with varying potential windows. These were all run on the same crystal at a scan rate of 20mVs^{-1} with electrolyte concentration of 0.01 M. It is noteworthy that in these CVs you see a characteristic '**double loop**'. Precisely what we were hoping to find with these CVs





The plots above include **one of the CVs** shown in the grouped plot to the left, presented with its **current** (<I>) **and frequency** (f3) **data over time**. These 5 dips in the frequency plot represent the change in resonance frequency of the quartz decreasing cyclically due to the very slight increase in surface mass (the Cu plated on the thin-film Au WE). And, as you would expect, the mass over time graph in the processed data is **the exact inverse shape** of this one.

CONCLUSIONS

Successfully **adapted setup** from a simplistic 3-electrode cell to a much more complex 3-electrode system while recording measurements in operando.

Successful development of **reproducible Cu plating and stripping** methodology within an EQCM system.

Successfully developed a method to **directly observe and quantify Cu plating** using an eQCM system.

SEM imaging was used in attempt to analyse surface morphology of the plated Cu. However, there was no opportunity to perform further study here due to focus being on methods.

FUTURE DIRECTIONS

Now that effective methods for a benchmark material have been implemented, the next step shifts our aim towards advances primarily with **Zn** (and potentially with Li later down the line).

Zn is SEI-forming but still has a simpler electroplating profile than Li. This makes it ideal for use as an intermediary model, used as a 'stepping stone' for the launch into deeper study of Li using Sauerbrey and QCM methods.

Further implementation of SEM could be used aimed at observing the plating morphology of the studied metal.

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Intern bio

Laurence is a currently a dedicated student entering his 4th year of an MChem degree program at the University of York. His project was undertaken within the Grey Group, located in the Yusuf Hamied Dept at the University of Cambridge.
His efforts have contributed to ongoing advancements in the Battery Technology and Energy Storage Sector, and he is committed to continue leveraging his knowledge and skills to drive progress in this rapidly evolving field.
He eagerly anticipates opportunities to continue his academic and professional journey in this area of scientific exploration.

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