

Using the SECM150 to Measure an NMC Battery Electrode

I – INTRODUCTION

Scanning Electrochemical Microscopy (SECM) allows the electrochemical nature of a sample, and the electrochemical processes occurring at a sample to be investigated. Over the last few years SECM has seen increasing popularity as a technique to investigate battery electrodes and battery materials. SECM has been used in battery research to investigate the Solid Electrolyte Interface (SEI) [1], Li intercalation [2], surface dissociation of species [3], solid electrolytes [4] and diffusion through porous electrodes [5].

In this note the SECM150, Bio-Logic's compact, value-oriented SECM, is used to demonstrate the applicability of SECM for the analysis of battery electrode inhomogeneity. This is shown by measuring a Lithium Nickel Manganese Cobalt oxide (NMC) battery cathode material provided by Dr Fu Ming Wang, NTUST, Taiwan.

Further applications of the Scan-Lab SECMs in the investigation of battery materials can be found in AN#7 [6], AN#10 [7], and AN#20 [8].

II – EXPERIMENTAL

The SECM150 was used to perform dc-SECM measurements on an NMC battery cathode. All measurements were performed in a Faraday cage. A small piece of NMC electrode was adhered to a resin blank using Parafilm which had been heated until tacky. All measurements were carried out in $5 \times 10^{-3} \text{ mol L}^{-1} \text{ K}_3[\text{Fe}(\text{CN})_6]$ in $0.1 \text{ mol L}^{-1} \text{ KCl}$ aqueous electrolyte. A $1 \text{ } \mu\text{m}$ Pt Ultra MicroElectrode (UME) probe, a Saturated Calomel Electrode (SCE) reference, and a Pt counter electrode were used for all measurements. All potentials are quoted against SCE.

In order to characterize the probe a Cyclic Voltammogram (CV) was first measured over

the resin blank to avoid any influence from the sample on the electrochemistry. The CV was performed between 0.75 and -0.25 V, using a scan rate of 0.05 V s^{-1} . The probe was then manually positioned over the sample using the x, y micrometers and a CV was performed using the same settings.

An approach curve to the NMC electrode surface was then performed to determine the most suitable z position of the measurement, as the proximity of the probe to the sample surface determines the magnitude of current change compared to the bulk measurement. This was performed by biasing the probe at 0.7 V, with an initial step size of $0.2 \text{ } \mu\text{m}$, and upon triggering a reduced step of $0.05 \text{ } \mu\text{m}$.

To verify the optimized probe position a line scan was performed over $50 \text{ } \mu\text{m}$ in the x axis. This was performed in Step Scan mode with a step size of $0.5 \text{ } \mu\text{m}$, and velocity of $25 \text{ } \mu\text{m s}^{-1}$. The probe was biased at 0.7 V throughout.

With the z position confirmed an area scan over a $50 \text{ } \mu\text{m} \times 50 \text{ } \mu\text{m}$ area was performed. As with the line scan this was performed in Step Scan mode with a step size of $0.5 \text{ } \mu\text{m}$ and a velocity of $25 \text{ } \mu\text{m s}^{-1}$. The probe was biased at 0.7 V throughout the measurement.

All area maps have been processed using the Gwyddion software [9].

III – RESULTS

Prior to performing any SECM measurements the UME probe is characterized with a CV in bulk solution. This allows the quality of the probe to be assessed, and selection of the measurement bias potential to ensure the reaction of interest is maximized. To ensure the bulk CV at the probe was not influenced by the cathode the probe was moved over the resin blank. The resulting CV, yellow curve in Fig. 1,

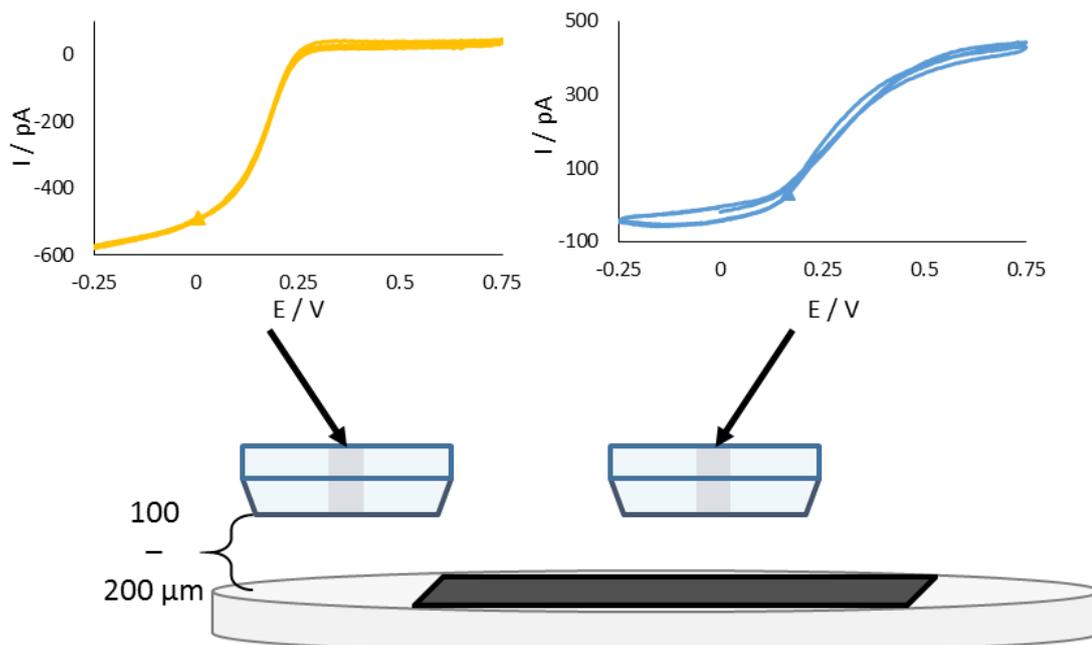


Figure 1: CV of 1 μm UME in bulk performed in bulk over the resin blank (yellow) and over the cathode sample (blue) in $5 \times 10^{-3} \text{ mol L}^{-1} \text{ K}_3[\text{Fe}(\text{CN})_6]$ in $0.1 \text{ mol L}^{-1} \text{ KCl}$ aqueous electrolyte. Scans were performed from 0.75 to -0.25 V , using a scan rate of 0.05 V s^{-1} .

shows the classic sigmoid shape expected for the reduction of $[\text{Fe}(\text{CN})_6]^{3-}$ in bulk, and a higher current magnitude at -0.25 V than at 0.75 V . This is not the case when the same CV is performed over the NMC electrode surface, blue curve in Fig. 1. In this case, even though the probe has not been approached to the electrode surface the CV does not match that expected for a bulk measurement of $[\text{Fe}(\text{CN})_6]^{3-}$. Instead the current magnitude for the reduction of $[\text{Fe}(\text{CN})_6]^{3-}$ falls to near 0 nA , while the oxidative current has a similar magnitude as for the reduction prior. This implies the unbiased sample reduces $[\text{Fe}(\text{CN})_6]^{3-}$ to $[\text{Fe}(\text{CN})_6]^{4-}$, which is then oxidized by the UME probe. Therefore in these experiments measurement is performed in Sample Generation/Tip Collection (SG/TC) mode, as shown graphically in Fig. 2. In this case a bias of 0.7 V was selected for all subsequent experiments.

To optimize the z position of the measurement an SECM approach curve was performed in the $-z$ direction to the electrode sample, an example is shown in Fig. 3. While globally the sample acts to generate $[\text{Fe}(\text{CN})_6]^{4-}$, the approach measured to the cathode sample

shows negative feedback. This implies an insulating or poorly conductive region within a heterogeneous sample, suggesting the probe was over an NMC particle. While there is no apparent contact between the UME and the NMC in order to avoid the probe contacting, and/or dragging through the NMC surface it is beneficial to use a z position away from the final point for subsequent line and area scans.

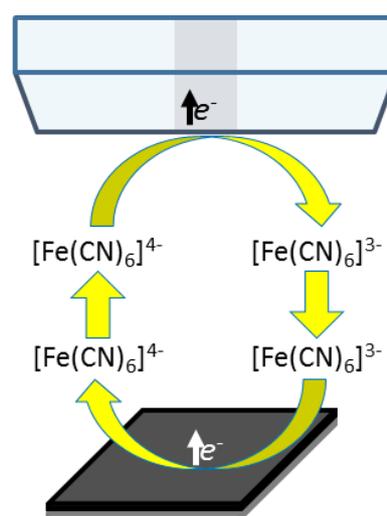


Figure 2: The reduction of $[\text{Fe}(\text{CN})_6]^{3-}$ to $[\text{Fe}(\text{CN})_6]^{4-}$ by the surface, and oxidation by the UME probe is shown.

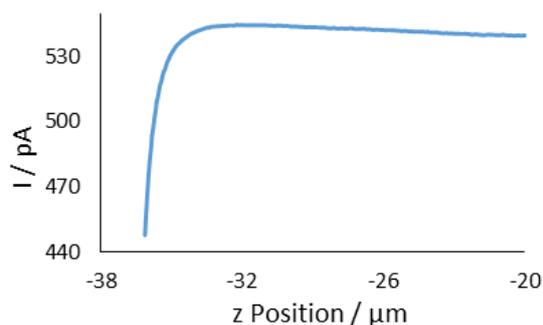


Figure 3: SECM approach curve performed to the NMC surface in $5 \times 10^{-3} \text{ mol L}^{-1} \text{ K}_3[\text{Fe}(\text{CN})_6]$ in $0.1 \text{ mol L}^{-1} \text{ KCl}$ aqueous electrolyte were performed at a bias of 0.7 V.

Before performing an area scan the selected z position was further verified by performing a line scan in x at the same y position three times, as shown in Fig. 4. Distinct low current features can be seen in these scans, which overlay well between each line scan. The agreement between the three scans implies the features are due to the interaction with the sample surface, and not from a measurement artefact. There is a slight reduction in current between the first and second scan, which may relate to a depletion in reactants.

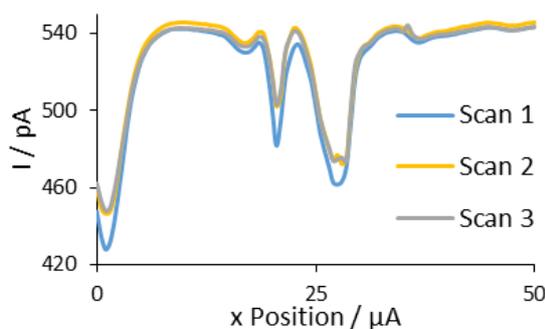


Figure 4: The NMC was measured by an x line scan in $5 \times 10^{-3} \text{ mol L}^{-1} \text{ K}_3[\text{Fe}(\text{CN})_6]$ in $0.1 \text{ mol L}^{-1} \text{ KCl}$ aqueous electrolyte. The measurement was performed at a probe bias of 0.7 V, over $50 \mu\text{m}$ with a $0.5 \mu\text{m}$ step size.

With the probe z position confirmed an area scan was performed over a $50 \mu\text{m} \times 50 \mu\text{m}$ area of the sample, Fig. 5. The resulting SECM measurement provides an indication of the homogeneity of the NMC sample. Distinct asymmetric features can be seen in the SECM measurement which likely arise from inhomogeneity in the electrode activity.

This inhomogeneity is a result of the mixture of low conductivity NMC agglomerates (blue regions), and higher conductivity additives (red regions). The degree of inhomogeneity seen is in turn a reflection of the mixing conditions during the electrode preparation process. SECM measurements of this kind can therefore aid in the optimization of electrode preparation.

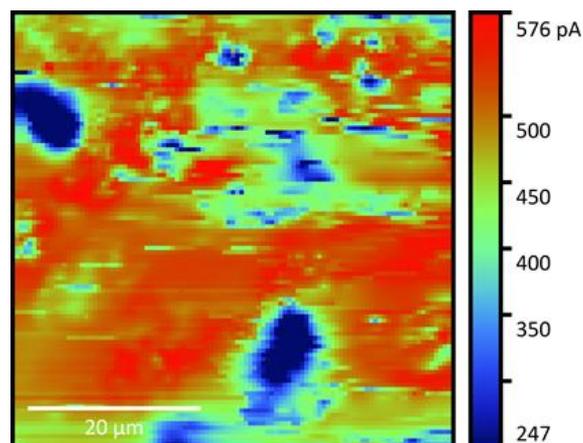


Figure 5: A $50 \mu\text{m} \times 50 \mu\text{m}$ area of NMC was measured in $5 \times 10^{-3} \text{ mol L}^{-1} \text{ K}_3[\text{Fe}(\text{CN})_6]$ in $0.1 \text{ mol L}^{-1} \text{ KCl}$ aqueous electrolyte. The $1 \mu\text{m}$ Pt UME probe was biased at 0.7 V, and a step size of $0.5 \mu\text{m}$ was used.

IV – CONCLUSION

The SECM150 has been used to assess the homogeneity of the NMC cathode material. SECM allows for the direct measurement of the electrochemical activity of the surface. Through such measurements the inhomogeneity of the electrode can be assessed on a micron scale. Utilizing such analysis can be useful for understanding how the electrode processing steps have affected the final electrode morphology. While the work presented here was performed in aqueous electrolyte, a similar approach could easily be used to perform measurements in non-aqueous electrolytes.

V – ACKNOWLEDGEMENTS

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9. Gwyddion data analysis software <http://gwyddion.net/>