The influence of PEMFC catalyst layer thickness on electro-chemical impedance spectroscopy signals and their equivalent circuits - SI

Maximilian Grandi [1], Kurt Mayer [1], Matija Gatalo [2], Gregor Kapun [2], Francisco Ruiz Zepeda [2], Bernhard Marius [1], Miran Gaberšček [2] and Viktor Hacker [1*]

Methodology for raw data analysis and data quality assessment

Kramers Kronig (K – K) analysis has been performed on the original untreated data from Figures S.1 and S.2. There were several points especially in the low frequency (5-0.1 Hz) spectrum that showed relative residuals of 2%, which indicate deviation from stationary behavior. For this reason, the following procedure has been followed to check if this deviation influences the overall results and drawn conclusions:

- The ZHIT – algorithm explained in reference [1,2] was used to ensure Impedance points at non - stationary conditions are removed from the spectra. This data analysis algorithm uses a two pole Hilbert transformation to check if the recorded impedance point represents stationary conditions or not. The K-K analysis was repeated on ZHIT converted data and relative residuals were below the acceptable range of 1%. This means remaining spectra now show stationary behavior.
- The equivalent circuits were fitted again to the stationary spectra and compared with raw data.
- Relative residuals of imaginary and real impedance values were calculated using Equation 1 and compared.

$$\widehat{\varepsilon_{1,Z}} = \frac{(Z_{exp} - Z_{sim})}{|Z_{exp}|} \qquad \text{(Equation 1)}$$

The K-K analysis residuals of the raw data and ZHIT reconstructed data is seen in Figures S.3 to S.4. Exemplary relative residuals of model data vs ZHIT Data can be found in Figures S.5 and S.6 Comparison of resistances values obtained with raw data and ZHIT reconstructed data are found in Figure S.7.

The trust in the data simulated with Model 2 is very high. At all current density points where impedance spectra where recorded and simulated the residuals showed <1% deviation. In contrast the simulation results of model 1 are doubtful as all residuals are very high for all recorded impedance spectra. Especially the capacitive values are questionable, as very high residuals were found in the Low frequency spectrum. Resistive values show very high deviations at low frequency explaining why Rmt values calculated by Model 1 show very irregular behavior in some cases.

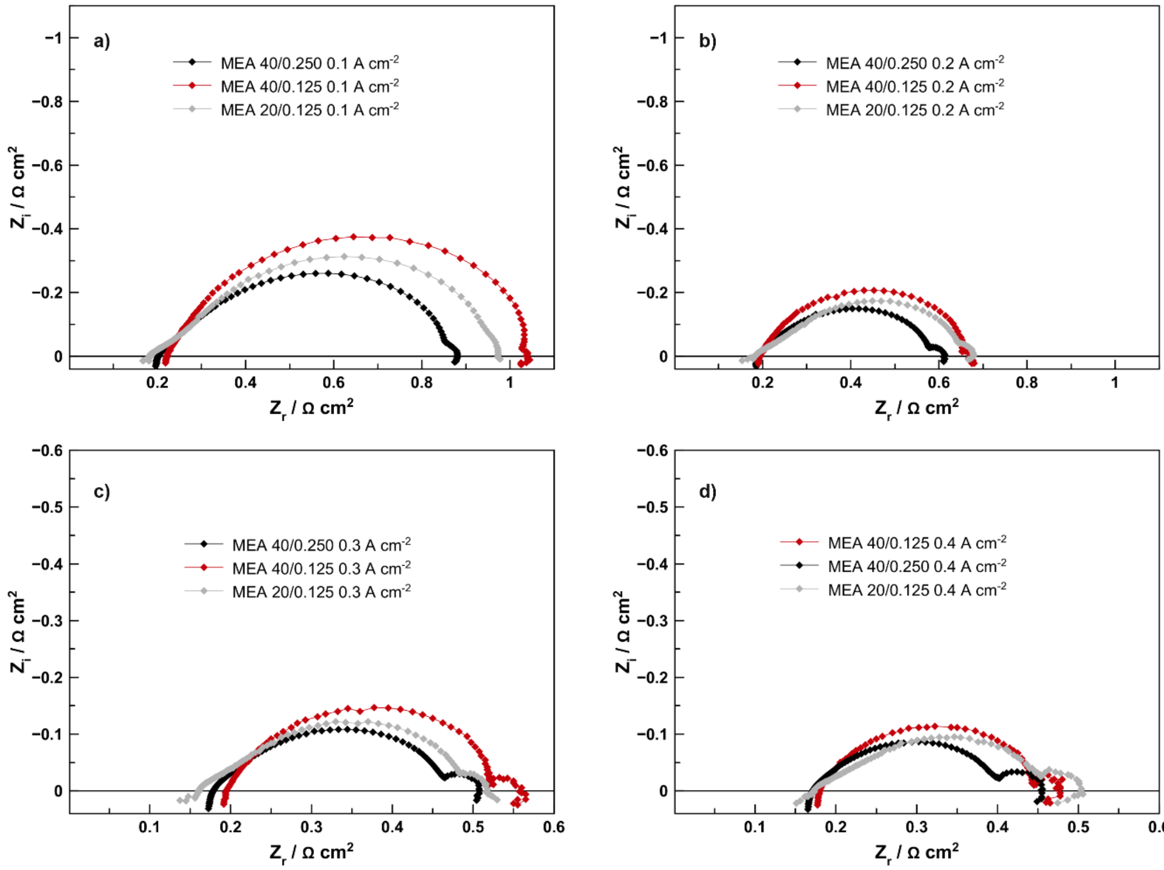

Figure S1. Experimental EIS data for every studied MEA recorded at 0.1 (a), 0.2 (b), 0.3 (c) and 0.4 (d) A cm^{-2}.

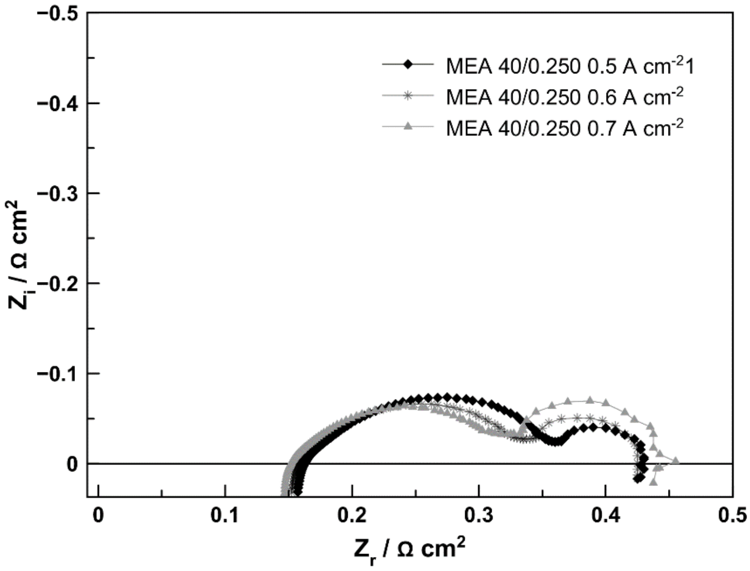

Figure S2. Experimental EIS data recorded at 0.5, 0.6 and 0.7 A cm^{-2} of MEA 40/0.250.

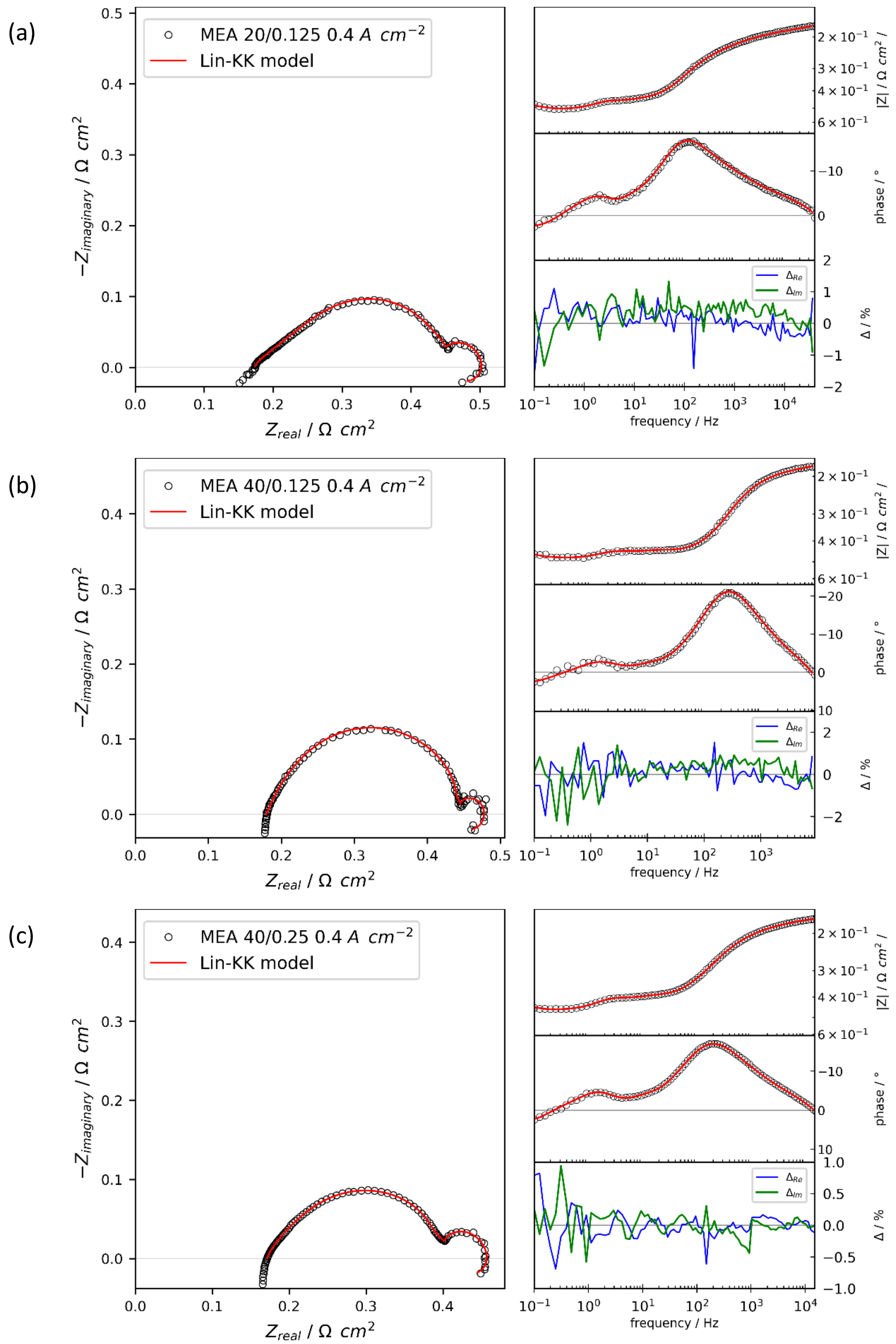

Figure S3. Linear Kramers-Kronig Analysis (red line) of the experimental data (black circles) at an operating point of 0.4 A cm-2 for (a) MEA 20/0.125, (b) MEA 40/0.125 and (b) MEA 40/0.25. On the left the Nyquist Plot is shown. At the top right the two diagrams show the Bode plot and the fitted lin-KK model. At the bottom right the real and imaginary residuals are presented.

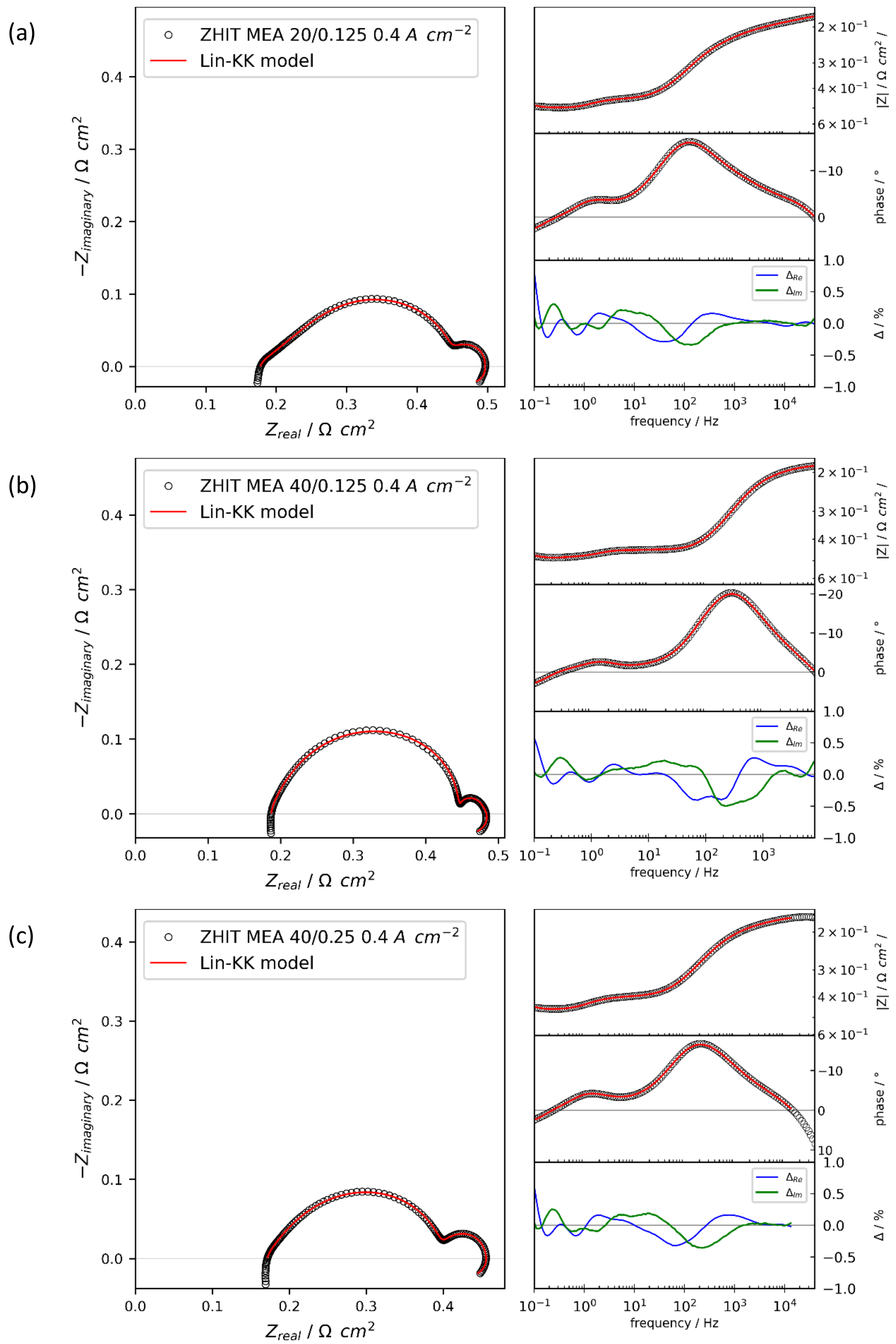

Figure S4. Linear Kramers-Kronig Analysis (red line) of the reconstructed data (ZHIT Algorithm is used; black circles) at an operating point of 0.4 A cm^{-2} for (a) MEA 20/0.125, (b) MEA 40/0.125 and (b) MEA 40/0.25. On the left the Nyquist Plot is shown. At the top right the two diagrams show the Bode plot and the fitted lin-KK model. At the bottom right the real and imaginary residuals are presented.

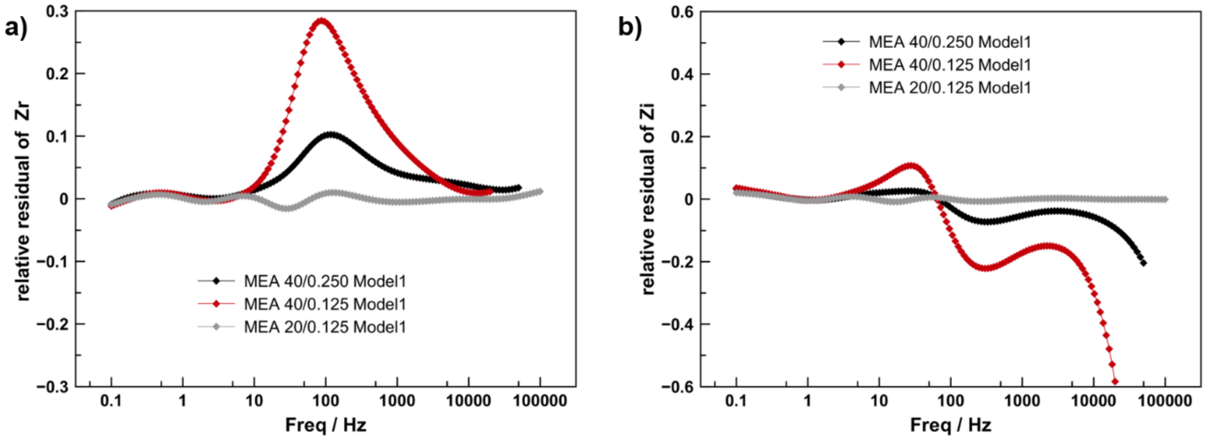

Figure S5. Residuals at 0.4 A cm-2 of Zr **(a)** and Zi **(b)** Model 1 compared to ZHIT reconstructed data. The Frequency range was selected to better show the frequency range of interest. The highest residuals were found in the low frequency range.

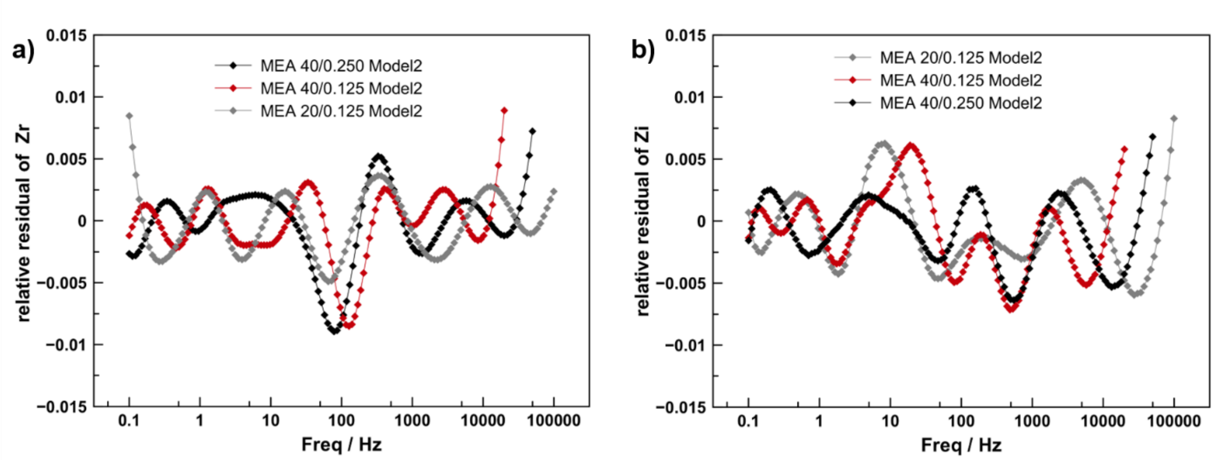

Figure S6. Residuals at 0.4 A cm-2 of Zr **(a)** and Zi **(b)** Model 2 compared to ZHIT reconstructed data. The Frequency range was selected to better show the frequency range of interest. The highest residuals were found in the low frequency range.

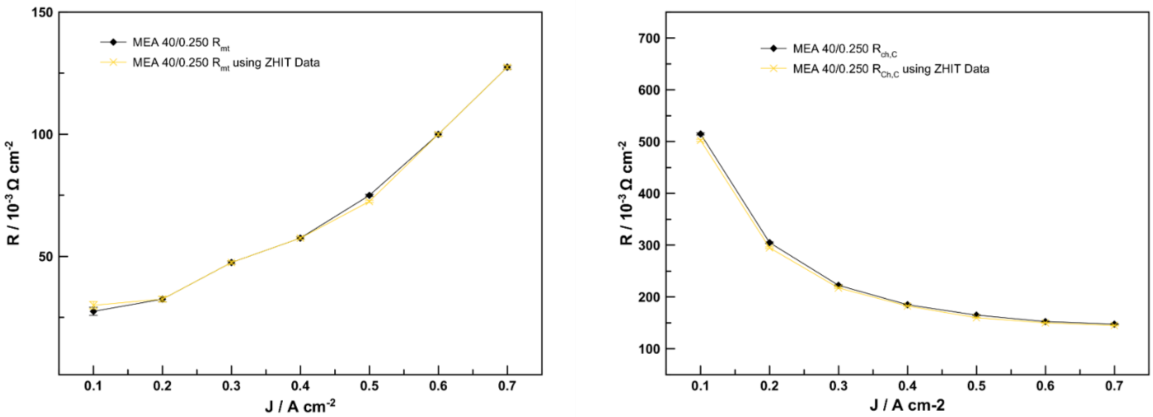

Figure S7. Comparison of Model 2 resistance calculation when using raw data vs ZHIT reconstructed data. No significant change in numerical values can be determined in neither R_{mt} nor $R_{Ch,C}$.

References

[1] Ehm, W. & Kaus, Rüdiger & Schiller, C.A. & Strunz, W.. (2001). New Trends in Electrochemical Impedance Spectroscopy and Electrochemical Noise Analysis. Electrochemical Society Inc. 2000.

[2] Schiller, C. A., Richter, F., Gülzow, E., & Wagner, N. (2001). Validation and evaluation of electrochemical impedance spectra of systems with states that change with time. Physical Chemistry Chemical Physics, 3(3), 374–378. https://doi.org/10.1039/B007678N