Supporting information on "The Double Layer Capacitance as a Sensitive Metric to Monitor the Formation of Solid Electrolyte Interphases for Li-Ion Batteries"

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1 Design of the experimental cell

Figure S1 shows the blueprint of the polypropylene (PP) body of the electrochemical cell used for the presented measurements. The glassy carbon electrode was pressed onto the bottom with M6 screws that were anchored into a stainless-steel plate below the glassy carbon plate. The heads of the four used M6 screws were hold in the PP body. The side drillings for the connections between the different electrolyte chambers were sealed with M5 screws with PTFE-sealing band around the threads. The holes for the working, counter, and reference electrode on top were sealed with rubber plugs for test tubes. For the counter and reference electrode chamber, titanium wires were pressed through these plugs, forming a seal tight pass for the wires.

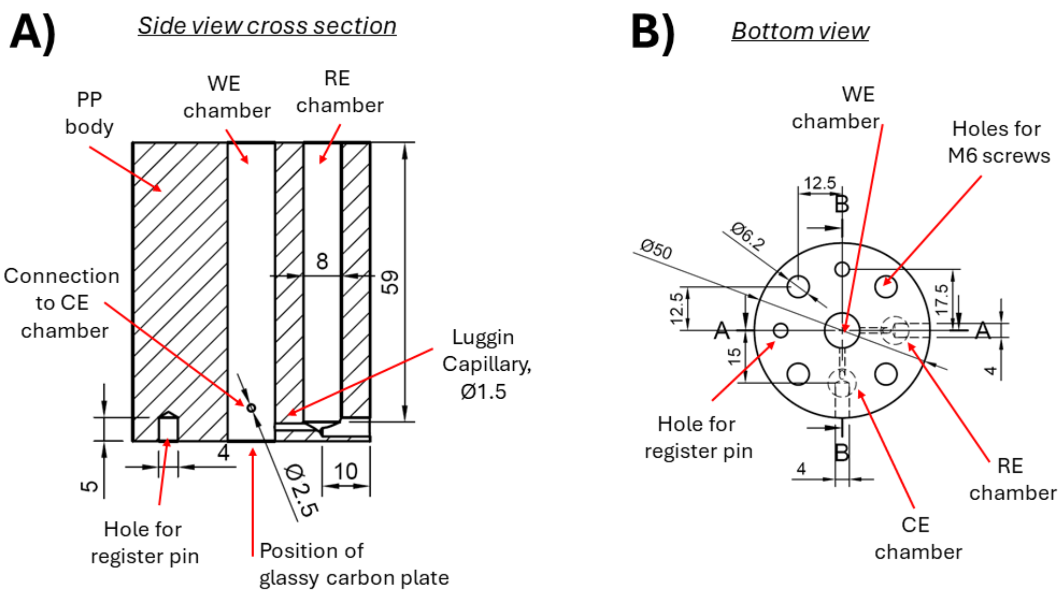

Figure S1:Blueprint of the polypropylene (PP) body of the electrochemical cell used for the measurements. WE = working electrode. RE = reference electrode. CE= counter electrode.

2 Open circuit potentials

Table S1 shows the open circuit potentials (OCPs) measured for the five different electrolytes at the glassy carbon electrode including the repetition measurements.

Table S1: Open circuit potentials (in V vs Li/Li⁺) measured for the first (M1) and second (M2) measurements with the five different electrolytes.

	M1	**M2**
EC-DMC	3.256	3.228
EC-DEC	3.266	3.227
DMC	2.998	3.258
PC	3.162	3.114
PC-DMC	3.142	3.224

Figure S2 shows the impedance spectra measured at the OCPs, showing the typical characteristics of a blocking electrode.

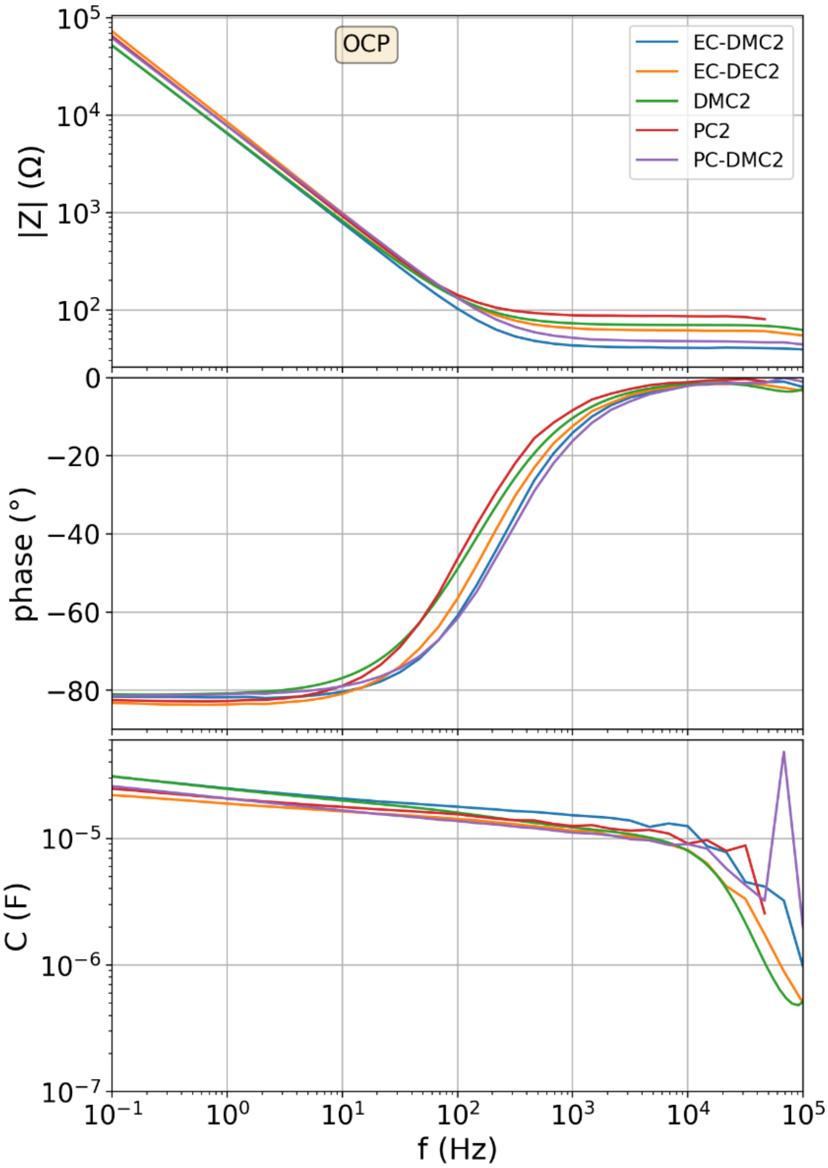

Figure S2: Measured impedance spectra f the five different electrolytes at open circuit potential.

3 Impedance data

Figure S3 to S7 show the impedance spectra of the first iteration of the measurement protocol. To avoid overloading of the graphs, the results of every second potential step are shown.

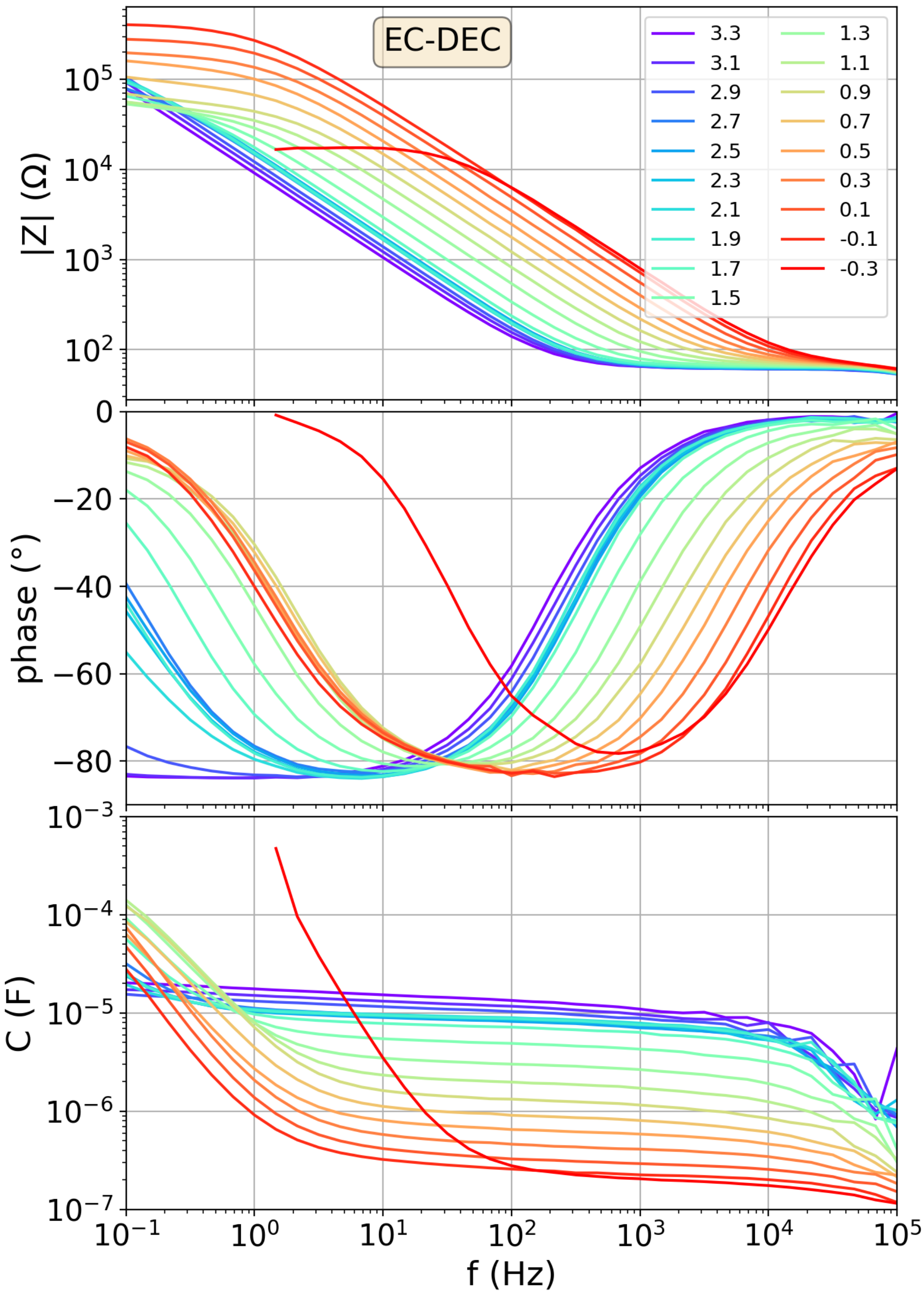

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Figure S3: Impedance spectra of the first iteration for every second potential iteration with the EC-DEC electrolyte. Colors and legend: Applied potential.

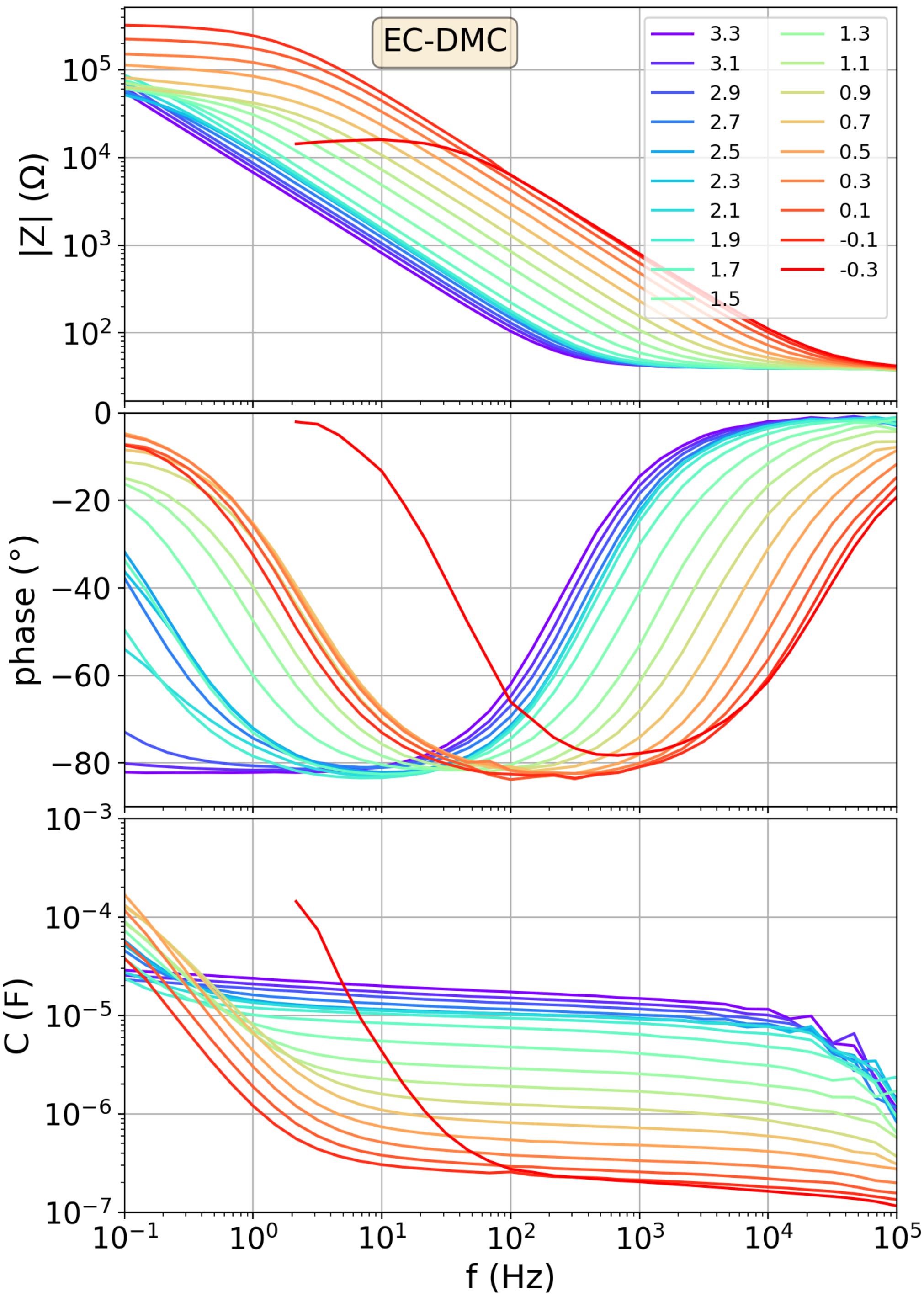

Figure S4: Impedance spectra of the first iteration for every second potential iteration with the EC-DMC electrolyte. Colors and legend: Applied potential.

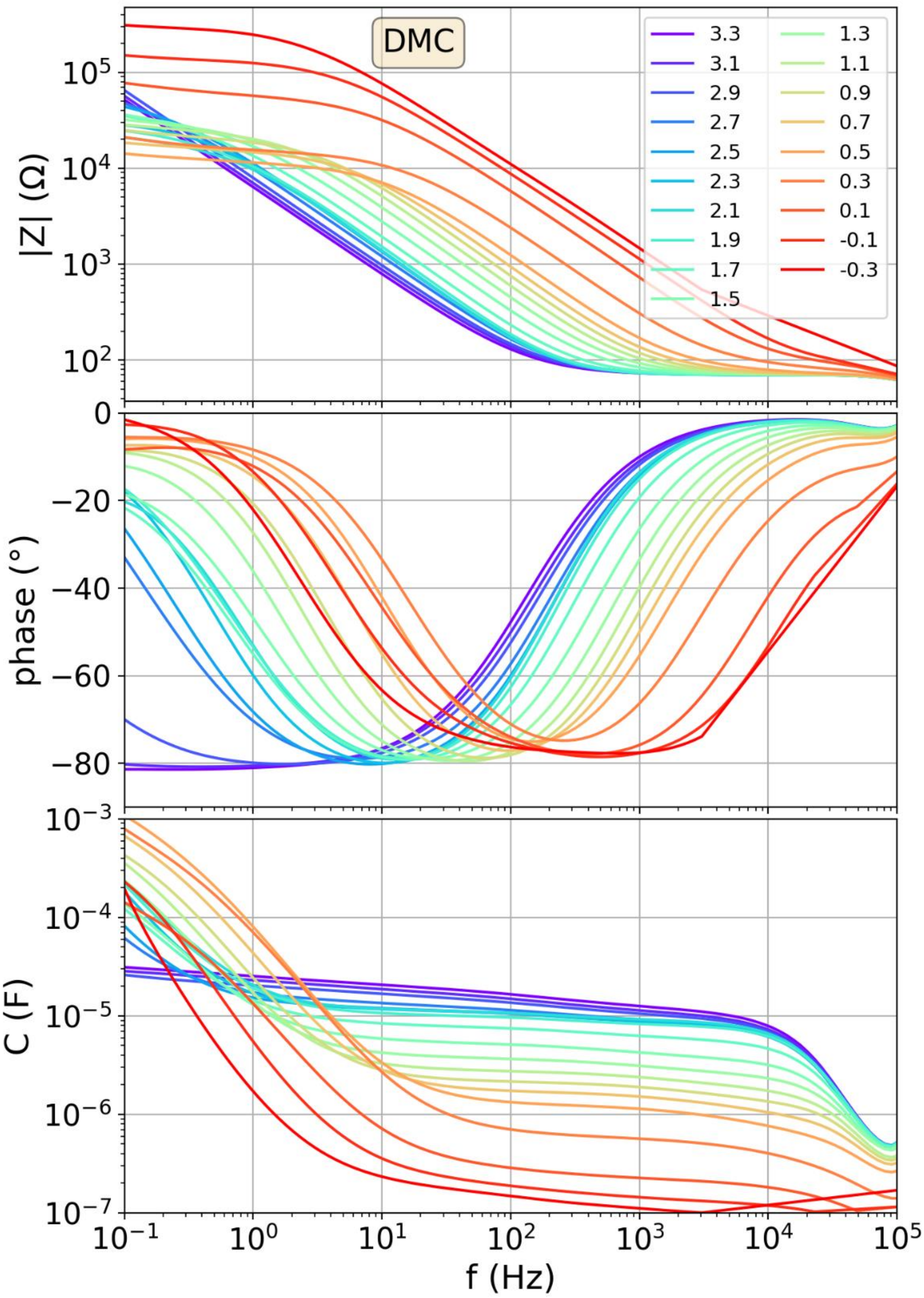

Figure S5: Impedance spectra of the first iteration for every second potential iteration with the DMC electrolyte. Colors and legend: Applied potential.

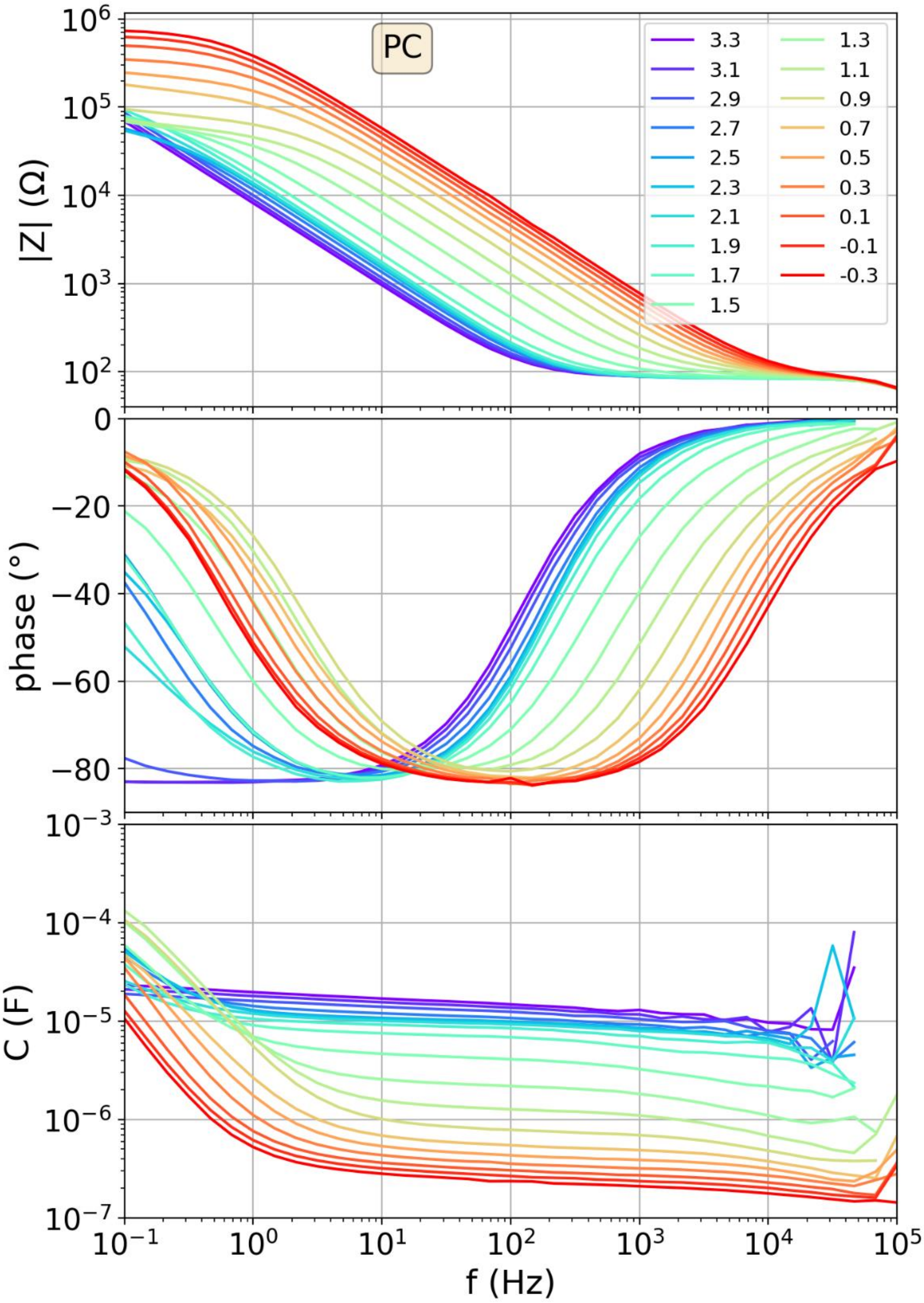

Figure S6: Impedance spectra of the first iteration for every second potential iteration with the PC electrolyte. Colors and legend: Applied potential.

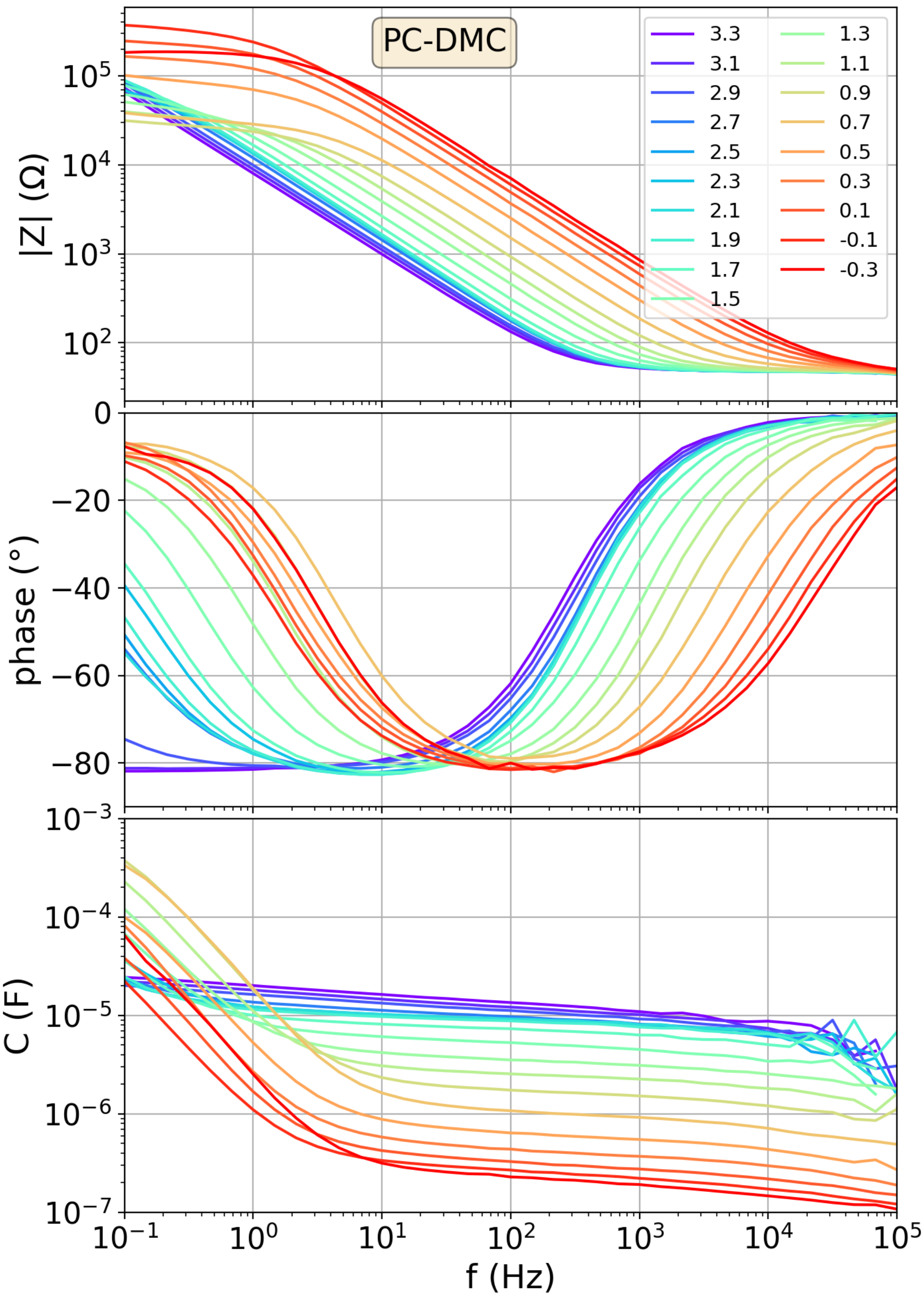

Figure S7: Impedance spectra of the first iteration for every second potential iteration with the PC-DMC electrolyte. Colors and legend: Applied potential.

4 Repetition measurements

Figure S8 to S12 show the metrics derived from the electrochemical step protocol of two measurements for every electrolyte, aiming to prove the reproducibility of the shown data.

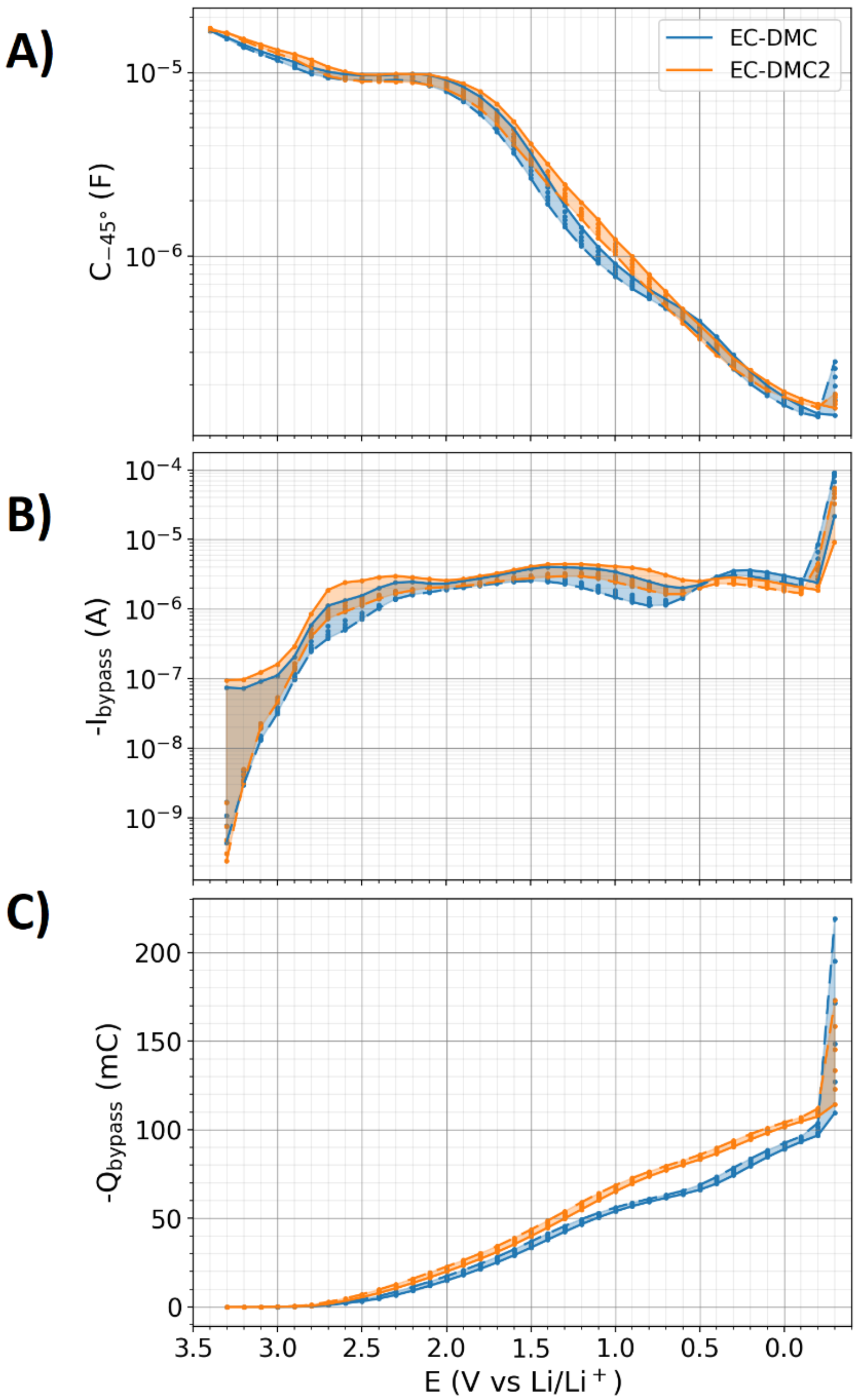

Figure S8: Metrics derived from the electrochemical step protocol for two measurements with the EC-DMC electrolyte.

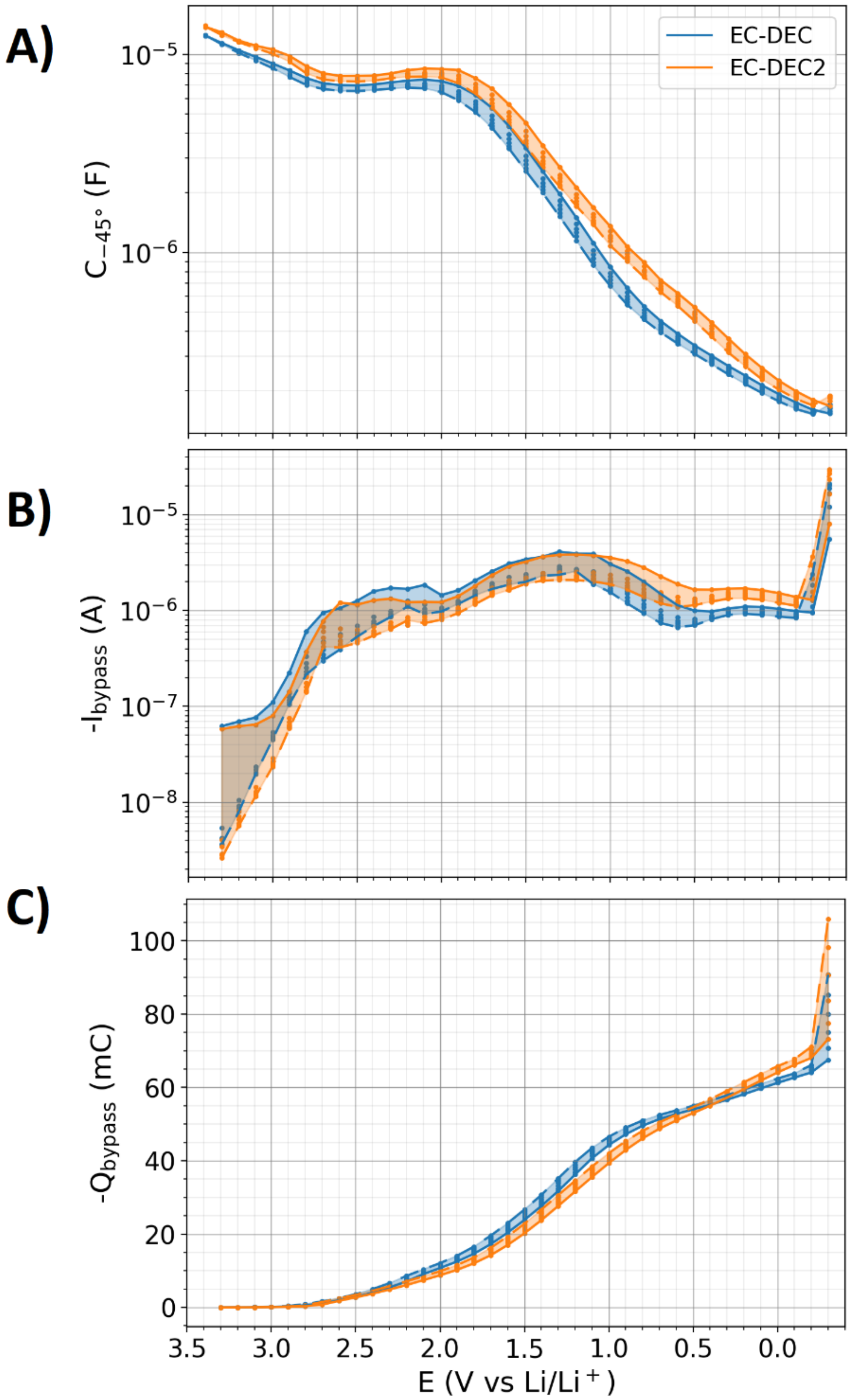

Figure S9: Metrics derived from the electrochemical step protocol for two measurements with the EC-DEC electrolyte.

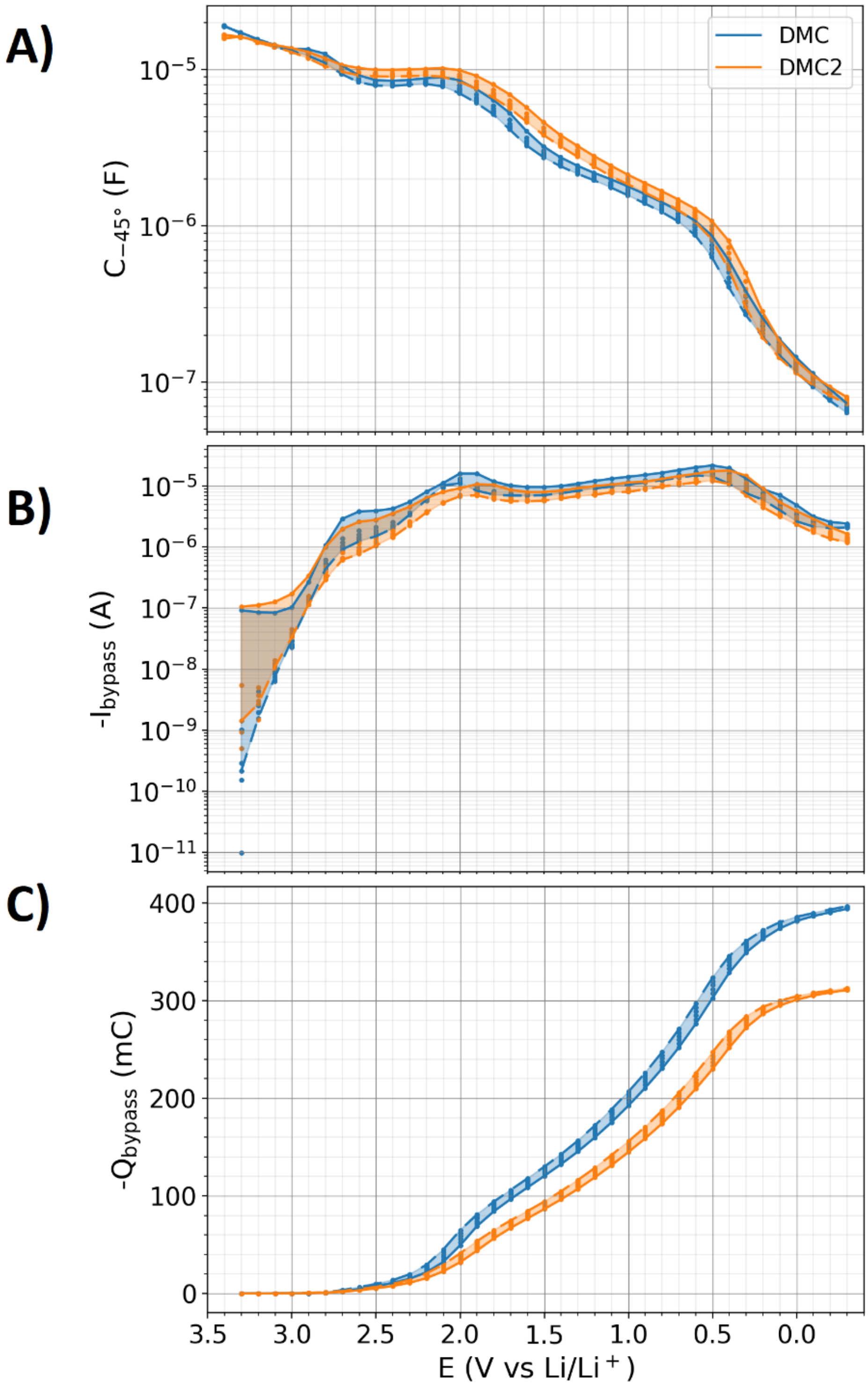

Figure S10: Metrics derived from the electrochemical step protocol for two measurements with the DMC electrolyte.

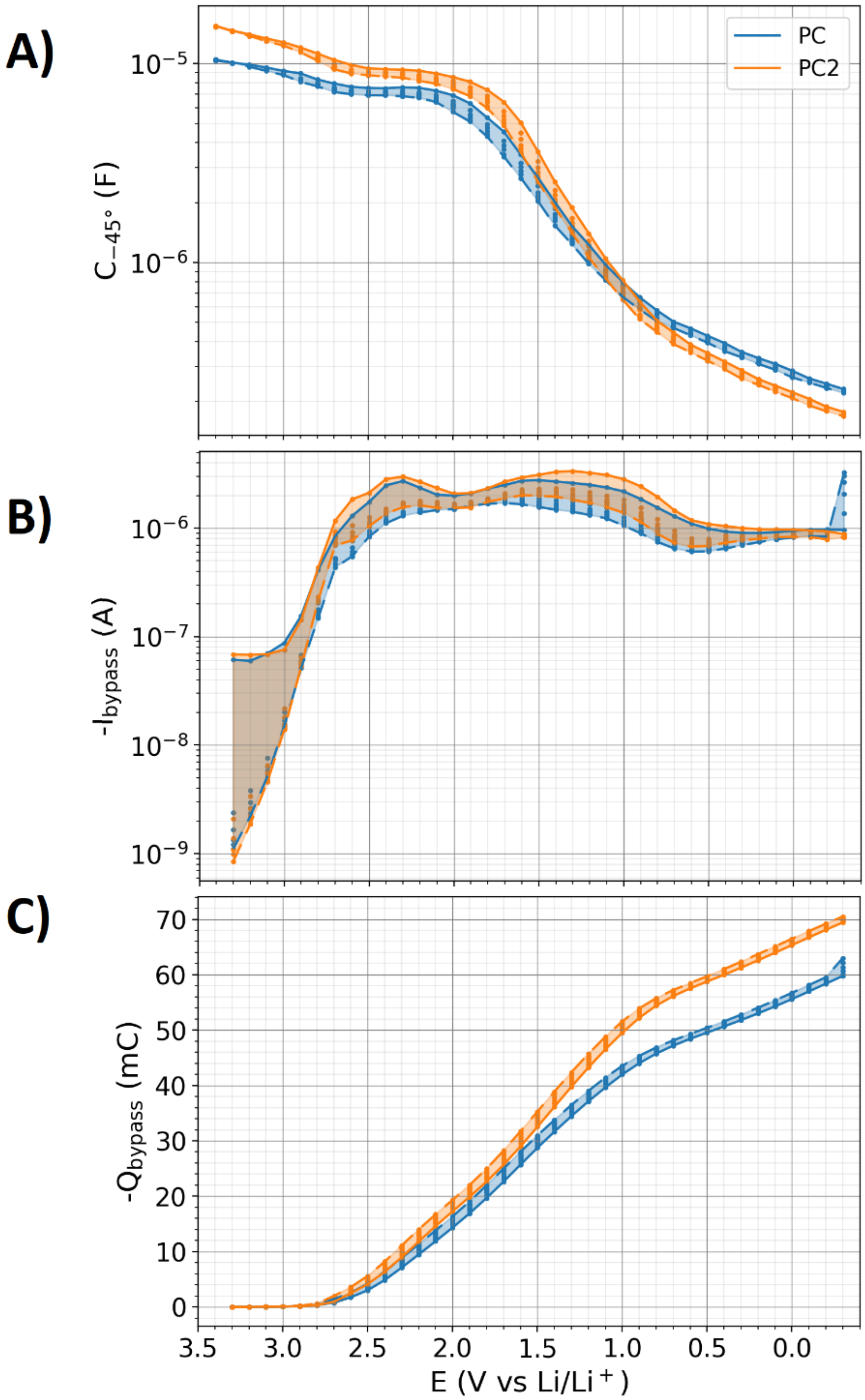

Figure S11: Metrics derived from the electrochemical step protocol for two measurements with the PC electrolyte.

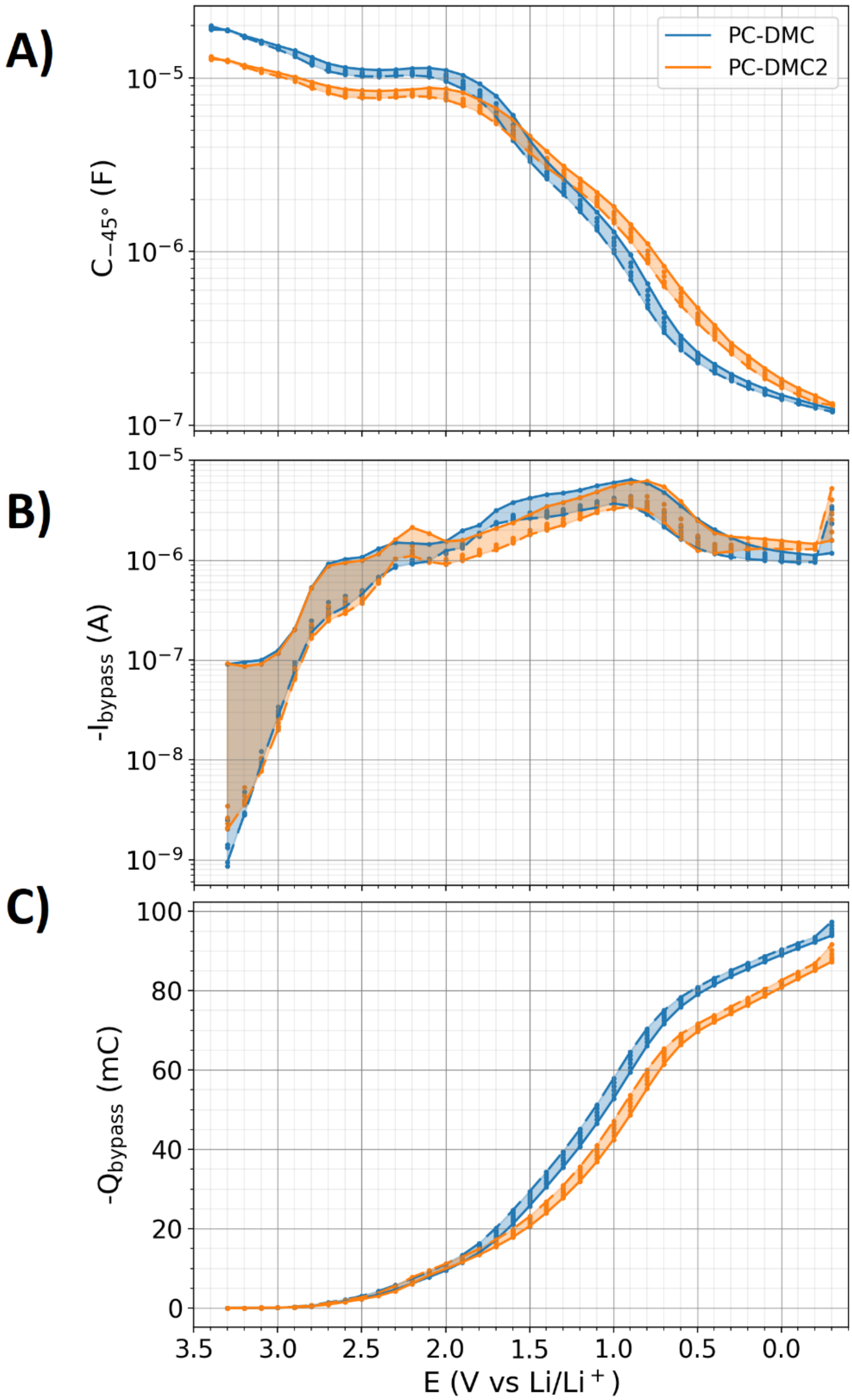

Figure S12: Metrics derived from the electrochemical step protocol for two measurements with the PC-DMC electrolyte.

5 Cyclic voltammetry data

In the following, first the full cyclic voltammetry data of the measurements shown in the manuscript are graphed individually for each electrolyte. Second, the data of the first scans are individually compared to repetition measurements.

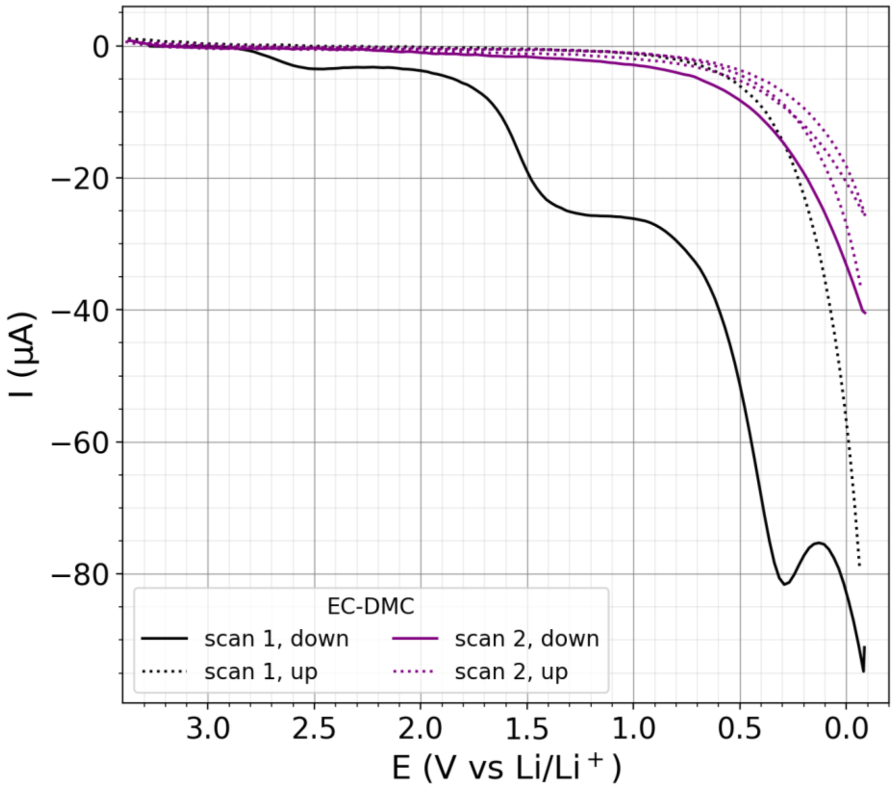

Figure S13: Full CV data with individual branches of the EC-DMC electrolyte.

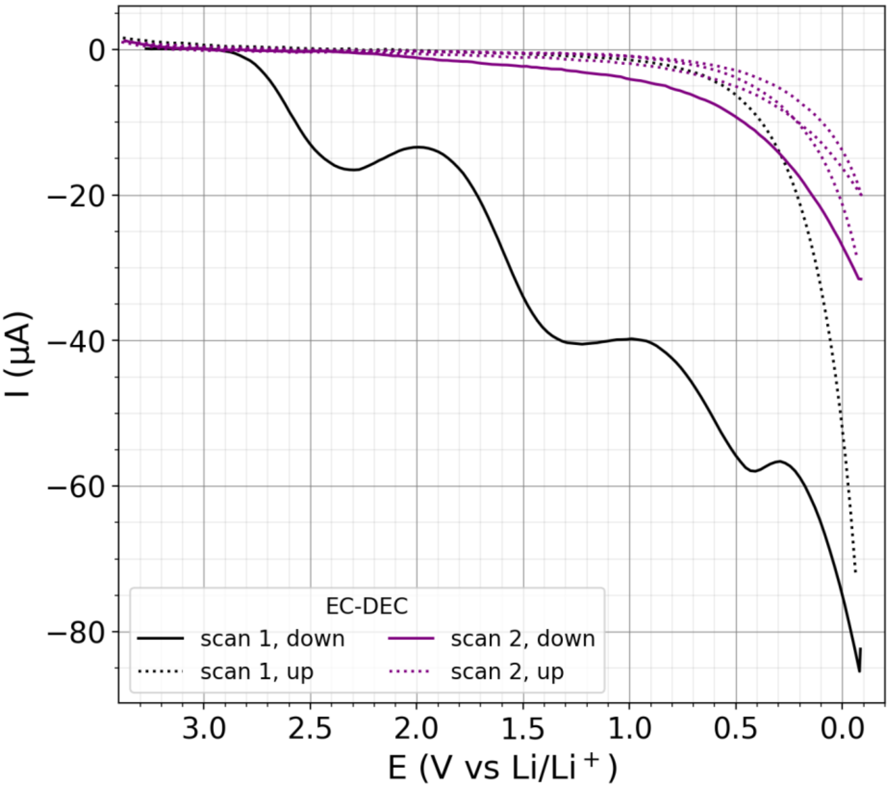

Figure S14: Full CV data with individual branches of the EC-DEC electrolyte.

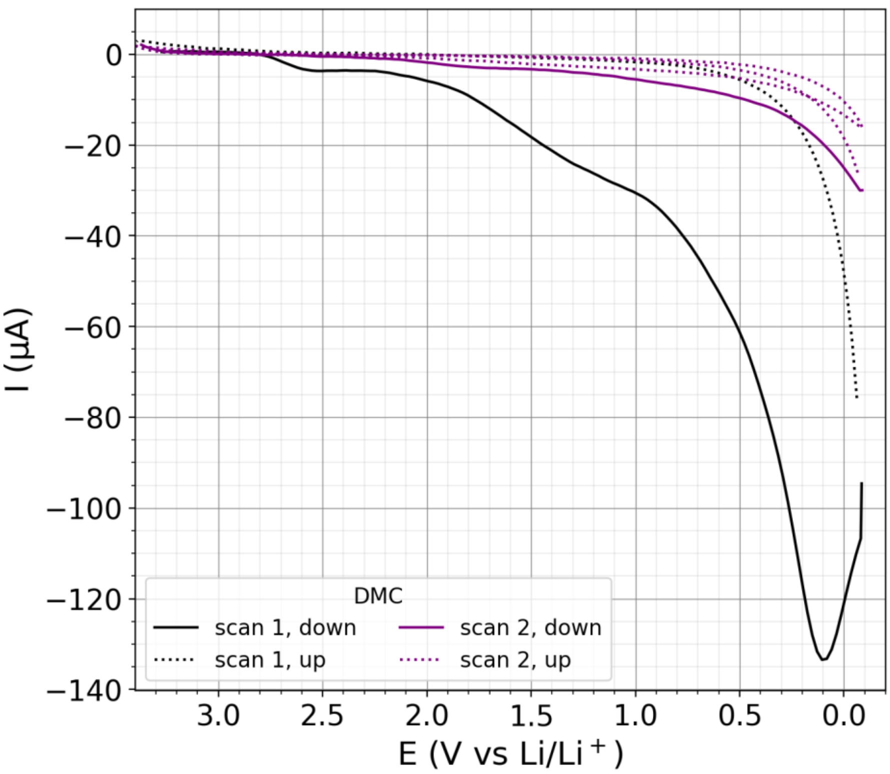

Figure S15: : Full CV data with individual branches of the DMC electrolyte.

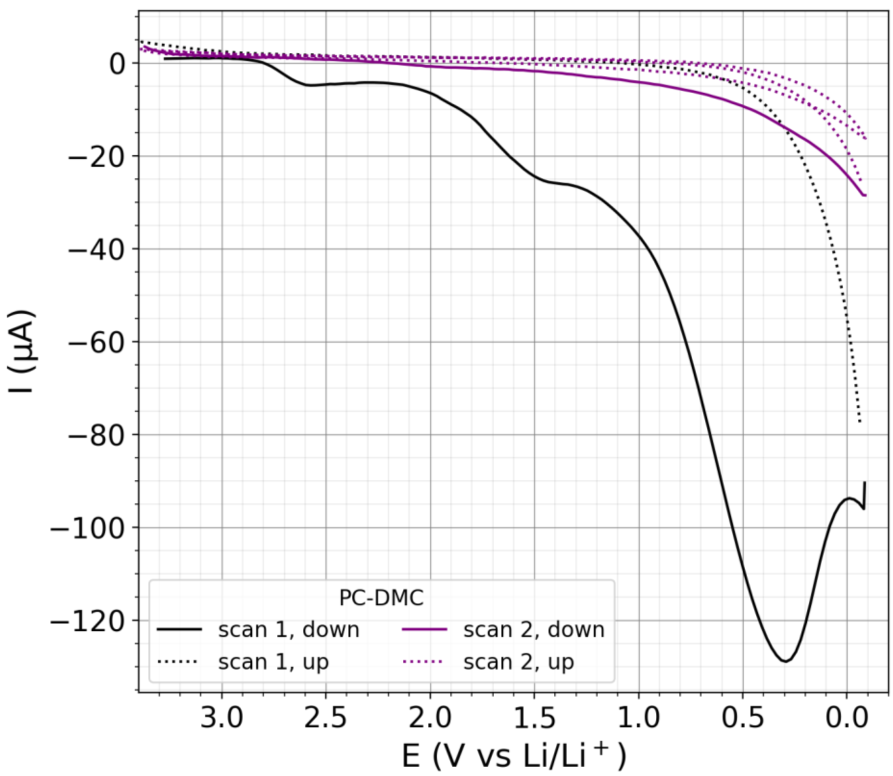

Figure S16: Full CV data with individual branches of the PC-DMC electrolyte.

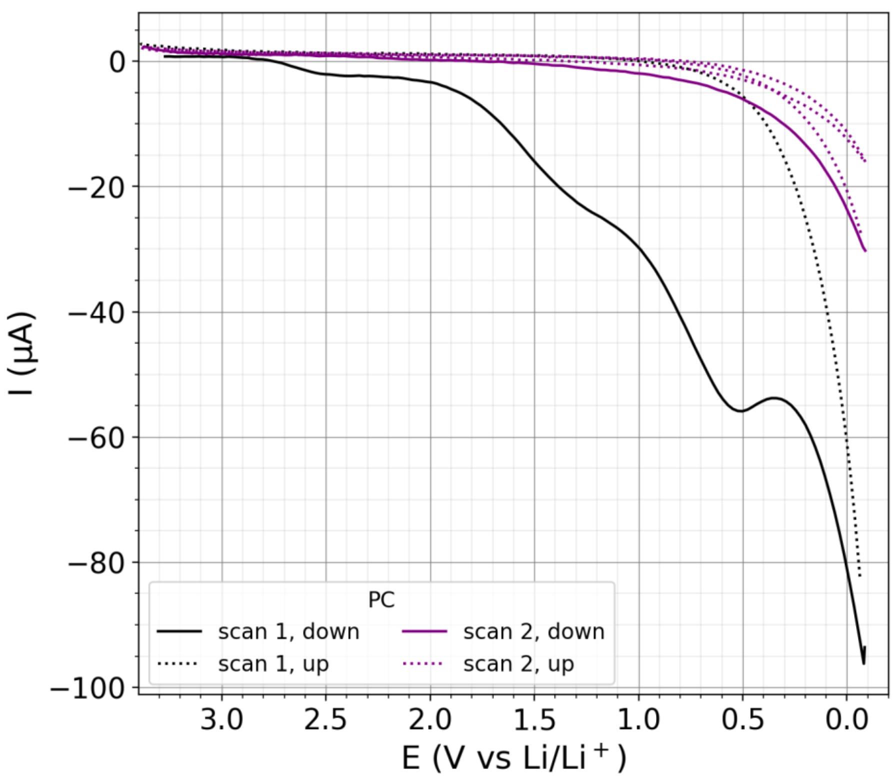

Figure S17: Full CV data with individual branches of the EC-DMC electrolyte.

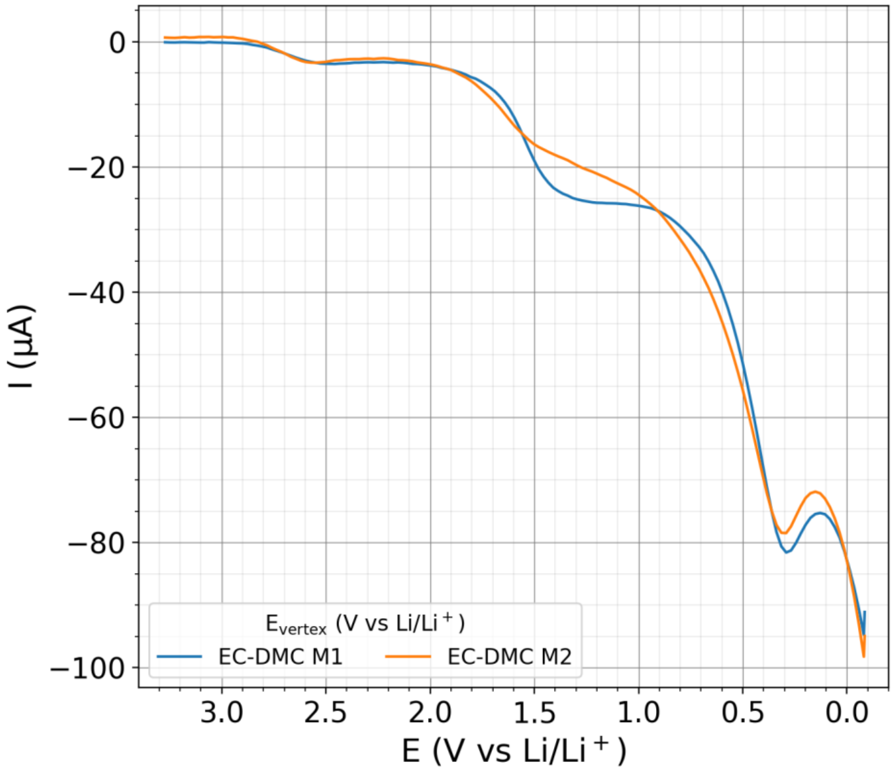

Figure S18: CV data of the data from the manuscript compared to a reproduction measurement.

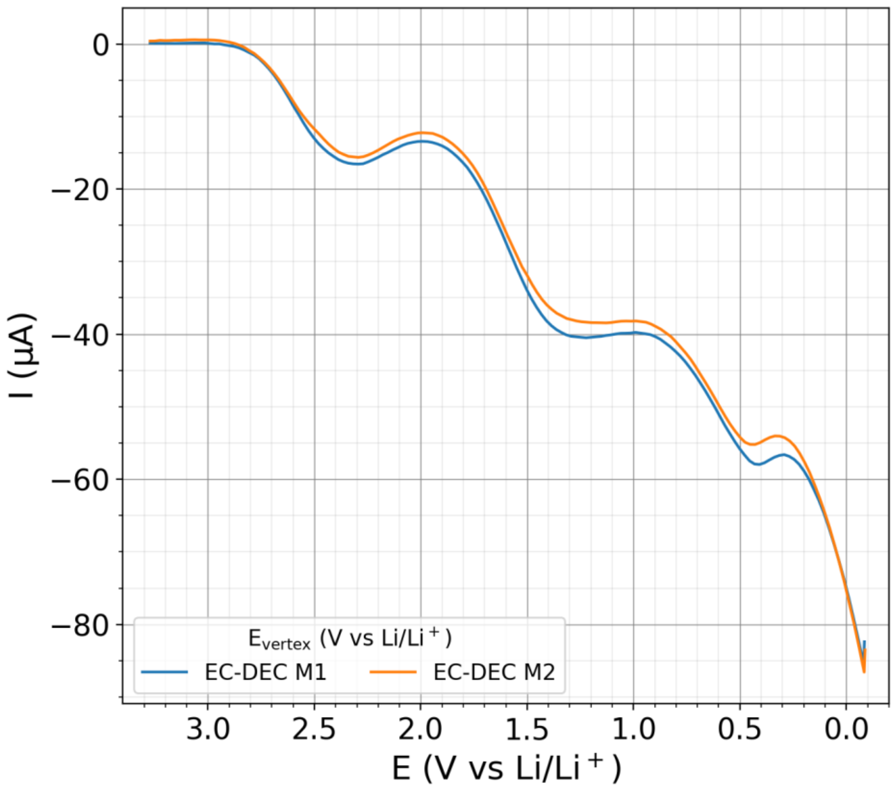

Figure S19: CV data of the data from the manuscript compared to a reproduction measurement.

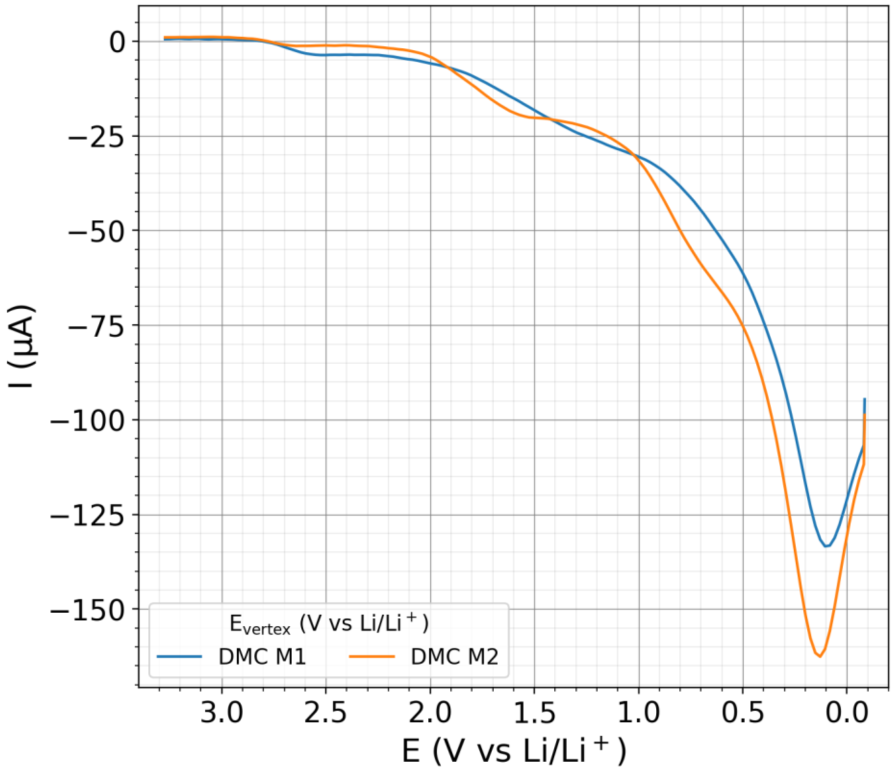

Figure S20: CV data of the data from the manuscript compared to a reproduction measurement.

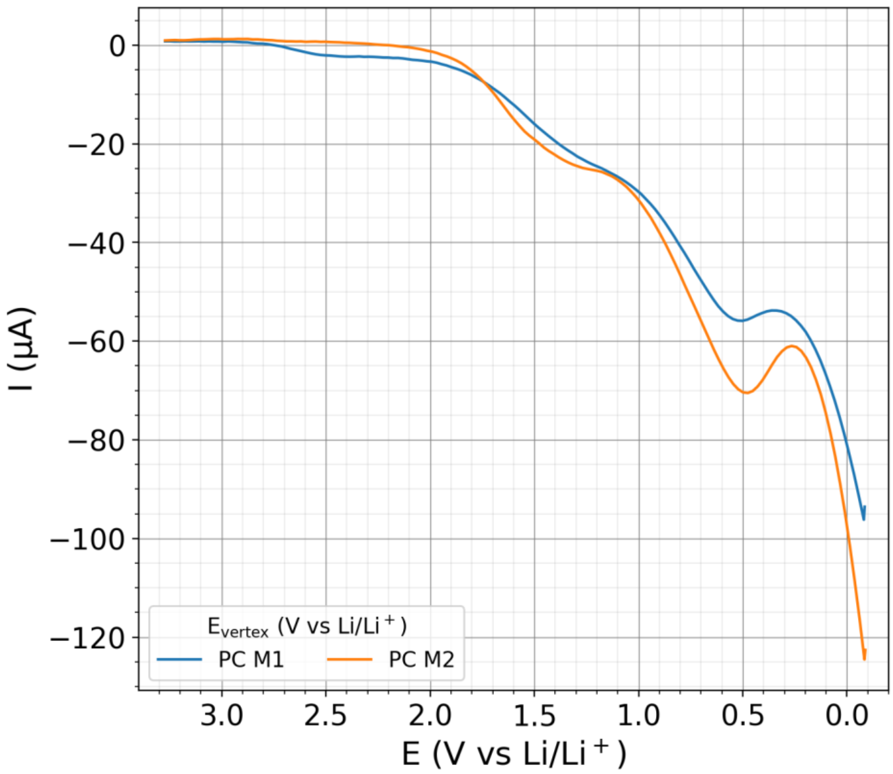

Figure S21: CV data of the data from the manuscript compared to a reproduction measurement.

6 Python codes

The following function was developed to extract the capacitance at the relaxation frequency from the impedance spectra.

```
def eval_df(df):
    # Determine the electrolyte resistance
    df = df.sort_values(by=['f'],ascending = False)
    df = df.reset_index(drop = True)

    # filter frequency range for evaluation
    df = df[df["f"]< 2e5]
    df = df[df["f"]> 0.1]

    # filter phase angle
    df = df[df["phase"]<0]

    # ist ja totaler quatsch!!!
    df_test = df.copy()
    df_test = df_test[df_test["f"]>1e3].copy()
    index_R_s = np.argmin(abs(df_test["phase"]))
    R_s = df_test.at[df_test.index[index_R_s],"Z_real"]

    # determine relaxation frequency
    df_r = df.copy()
    iindex_phase_min = np.argmin(df_r["phase"])
    index_phase_min = df_r.index[iindex_phase_min]
    df_r = df_r[df_r.index<=index_phase_min]
    index_relax = np.argmin(abs(df_r["phase"] +45))
    low = index_relax-1
    high = index_relax+1
    f_relax = np.interp(45, -df_r["phase"].iloc[low:high], df_r["f"].iloc[low:high])
    C_relax =  np.interp(45, -df_r["phase"].iloc[low:high], df_r["C"].iloc[low:high])

    phase_min = df_r["phase"].min()
    index_1Hz = np.argmin(abs(df["f"] -1))
    C_1Hz = df.at[df.index[index_1Hz],"C"]

    index_10Hz = np.argmin(abs(df["f"] -10))
    C_10Hz = df.at[df.index[index_10Hz],"C"]

    index_01Hz = np.argmin(abs(df["f"] -0.1))
    Z_real_01Hz = df.at[df.index[index_01Hz],"Z_real"]
    phase_01Hz = df.at[df.index[index_01Hz],"phase"]
    return [R_s,phase_min, f_relax, C_relax*1e6,C_1Hz*1e6,phase_01Hz,Z_real_01Hz]
```