Supporting Information for

Temperature Reduction as Operando Performance Recovery Procedure for Polymer Electrolyte Membrane Fuel Cells

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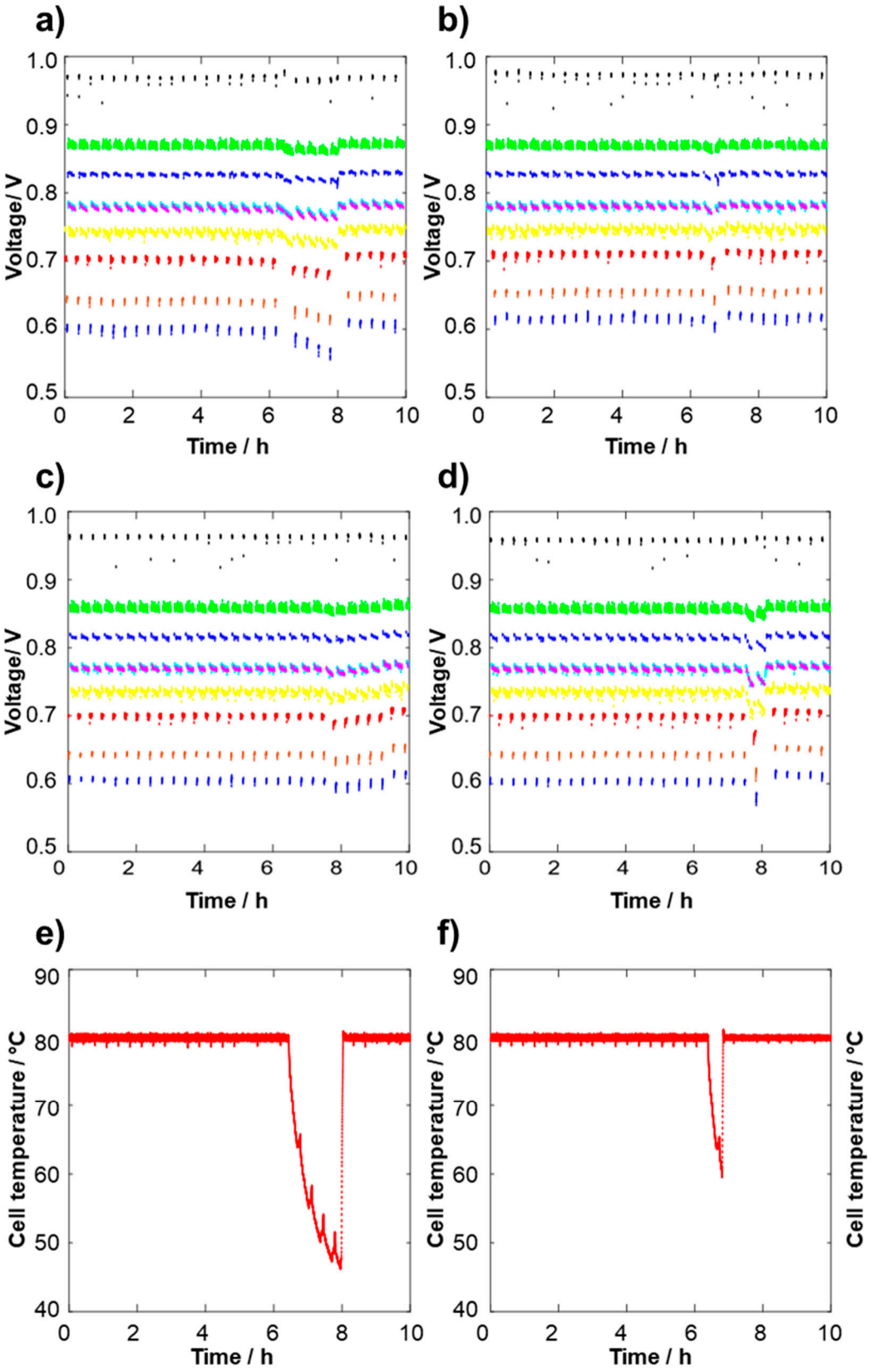
JRC recovery protocol:

Upon the load switching off, the air flow and cathode outlet are closed. The hydrogen flow on the anode side is maintained until the cell voltage drops below 0.1 V, which takes about 25 min. After that, dry N_2 purges both the anode and cathode for 30 min, followed by dry air purging for another 30 min. Subsequently, the gas supply to both anode and cathode is switched off while keeping the gas outlet valves closed. For the next 8 h, the cell heating is shut down, allowing the cell to cool to ambient temperature. Upon restarting of the cell, both the anode and cathode are purged with humified N_2 for 30 min while heating the cell to 80 °C. The entire procedure, including the restart, takes 10 h 25 min in our lab.


a)
b)
c)
d)
e)
f)
Voltage/ V
Time / h
Cell temperature / °C
1.0
0.9
0.8
0.7
0.6
0.5
90
80
70
60
50
40
0
2
4
6
8
10

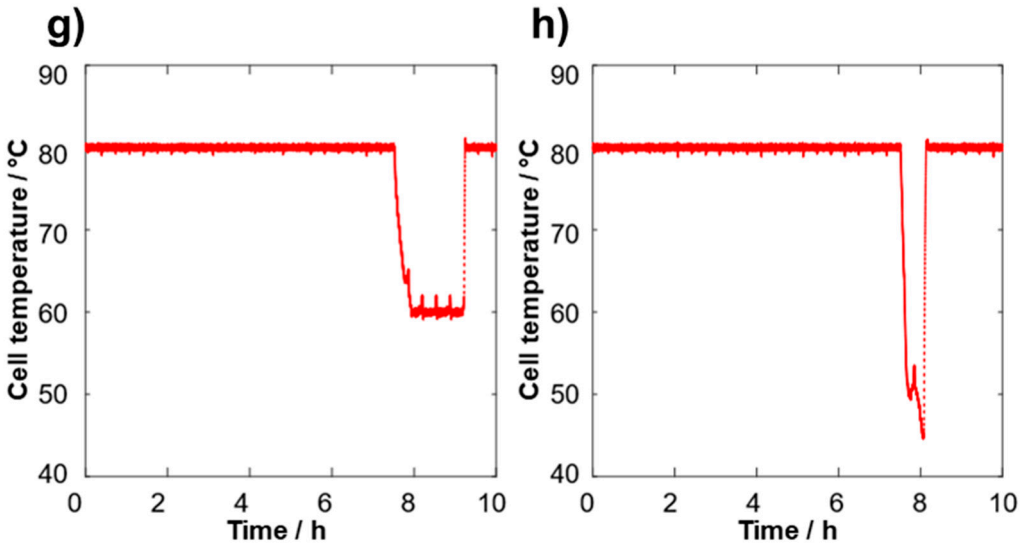


Figure S1. Voltage changes during the operando temperature reduction: (**a**,**e**) correspond to the Recovery 1, 80 °C to 45 °C (95 min); (**b**,**f**) correspond to the Recovery 2, 80 °C to 60 °C (35 min); (**c**,**g**) correspond to the Recovery 5, 80 °C to 60 °C (95min); (**d**,**h**) correspond to the Recovery 6, 80 °C to 45 °C (35 min). Recovery 3 and 4 are repetition of Recovery 1 and 2, which show similar results and are not presented here.

Irreversible degradation rate:

To calculate the irreversible performance degradation rate of the MEA during the durability test, voltage values (belonging to each current density level of the FC-DLC operation) at the beginning of each test block (i.e., after the JRC recovery protocol) were used to perform a linear regression. An example is provided in Figure S2a) for a current density of 1 A·cm^{-2}, represented by the red data points (voltage at the beginning of each test block) and the red dash line (linear fit). It is noted that the irreversible degradation defined by the slope of the linear fit refers to operation time (i.e., test time without all non-operando periods). The calculated irreversible degradation rates versus current density are provided in Figure S2b).

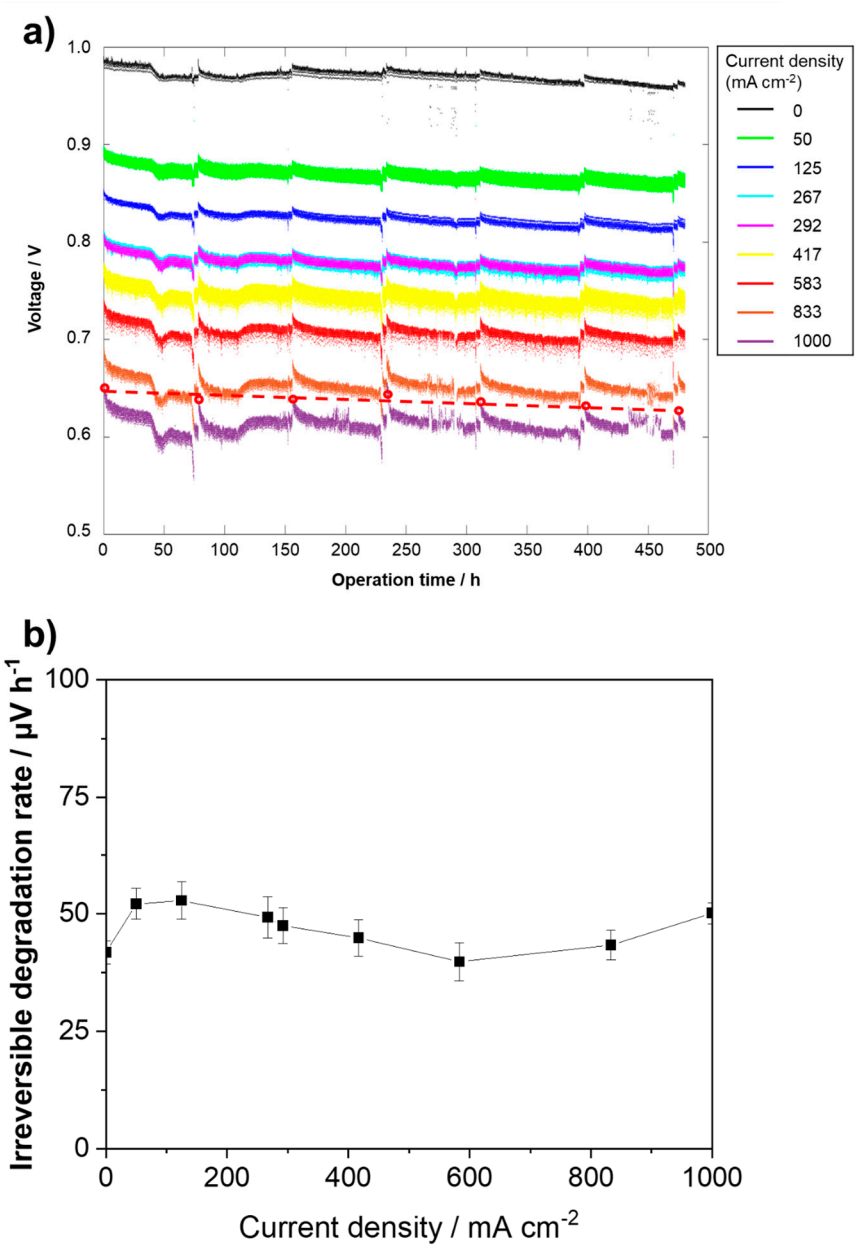
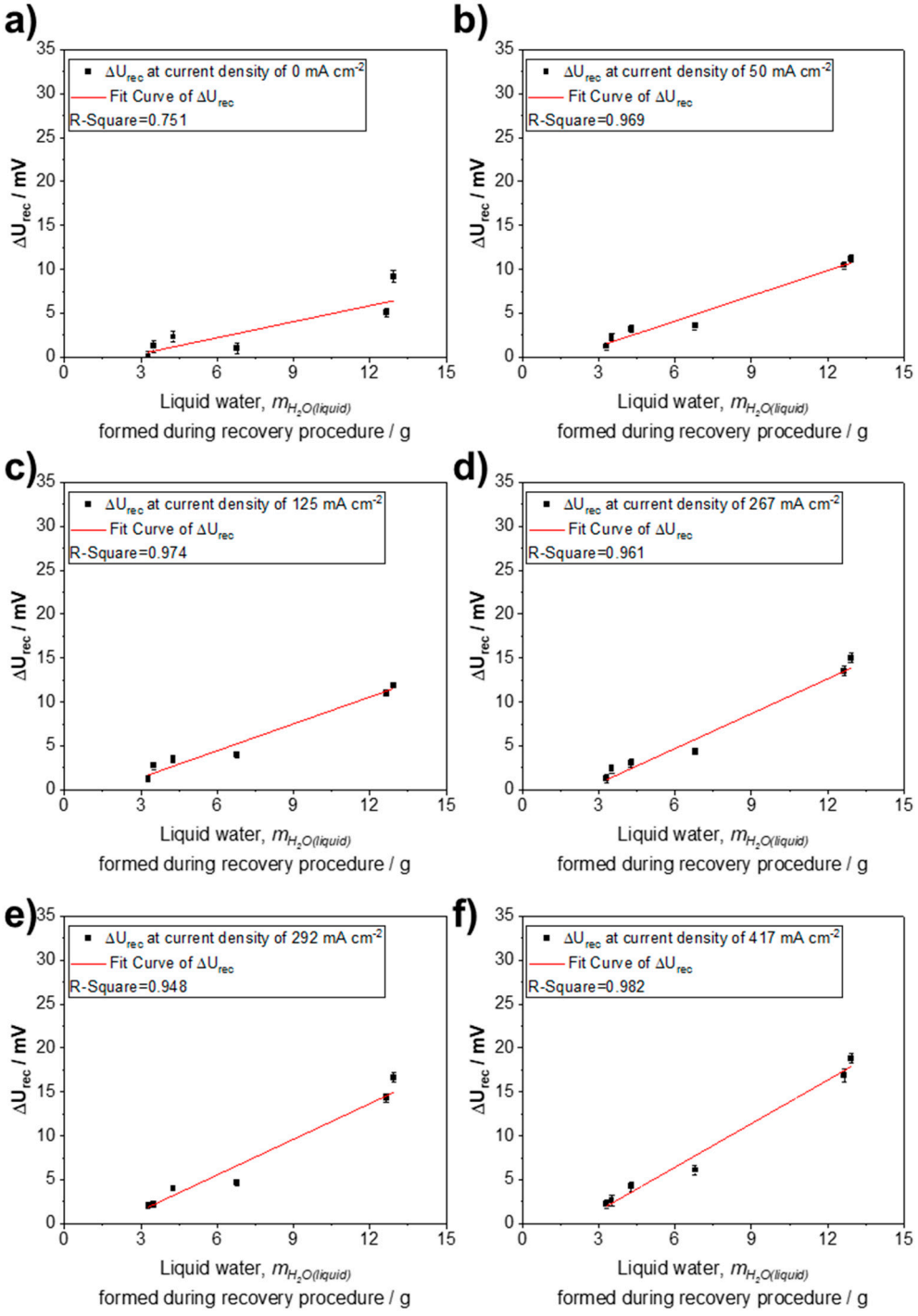


Figure S2. (**a**) Cell voltage recorded during the durability test for the investigation of recovery procedures based on operando temperature reduction. The red points are the cell voltage at the beginning of each test block at 1 A cm^{-2}. (**b**) Irreversible degradation rate at the current density range from 0 to 1 A cm^{-2}.


a)
ΔU_rec at current density of 0 mA cm-2
Fit Curve of ΔU_rec
R-Square=0.751
b)
ΔU_rec at current density of 50 mA cm-2
Fit Curve of ΔU_rec
R-Square=0.969
c)
ΔU_rec at current density of 125 mA cm-2
Fit Curve of ΔU_rec
R-Square=0.974
d)
ΔU_rec at current density of 267 mA cm-2
Fit Curve of ΔU_rec
R-Square=0.961
e)
ΔU_rec at current density of 292 mA cm-2
Fit Curve of ΔU_rec
R-Square=0.948
f)
ΔU_rec at current density of 417 mA cm-2
Fit Curve of ΔU_rec
R-Square=0.982
ΔU_rec / mV
Liquid water, m_H2O(liquid)
formed during recovery procedure / g

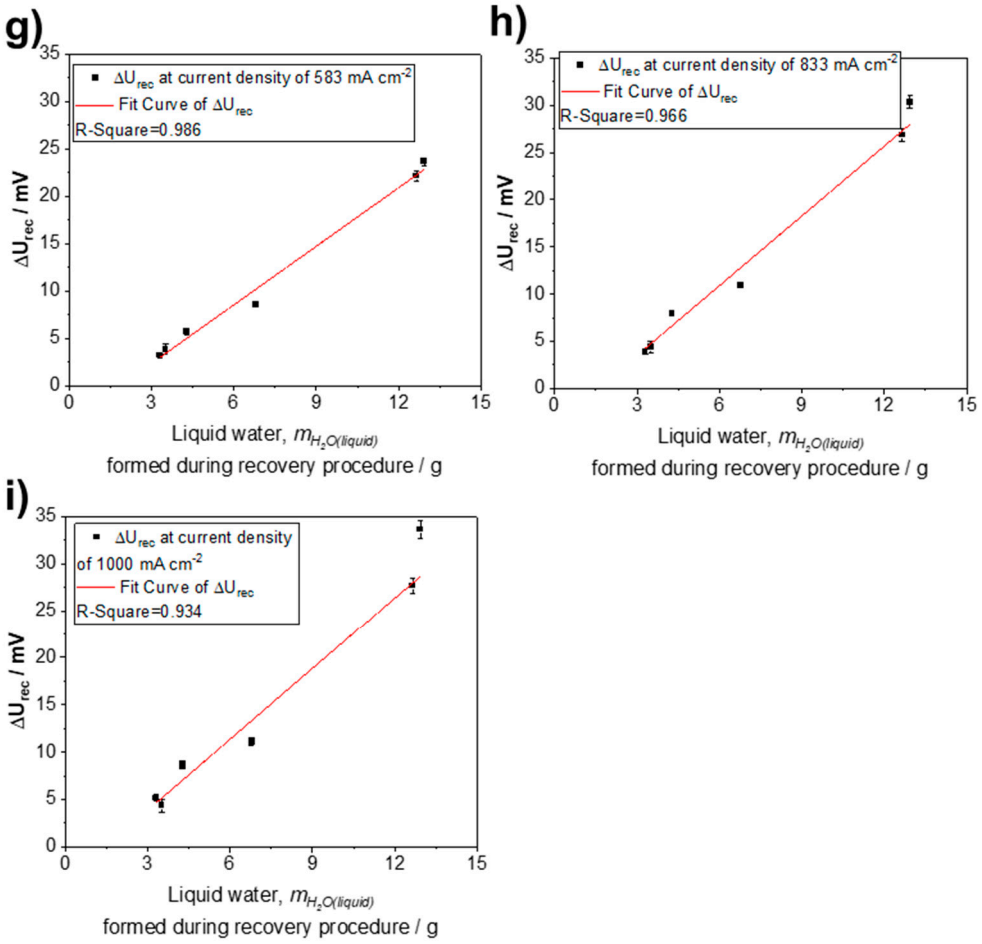


Figure S3. Absolute recovered voltage versus total amount of liquid water formed during operando recovery at all the evaluated current densities from 0 to 1 A cm^{-2}. Recovered voltage corresponds to data from Figure 3b.

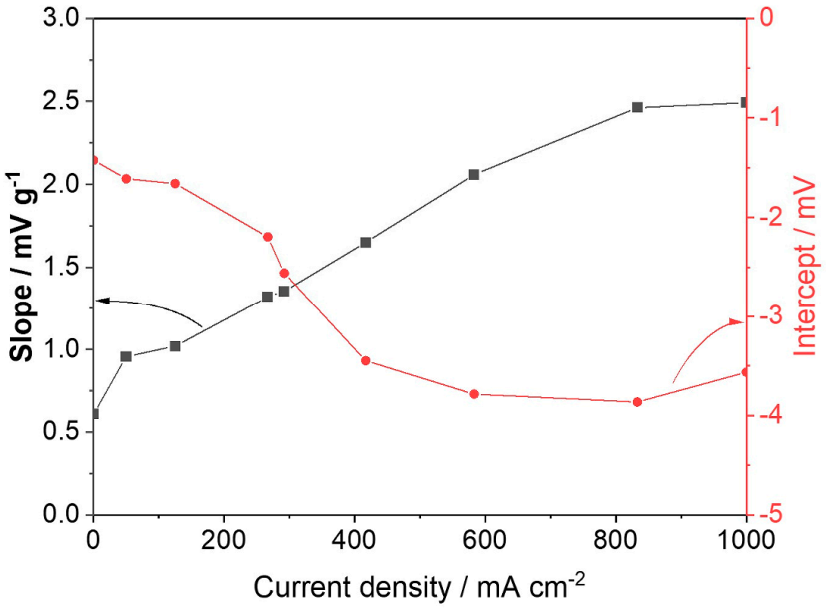


Figure S4. Slope and intercept of the linear fitting results between the absolute recovered voltage and the formed liquid water during each operando recovery procedure at different current densities.

Recovery effect of the non-operando performance recovery procedures with temperature reduction:

Figure S5 a) shows the cell voltages at various current density levels according to Figure 5, excluding all the recovery procedures and performance characterization measurements. Similar to Figure S2, the slope of the dashed red line presents the irreversible performance degradation rate of the fuel cell upon the 400-h FC-DLC operation. According to Figure 5 b), the irreversible performance degradation rate at the current density range from 0 to 1 A cm^{-2} varies between 75 and 125 $\mu V\,h^{-1}$. Additionally, the average reversible performance degradation rate of each test block, calculated using $\Delta U_{i=n}^{rev}$ from Figure 6, is 430 $\mu V\,h^{-1}$ at 1 A cm^{-2}. The similarity in average rates of reversible performance degradation in the two durability tests can be attributed to the same test hardware and operation parameters. On the other hand, the irreversible performance degradation rate in the durability test with the non-operando recovery procedure, although still much lower than the rates reported in the literature, is significantly higher than that observed with operando recovery procedures. This discrepancy is ascribed to the OCV periods during the recovery process.

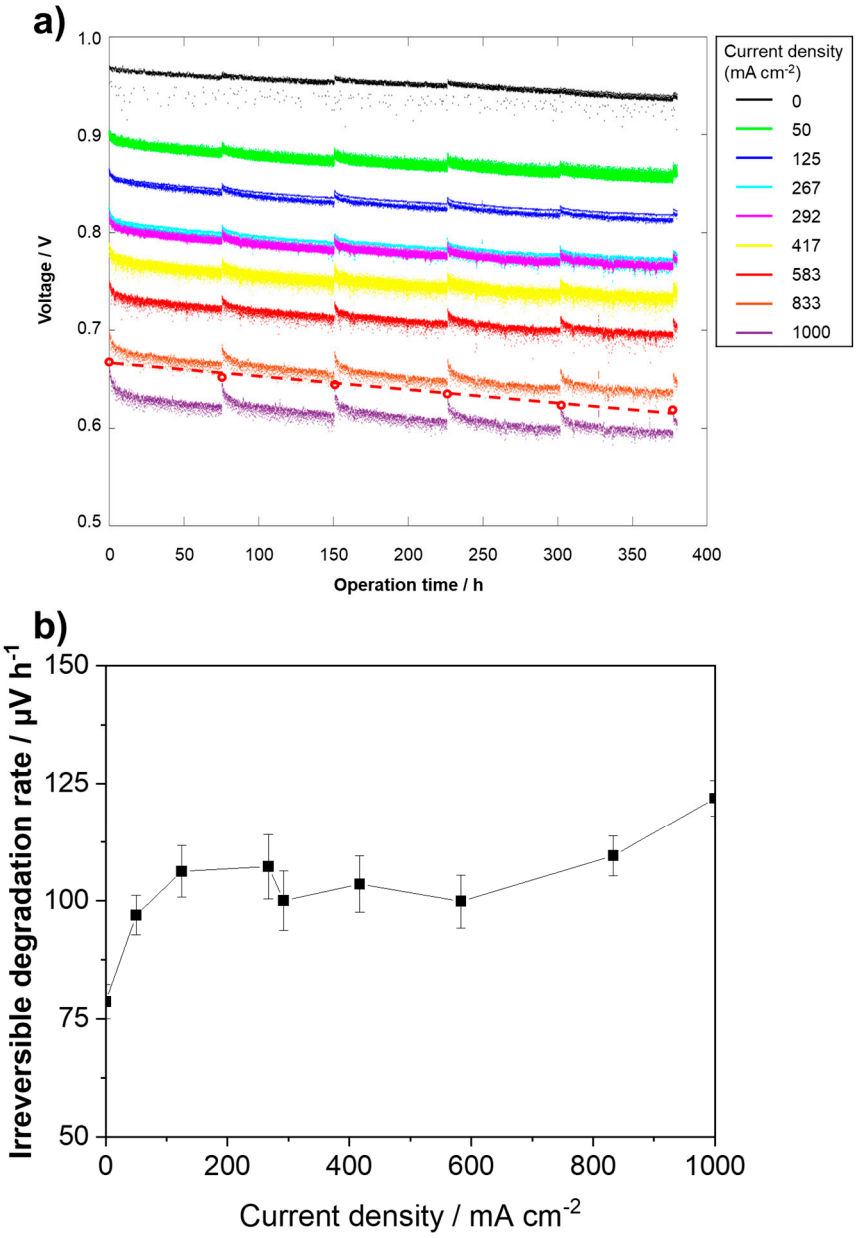


Figure S5. (**a**) Cell voltage recorded during the durability test for the investigation of recovery procedures based on non-operando temperature reduction. The red points are the cell voltage at the beginning of each test block at 1 A cm^{-2}. (**b**) Irreversible degradation rate at the current density range from 0 to 1 A cm^{-2}.

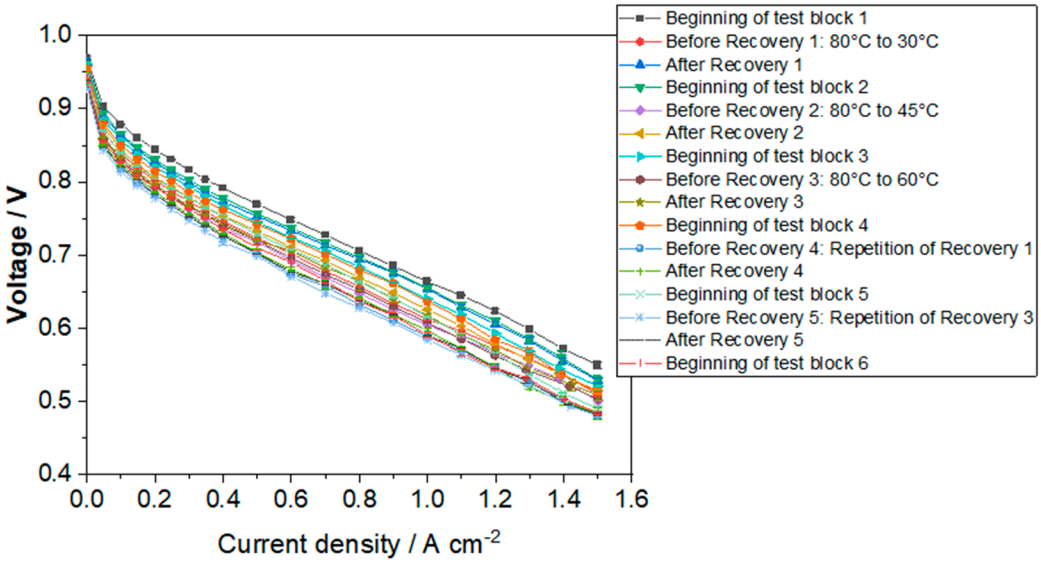
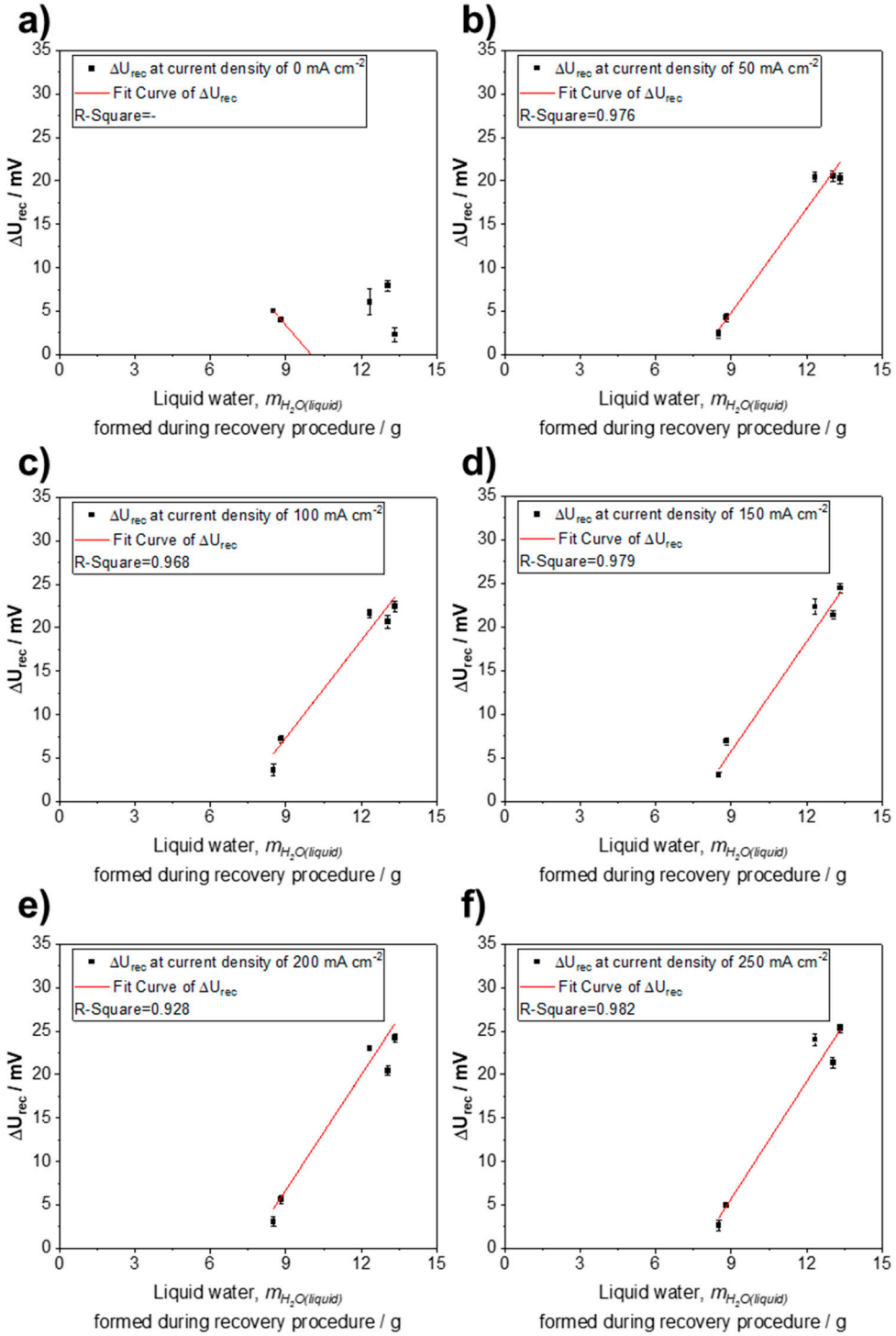
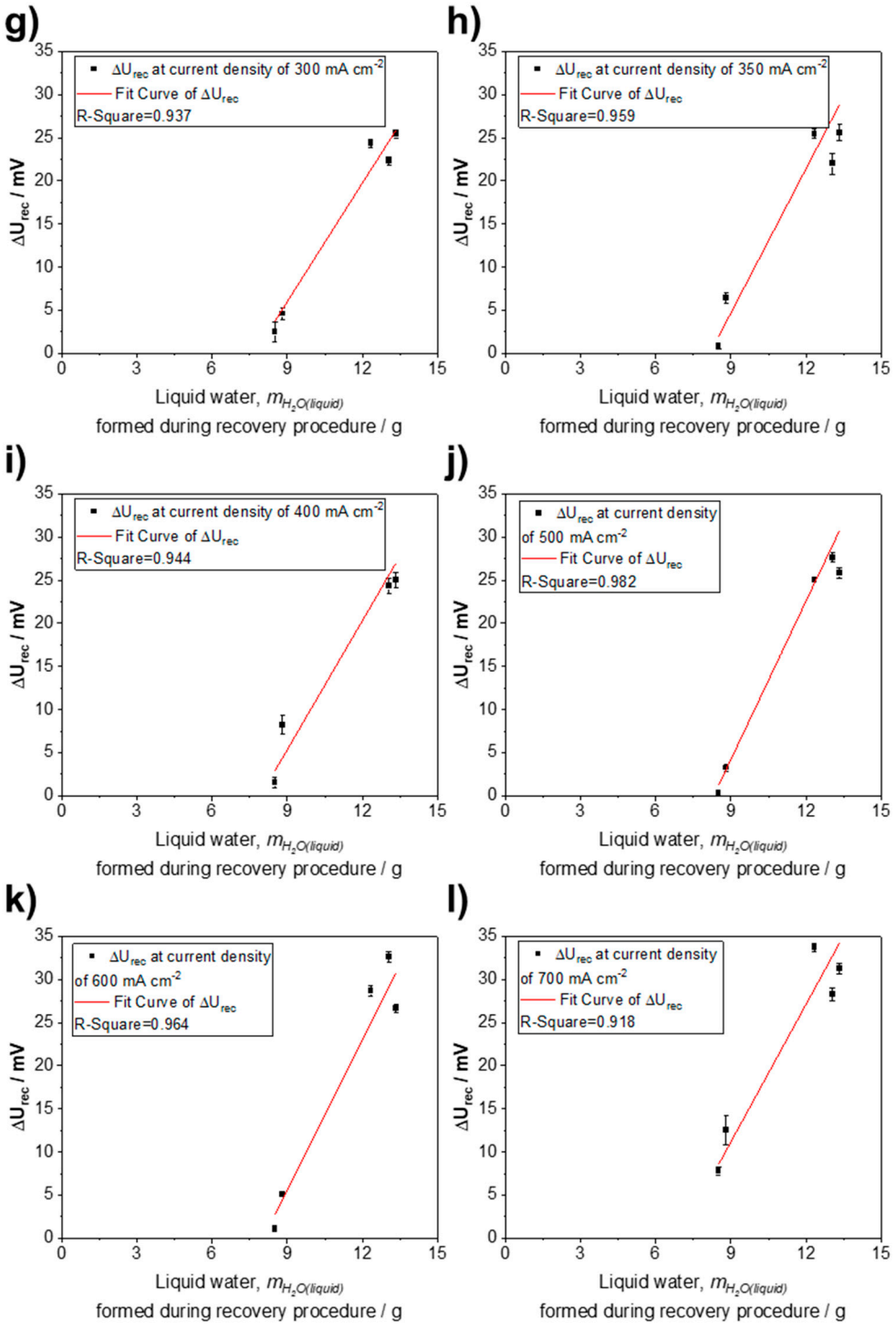
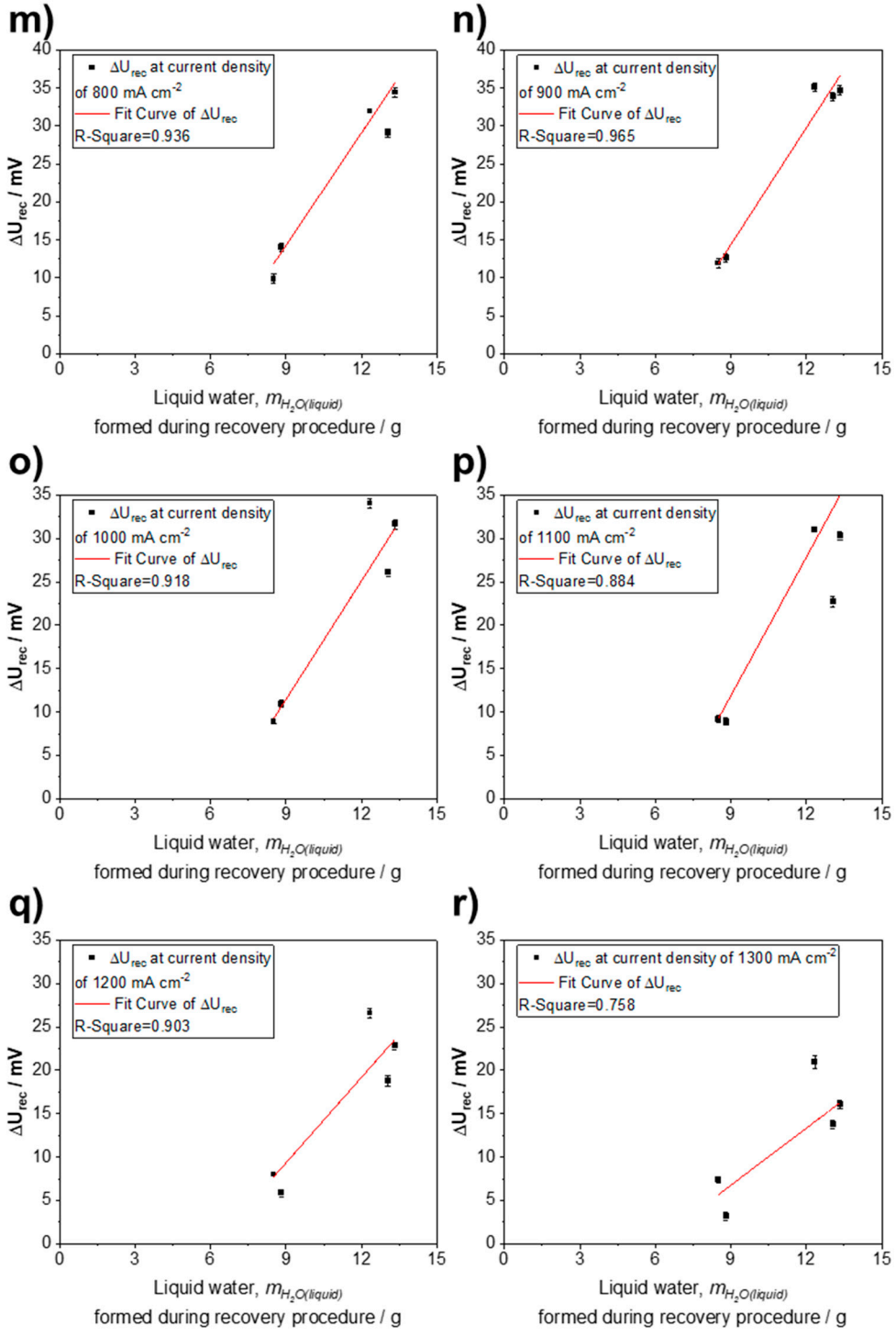


Figure S6. Polarization curves measured during the durability test with non-operando temperature reduction. The error bars correspond to the standard deviation from the average of the last 30 s of the dwell time of each tested current density step.


a)
ΔU_rec at current density of 0 mA cm^-2
Fit Curve of ΔU_rec
R-Square=-
b)
ΔU_rec at current density of 50 mA cm^-2
Fit Curve of ΔU_rec
R-Square=0.976
c)
ΔU_rec at current density of 100 mA cm^-2
Fit Curve of ΔU_rec
R-Square=0.968
d)
ΔU_rec at current density of 150 mA cm^-2
Fit Curve of ΔU_rec
R-Square=0.979
e)
ΔU_rec at current density of 200 mA cm^-2
Fit Curve of ΔU_rec
R-Square=0.928
f)
ΔU_rec at current density of 250 mA cm^-2
Fit Curve of ΔU_rec
R-Square=0.982
ΔU_rec / mV
Liquid water, m_H2O(liquid)
formed during recovery procedure / g


g)
h)
i)
j)
k)
l)
ΔU_rec at current density of 300 mA cm^-2
Fit Curve of ΔU_rec
R-Square=0.937
ΔU_rec at current density of 350 mA cm^-2
Fit Curve of ΔU_rec
R-Square=0.959
ΔU_rec at current density of 400 mA cm^-2
Fit Curve of ΔU_rec
R-Square=0.944
ΔU_rec at current density of 500 mA cm^-2
Fit Curve of ΔU_rec
R-Square=0.982
ΔU_rec at current density of 600 mA cm^-2
Fit Curve of ΔU_rec
R-Square=0.964
ΔU_rec at current density of 700 mA cm^-2
Fit Curve of ΔU_rec
R-Square=0.918
ΔU_rec / mV
Liquid water, m_H2O(liquid) formed during recovery procedure / g


m)
ΔU_rec at current density of 800 mA cm-2
Fit Curve of ΔU_rec
R-Square=0.936
n)
ΔU_rec at current density of 900 mA cm-2
Fit Curve of ΔU_rec
R-Square=0.965
o)
ΔU_rec at current density of 1000 mA cm-2
Fit Curve of ΔU_rec
R-Square=0.918
p)
ΔU_rec at current density of 1100 mA cm-2
Fit Curve of ΔU_rec
R-Square=0.884
q)
ΔU_rec at current density of 1200 mA cm-2
Fit Curve of ΔU_rec
R-Square=0.903
r)
ΔU_rec at current density of 1300 mA cm-2
Fit Curve of ΔU_rec
R-Square=0.758
ΔU_rec / mV
Liquid water, m_H2O(liquid) formed during recovery procedure / g

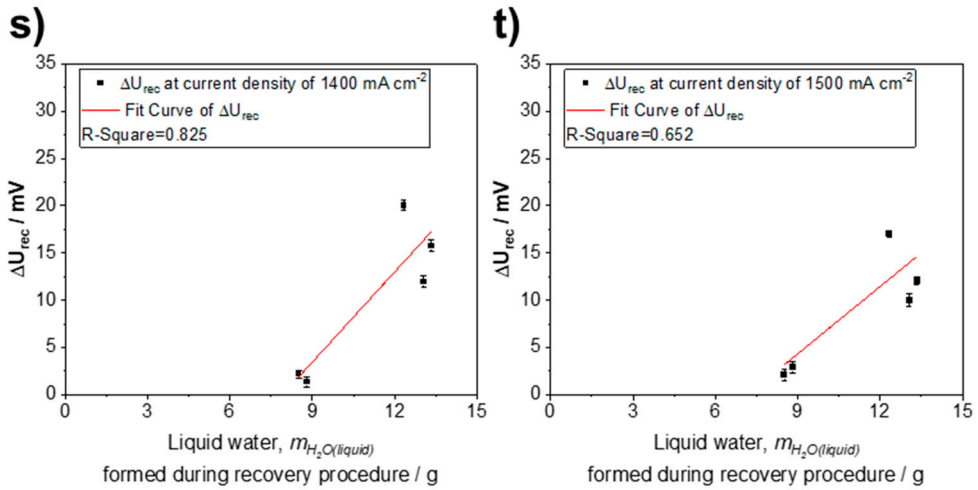


Figure S7. Absolute recovered voltage versus total amount of liquid water formed during non-operando recovery at all the evaluated current densities from 0 to 1.5 A cm^{-2}. Recovered voltage corresponds to data from Figure 6b.

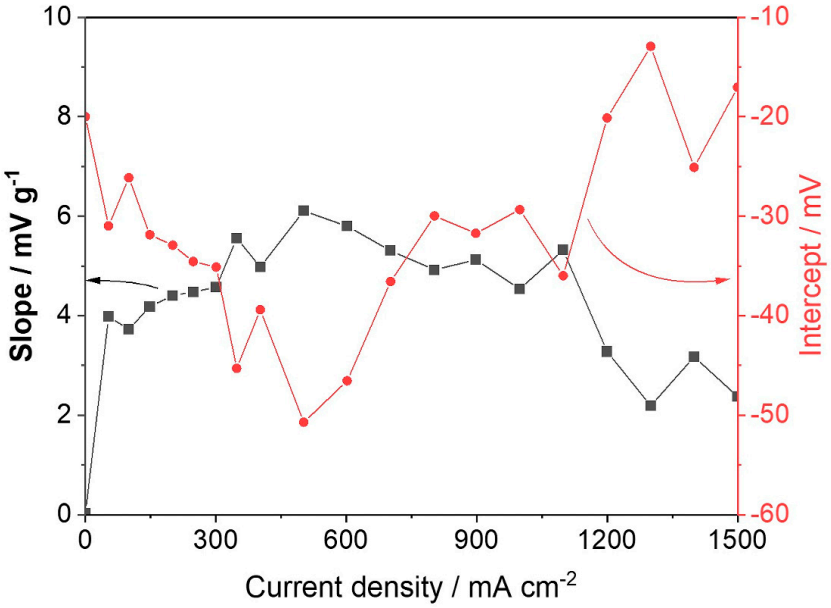


Figure S8. Slope and intercept of the linear fitting results between the absolute recovered voltage and the formed liquid water during each non-operando recovery procedure at different current densities.