

Three-Electrode Cell Calorimeter for Electrical Double Layer Capacitors

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A calorimeter was built to measure the heat from a porous capacitive working electrode connected in a three-electrode configuration. This makes it possible to detect differences between cathodic and anodic heat production. The electrochemical cell contains a large electrolyte solution reservoir, ensuring a constant concentration of the salt solution probed by the reference electrode via a Luggin tube. A heat flux sensor is used to detect the heat, and its calibration as a gauge of the total amount of heat produced by the electrode is done on the basis of the net electrical work performed on the working electrode during a full charging-discharging cycle. In principle, from the measured heat and the electrical work, the change in internal energy of the working electrode can be determined as a function of applied potential. Such measurements inform about the potential energy and average electric potential of ions inside the pores, giving insight into the electrical double layer inside electrode micropores. Example measurements of the heat are shown for porous carbon electrodes in aqueous salt solution.

I. INTRODUCTION

Capacitive porous electrodes are of interest for instance as supercapacitors in power delivery systems¹ and as reversible salt adsorbants in water desalination.² During charging of a porous electrode, electrical energy and ions are stored in the electrical double layer (EDL). Experimental characterization of the EDL helps to elucidate the energetic or ionic uptake capacity of the electrode. Changes in the amount of charge can be measured in the external electrical circuit.^{3,4} Additional information on the charging mechanism and the amounts of ions inside the pores can for instance be obtained from in situ NMR spectroscopy,^{5–8} infrared spectroscopy,^{9,10} and small-angle neutron scattering.^{11,12} Here, we will focus on a thermodynamic characterization approach that consists of measuring the heat exchanged while the electrode is being charged or discharged.

Electrodes in any electrochemical cell produce heat, although this is generally not the intended outcome. One example is heat generation during electrolysis reactions.¹³ Another is Joule heat produced by supercapacitors,¹⁴ which can cause a strong temperature rise that can be damaging for their performance.^{15–17} When it is possible to determine the reversible heat, this provides valuable information on the change in thermodynamic state of the system. The reversible heat can for example correspond to the enthalpy changes due to the electrochemical processes^{18,19} or to the entropic heat from batteries, in agreement with the temperature dependence of their open circuit voltage.²⁰ For supercapacitors, the reversible heat has been interpreted in different ways, as the entropic heat from the confinement of ions into the pores of the electrodes,²¹ or as changes in the entropic part of the grand potential energy,^{22,23} or as due to several entropic and enthalpic contributions because of mixing as well as electrical and steric

interactions of the ions,^{24–26} or as due to nonzero potential energy of the ions in the pores.²⁷

Measuring heat from porous electrodes requires a different measurement approach than measuring heat from submonolayer changes at a flat electrode,²⁸ which result in very little heat, produced very briefly.²⁹ This requires highly sensitive and rapid detection, which can for instance be achieved using lithium tantalate-based sensors.³⁰ Porous electrodes have a much higher surface area and slow ionic transport in an extensive porous network,^{31,32} resulting in much more heat production but spread out over a much longer time. Due to the long duration of heat production, the measurement requires a very stable background temperature to differentiate from heat exchange due to temperature changes in the environment.

Here, a setup is presented that measures the heat of charging and discharging from a capacitive porous carbon³³ electrode, connected in a 3-electrode configuration. The setup was first used in Ref. 27, where it was described much more briefly. Earlier experiments on capacitive porous electrodes were done on 2-electrode cells, by measuring the temperature of the complete cell using a resistance temperature detector,^{21,34} or by measuring the separate heats of both electrodes, using heat flux sensors.^{25,35} When the heat of a complete cell is measured, differences between cathodic and anodic heat production cannot be distinguished. This limitation disappears when the heat of individual electrodes is measured. However, when the cell has only two electrodes, even though it is clear that the charge that exits one electrode enters the other electrode, it is more difficult to clarify differences between cathodic and anodic behavior, because the potentials applied to each electrode are not determined against a constant reference. In the setup presented here, a reference electrode is introduced as the third electrode. The current still flows from the working electrode to a counter electrode, but the potential on the working electrode is applied and measured with respect to an invariant reference electrode. A three-electrode cell is commonly used in electrochemistry,³⁶ but not for measurements on commercial batteries or supercapacitors. In Section II, the design and operation of the setup are presented, and

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typical measurements are shown in Section III.

II. DESIGN AND OPERATION

A. Electrochemical setup

The electrochemical cell developed to measure heat effects of capacitive porous electrodes in a 3-electrode configuration is shown in Fig. 1. The cell has three glass parts. The central part consists of a horizontal cylinder (6.4 cm in length, 2.5 cm in external diameter) whose extremities are glued into the central hole (2.5 cm diameter) of square blocks (5 cm by 5 cm, 5 mm thick). These glued square blocks of the central part are connected to two outer square parts of the cell via plastic screws inserted into four holes at the corners of the squares, see Fig. 1(a). One of the outer square parts contains the counter electrode (CE), and the other contains the working electrode (WE) and the heat flux sensor (HFS). The WE and CE are mounted vertically, allowing gas to escape from the electrode surface. The separation of 6.4 cm between the electrodes ensures that no measurable heat of the CE reaches the heat flux sensor mounted behind the WE (given the thermal diffusivity of water³⁷, the timescale for heat diffusion across 6.4 cm of water is more than an hour). The volume of the cylinder (30 mL) is sufficiently large that the salt concentration remains approximately constant. The reference electrode (RE) senses the potential of the solution near the WE via a Luggin tube. Typically, a Radiometer Analytical REF201 Red Rod Ag/AgCl/saturated KCl is used as RE.

The WE and the CE each consist of a disk of porous carbon with a diameter of 22 mm and a thickness of typically 0.4 mm. Compared to a Pt CE, a porous carbon CE has the advantage that it does not produce hydrogen or oxygen gas under our measurement conditions, gases which can be oxidized or reduced at the WE, leading to faradaic currents which complicate the interpretation. At the center, these electrodes are glued to a nonporous carbon disk of 25 mm in diameter using a minimal amount of nonconductive Bison Kombi Snel epoxy glue. Mechanical contact between the WE and the current collector (a nonporous carbon disk of the same dimensions) is realized by pushing them together at their outer rims with a flat 50 μ m thick Teflon ring itself pushed by a 2 mm thick rubber O-ring with a diameter of 21 mm. The central part of the electrode exposed to the solution has a diameter of 18.5 mm. An electrically insulated copper wire is glued to the back side of the current collector using silver epoxy glue (Chemtronics[®] CW2400 conductive epoxy), ensuring electrical contact. This is topped off with nonconductive epoxy glue to insulate electrically the outer portion of the silver epoxy glue. The HFS (greenTEG gSKIN[®] XP 26 9C, earlier used to measure heat from supercapacitor electrodes by Munteshari et al.³⁵), is placed behind the WE in a separate glass compartment with walls of 0.15 mm in thickness. This compartment is an additional protection of the sensor (which must remain dry) against salt solution leaking around the outer rim of the current collector. The 1 cm \times 1 cm surface of the HFS faces the electrode and current collector and is centered with respect to

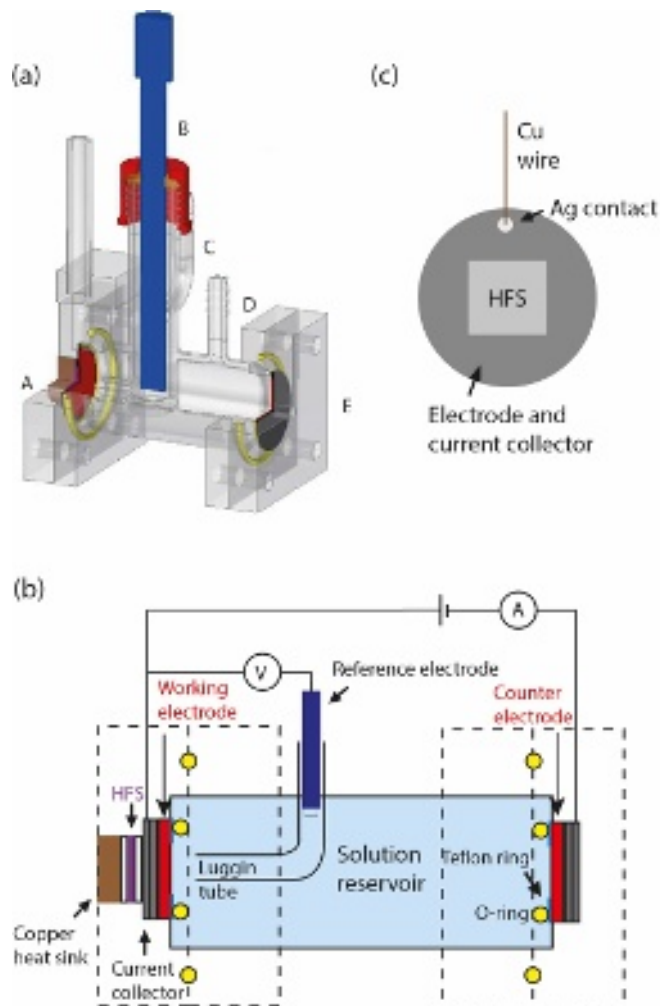


FIG. 1. (a) Technical drawing of the electrochemical cell used for heat measurements on a porous electrode, connected in a 3-electrode configuration. A 3D pdf of this figure is provided in the Supporting Information; A = outer square part containing the working electrode, with the HFS in purple behind it; the HFS is thermally stabilized by a copper block at the back; B = reference electrode; C & D = electrolyte solution in- and outlets; E = outer square part containing the counter electrode. (b) Schematic overview of the cell and its connections to the potentiostat. The yellow circles are cross-sections of the O-rings seen in part (a) of the figure. (c) Position of the HFS with respect to the electrode, the current collector, and the ohmic contact.

them. In contrast, the ohmic contact between current collector and copper wire is more to the side, see Fig. 1(c).

The HFS voltage is sampled twice per second using a Keithley 2182A Nanovoltmeter, connected to a personal computer via a GPIB interface. The electric potential is applied between the WE and the CE using a channel of an AMETEK PARSTAT MC-1000 multichannel potentiostat, with a feedback loop to keep the electrical potential of the WE stable with respect to the RE. The same instrument measures the resulting current between the WE and the CE.

B. Temperature stabilization

The electrochemical cell is in a controlled thermostatic environment to ensure a stable background level of the heat flux signal. The HFS is in thermal contact with a copper heat sink of 5.5 mm in thickness and 15.3 mm in diameter, in contact with water that surrounds the electrochemical cell. The cell is submerged in a 2 L glass beaker, filled with tap water up to the breathing hole of the reference electrode. This beaker is positioned at the center of a copper cylinder (34 cm height by 24 cm width), itself at the center of a thermostated box of 50 cm by 50 cm by 45 cm in height. Copper tubing is welded to the copper cylinder for good heat contact, and connected to a Julabo F25-HE Refrigerated/heating circulator bath via PVC tubes, pumping thermostated water through the copper cylinder. The box is closed with a lid measuring 50 cm in length and width and 24 cm in thickness and consisting of wood and styrofoam. The large heat capacity of the water in the glass beaker and an air gap of 5 cm between the beaker and the copper walls dampen temperature fluctuations of the thermostatic bath. To verify temperature stability and independence from environmental artifacts, the temperatures of the water in the glass beaker, of the water in the thermostatic bath, and of the air in the room are monitored using Pt100 sensors, whose signals are acquired via a Pico[®] Technology PT-104 Platinum Resistance Data Logger. The water bath has a temperature range of 5 °C to 70 °C. Due to the large heat capacity, it takes up to 48 hours before the thermostatic box reaches a stable temperature after closing the lid. Typically, the temperature of water in the glass beaker is constant within a standard deviation of 0.0045 °C on a short time scale (10² s) and 0.0058 °C on a long time scale (10⁵ s).

C. Operation and Calibration

The standard measurement protocol is the same as in Ref. 27. The temperature is stabilized and the difference between the potential of the WE and that of the RE at open circuit—the open circuit potential (V_{OCP})—is measured for several hours, until this potential has also stabilized, at around 0.2 V vs. RE in the case of the studied carbon electrodes in aqueous NaCl solution. A cyclic voltammogram is measured to verify that the electrical behavior of the WE is largely capacitive, without oxidative or reductive peaks indicating faradaic processes. Then, the same potential as was measured at equilibrium at open circuit, $V_{\text{OCP}} = 0.2$ V vs. RE, is applied actively to the WE for ≥ 1 hour until the current becomes minimal (< 20 A). The applied potential is then changed by ΔV , resulting in peaks of electrical current and HFS voltage, V_{HFS} . After 1 to 2 hours, 0.2 V vs. RE is reapplied. The charging-discharging cycle is repeated for $\Delta V = +0.5$ V to $+0.1$ V and $\Delta V = -0.5$ V to -0.1 V vs. RE, and this potential series is repeated at least once.

In principle, calibration can be done based on the specifications of the HFS (12.7 V per heat flux in W/m² for the sensor used here). In that case, it must be known which fraction of the heat produced by the electrode is measured by the HFS.

This can be calculated by assuming that half of the electrode heat is produced in the direction of the HFS and by taking into account the different surface areas of the electrode and the HFS. However, differences in the distance between electrode and HFS in early prototypes of the cell, as well as differences in heat contact from one electrode to the other, can render the calibration unreliable by a factor of order 2. Therefore, we chose to calibrate on another basis: the Joule heat of a complete charging-discharging cycle.²⁷

When a known potential ΔV is applied vs. V_{OCP} , a charge ΔQ builds up in the electrode during charging. As explained in Ref. 27, for a full cycle of charging and discharging, the total reversible heat is zero and the net measured heat is the irreversible heat, equal to the net electrical work performed on the electrode during the cycle:

$$q_{\text{ch}} + q_{\text{dis}} = -\Delta Q \Delta V, \quad (1)$$

where q_{ch} is the heat during charging and q_{dis} the heat during discharging. This equation stems from the knowledge that the internal energy of the electrode is the same before and after a full cycle of charging and discharging, since the electrode comes back to its initial state. The total integrated surface area of the two HFS voltage peaks in a charging-discharging cycle is proportional to $-\Delta Q \Delta V$ and the ratio of the two gives the calibration constant K , the total amount of heat produced by the electrode per integrated HFS signal:

$$-\Delta Q \Delta V = K \int V_{\text{HFS}} dt \quad (2)$$

Separate heats of charging and discharging in energy units can now be calculated from integrated HFS signals in units of Vs, using the calibration constant in units of J/(Vs). This assumes that the HFS has the same sensitivity for the reversible heat and for the Joule heat, an assumption which will be discussed in the next section.

III. TEST MEASUREMENTS

A. Experimental Results

Test measurements were done on porous carbon electrodes cut from sheets of electrode material produced by Voltea B.V. (Amstelveen, The Netherlands). The material had a density of 0.58 gmL⁻¹, a porosity of 65%, and a Brunauer-Emmett-Teller surface area of 88 m² per electrode.²⁷ This material was comparable to that prepared in Ref.4, with activated carbon (YP-50F, Kuraray, Japan), carbon black (Vulcan XC72R, Cabot Corp., Boston, MA) and a binder (85:5:10 in weight ratio). The electrolyte solution consisted of 1 M NaCl (for molecular biology, $\geq 98\%$, Sigma), degassed using a Branson 8800 Series Ultrasonic Cleaner.

In Fig. 2, results of a typical measurement series are shown. Within minutes of changing the potential applied to the working electrode, current and heat flux were close to zero, but to ensure that equilibrium was attained and to have a reliable baseline, measurements were continued for at least one hour

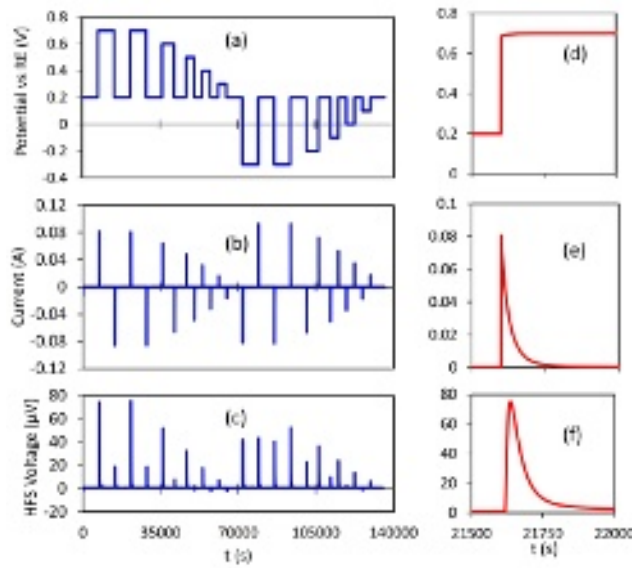


FIG. 2. Typical measurements on a porous carbon electrode in 1 M aqueous NaCl with (a) the measured applied potential, (b) the resulting current, and (c) the HFS voltage. (d)-(f) Shape of the signals in (a)-(c), respectively, during charging from 0.2 V to 0.7 V (potentials versus RE; 0.2 V is the open circuit potential).

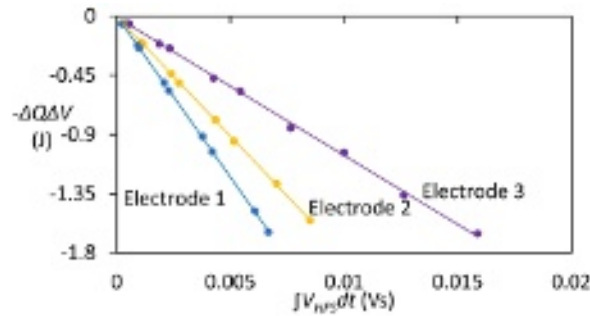


FIG. 3. Typical calibration results for 1 M NaCl using different electrodes, with $K_1 = (-245.2 \pm 0.8) \text{ J V}^{-1} \text{ s}^{-1}$, $K_2 = (-182.1 \pm 0.6) \text{ J V}^{-1} \text{ s}^{-1}$, and $K_3 = (-104.9 \pm 1.3) \text{ J V}^{-1} \text{ s}^{-1}$, the calibration constants for electrodes 1, 2, and 3, respectively.

after each change of applied potential. The signal-to-noise ratio of the highest HFS voltage peak (75 V) was 2850:1 in Fig. 2. In general, the signal-to-noise ratio was about two orders of magnitude higher than in the 2-electrode thermometer setup of Ref. 34.

Figure 3 shows the effect of different electrodes on the calibration according to Eq. 2. The main difference between the electrodes is how they were mounted in the cell, affecting their heat contact with the HFS. As noted in Ref. 27, the calibration assumes that the HFS was equally sensitive to Joule heat and to reversible heat produced in the porous network, which was not necessarily the case.

Figure 4 shows the data analysis of HFS voltage peaks of the type in Fig. 2(c), with heats of charging on the left and heats of discharging on the right. Time-integrated HFS voltages are in Fig. 4(a-b). When these units are scaled using the

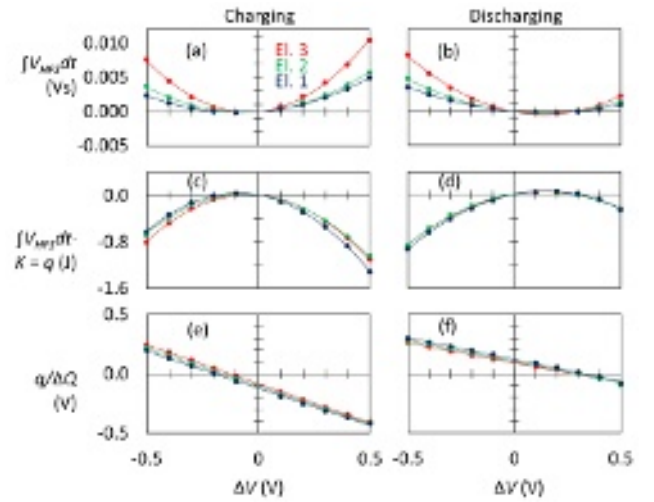


FIG. 4. Typical HFS measurement results during charging and discharging for different electrodes, (a-b) integrated heat flux, (c-d) calibrated heat, (e) calibrated charging heats divided by ΔQ . A least squares fit to Eq. 3 gives $\Delta V_{\text{att}} = (-0.102 \pm 0.007) \text{ V}$ and $[-\frac{1}{2} - \frac{3}{2}f] = -0.640 \pm 0.002$. (f) Calibrated discharging heats divided by ΔQ . A least squares fit to Eq. 4 gives $\Delta V_{\text{att}} = (-0.105 \pm 0.007) \text{ V}$ and $[\frac{1}{2} - \frac{3}{2}f] = -0.354 \pm 0.002$.

calibration factors determined in Fig. 3, the results are much closer to each other (Fig. 4(c-d)).

In Ref. 27, formulas for the heat of charging, q_{ch} , and the heat of discharging, q_{dis} , were derived in terms of the electrode capacitance, the applied potential ΔV , an average electric potential $f\Delta V$ of ions inside the pores, and a potential-independent ΔV_{att} , which corresponds to an energy per unit charge due to attraction of the ions to the electrode surface. From those equations, dividing q_{ch} and q_{dis} by the measured charge $C\Delta V$ yields the following expressions:

$$\frac{q_{\text{ch}}}{C\Delta V} = \Delta V \left[-\frac{1}{2} - \frac{3}{2}f \right] + \Delta V_{\text{att}} \quad (3)$$

$$\frac{q_{\text{dis}}}{C\Delta V} = \Delta V \left[-\frac{1}{2} + \frac{3}{2}f \right] - \Delta V_{\text{att}}. \quad (4)$$

On the basis of these two formulas, parameters f and ΔV_{att} can be obtained from linear fits of $q/(C\Delta V)$ vs. ΔV , much like the linear fit of $\Delta U/(C\Delta V)$ discussed in Ref. 27. In Figs. 4(c) and 4(f), plots of the heat of charging and discharging, divided by $\Delta Q = C\Delta V$ indicate the same values of ΔV_{att} . When the same measurements were performed using resistance temperature detectors instead of a heat flux sensor, similar results were obtained (but with lower signal-to-noise ratio), supporting the validity of the presented calibration approach, see SI.³⁸

B. HFS sensitivity for reversible heat

Our calibration approach assumes that the HFS has the same sensitivity for reversible heat and Joule heat, even

though in practice, these two contributions to the total heat are not produced at the same location with respect to the HFS. In our test measurements, the reversible heat was fully produced in the porous network. The Joule heat, however, was generated in different resistive parts of the system. Part of the heat was generated by the silver epoxy glue contact at the side of the electrode, see Fig. 1(c), whose resistance was $<0.5 \Omega$. Another part of the Joule heat was generated by electrical current through the bulk solution between the Luggin tube and WE, farther away from the HFS than the porous network. This can be concluded from the concentration dependence of the total cell resistance, equal to 3.3Ω at 5 M NaCl, 5.7Ω at 1 M NaCl, and 20.8Ω at 0.1 M NaCl, for measurements on a typical electrode. These resistances correspond to a concentration-independent contribution of about 2.5Ω plus the resistance of the liquid solution between Luggin tube and WE, given by $R = d/(\kappa A)$, where $1/\kappa$ is the concentration-dependent resistivity of aqueous NaCl solution obtained from Ref. 39, $d \approx 0.6$ cm is the distance between Luggin tube and WE, and $A \approx \pi(0.925 \text{ cm})^2$ is the external area of the WE exposed to bulk electrolyte solution. The thus calculated R is equal to 0.7Ω at 5 M, 2.2Ω at 1 M, and 17.5Ω at 0.1 M. Therefore, the resistance in the bulk electrolyte solution is dominant at 0.1 M NaCl, and it is about 40 % of the total resistance at 1 M NaCl and about 20% at 5 M NaCl.

The calibration constant was also concentration-dependent, indicating a sensitivity of $(-5.23 \pm 0.04) \times 10^{-3}$ Vs/J at 5 M, $(-5.88 \pm 0.06) \times 10^{-3}$ Vs/J at 1 M, and $(-6.72 \pm 0.02) \times 10^{-3}$ Vs/J at 0.1 M NaCl. This can be understood in terms of where most of the Joule heat was produced. The lower the concentration, the more Joule heat was produced in bulk electrolyte solution, and the higher the sensitivity of the HFS to the Joule heat. The bulk solution is better centered with respect to the HFS than the resistive elements that give concentration-independent contributions to the total resistance, which are more to the side of the electrode, possibly not facing the HFS.

Reversible heat produced in the porous network will flow partly toward bulk solution and partly toward the HFS. However, toward the HFS, the thermal conductivity of the glassy carbon current collector is higher ($0.7\text{-}4 \text{ W/m/K}$)⁴⁰ than toward bulk solution, mostly consisting of water (0.6 W/m/K)³⁷. This favors the flow of reversible heat in direction of the HFS. For 1 M NaCl, in the extreme case that all the reversible heat and all the Joule heat produced in the concentration-independent 2.5Ω resistive elements would flow in the direction of the HFS, and only half of the Joule heat produced in the bulk electrolyte solution would flow in the direction of the HFS, the HFS would detect 75 % of the Joule heat and 100 % of the reversible heat. This would lead to an overestimation of the reversible heat by 33 %, since our calibration is only on the Joule heat. In reality, the flow of reversible heat and Joule heat is likely to be more evenly distributed between the directions toward and away from the HFS, resulting in a lower overestimation of the reversible heat via our calibration method.

IV. CONCLUSION

With the presented setup, the heat of charging and discharging of a capacitive electrode can be determined as a function of electrode potential with respect to a reference electrode. In this way, differences between heat production in the anodic and cathodic ranges can be investigated. The heat flux sensor is calibrated using the Joule heat produced in a full cycle of charging and discharging. This partly solves the problem of not knowing which fraction of electrode heat flows in the direction of the sensor.

V. SUPPLEMENTARY MATERIAL

See Supplementary material (URL will be inserted) for a 3D pdf of the electrochemical cell and a description of comparable measurements performed using an alternative setup in which resistance temperature detectors were used instead of a heat flux sensor.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

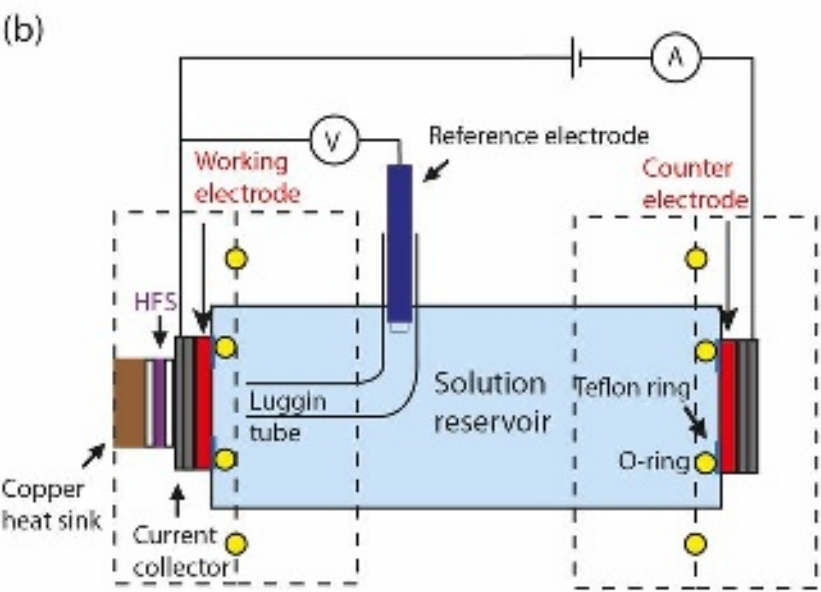
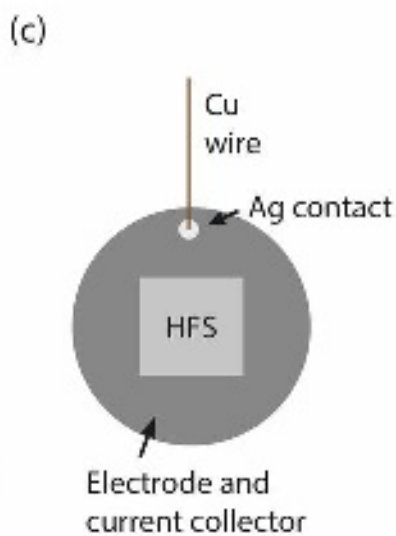
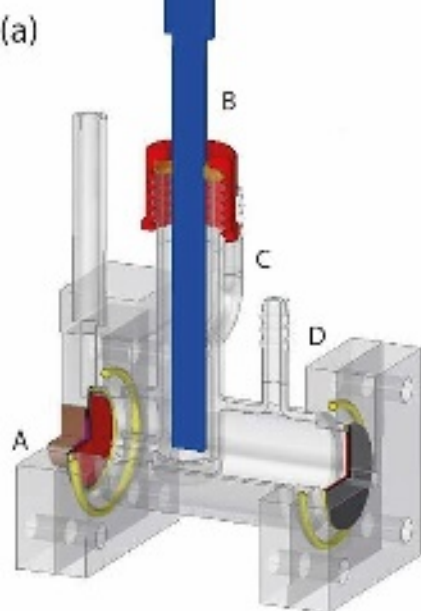
Joren Vos: Formal analysis (lead); investigation (lead); methodology (supporting); supervision (equal); writing – original draft (equal); writing – review and editing (supporting). **Henrik Rodenburg:** Formal analysis (supporting); investigation (supporting); software (equal); writing – review and editing (supporting). **Danny Inder Maur:** Formal analysis (supporting); investigation (supporting); software (equal); writing – review and editing (supporting). **Ties Bakker:** Formal analysis (supporting); software (equal); writing – review and editing (supporting). **Henkjan Siekman:** Methodology (lead); writing – review and editing (supporting). **Ben Erné:** Conceptualization (lead); funding acquisition (lead); methodology (supporting); supervision (equal); writing – original draft (equal); writing – review and editing (lead).

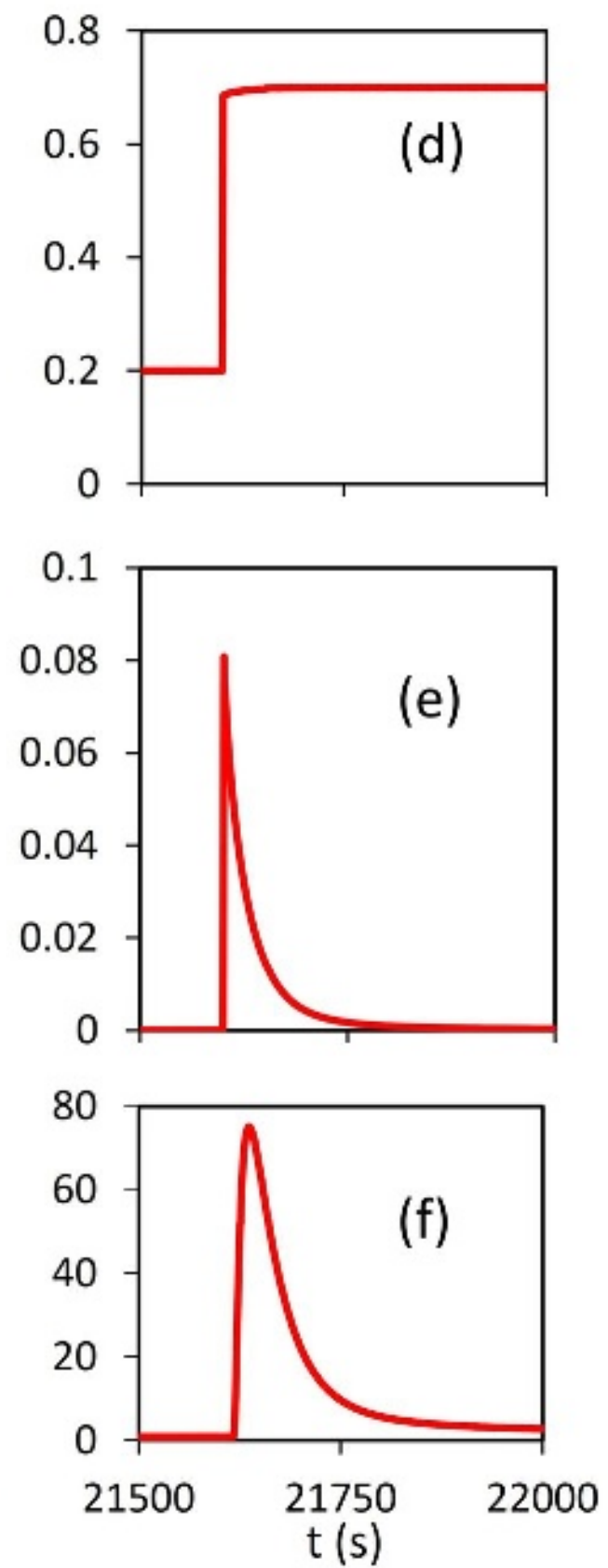
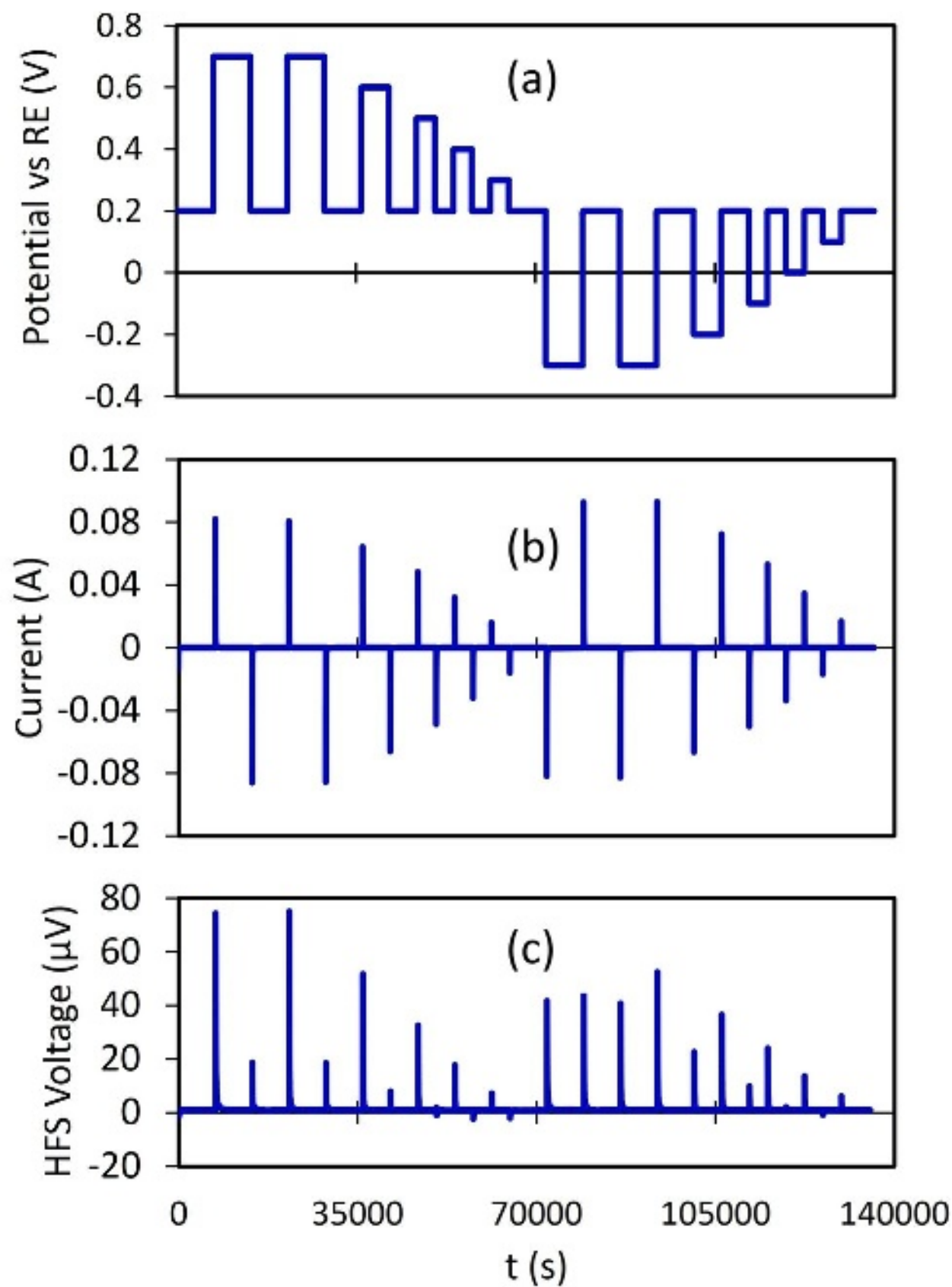
DATA AVAILABILITY

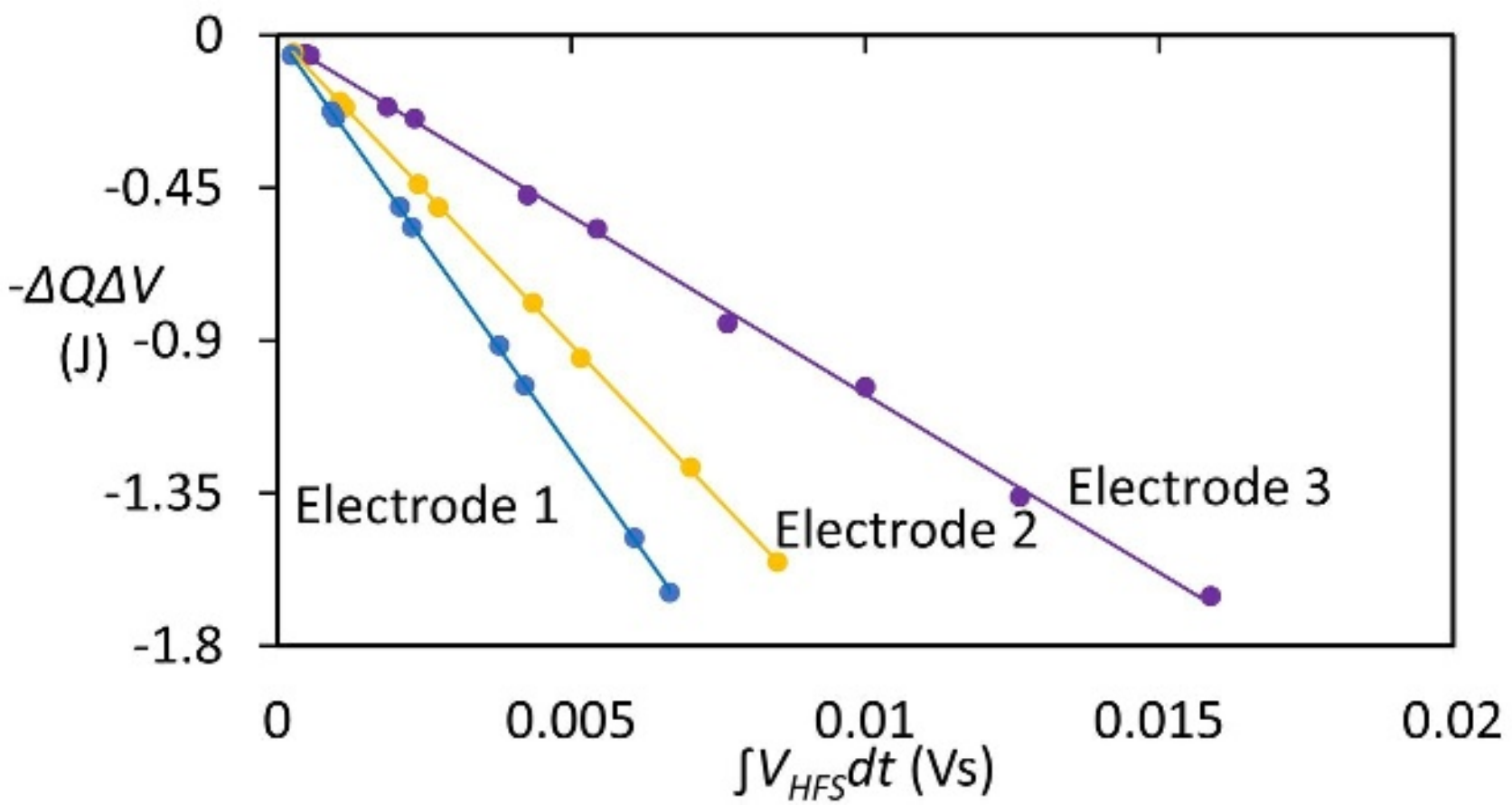
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Charging

Discharging

