

Heat Generation in Electric Double Layer Capacitors with Neat and Diluted Ionic Liquid Electrolytes Under Large Potential Window Between 5 and 80 °C

Ampol Likitchatchawankun^a, Ryan H. DeBlock^b, Grace Whang^b,
Obaidallah Munteshari^{a,c}, Matevž Frajnkovič^a, Bruce S. Dunn^{b,d}, and
Laurent Pilon^{a,d,e,+}

^aMechanical and Aerospace Engineering Department, Henry Samueli School of Engineering
and Applied Science, University of California, Los Angeles, CA 90095, USA

^bMaterials Science and Engineering Department, Henry Samueli School of Engineering and
Applied Science, University of California, Los Angeles, CA 90095, USA

^cMechanical Engineering Department, King Fahd University of Petroleum and Minerals
(KFUPM), Dhahran 31261, Saudi Arabia

^dCalifornia NanoSystems Institute, University of California, Los Angeles, Los Angeles,
California 90095, USA

^eInstitute of the Environment and Sustainability, University of California, Los Angeles, Los
Angeles, California 90095, USA

⁺Corresponding Author: Phone: +1 (310)-206-5598, Fax: +1 (310)-206-2302

E-mail: pilon@seas.ucla.edu

August 2, 2020

Abstract

This study investigates the effect of temperature on the heat generation and the associated electrochemical phenomena occurring in IL-based EDLCs. The EDLCs consisted of two identical activated carbon electrodes with neat Pyr₁₄TFSI or Pyr₁₄TFSI diluted in propylene carbonate (PC) as electrolytes. The instantaneous heat generation rate at each electrode was measured by isothermal calorimetry between 5 and 80 °C under constant current cycling and potential window of 2.5 V. First, the instantaneous heat generation rate was similar at each electrode in neat IL. However, it was smaller at the negative electrode in diluted IL and featured endothermic dips growing with increasing temperature > 40 °C due to overscreening effects, ion desolvation, and/or decomposition of PC. The irreversible heat generation was similar in each half-cell and decreased with increasing temperature due to the reduction in internal resistance, particularly with neat IL. The irreversible heat generation exceeded Joule heating in all cases, especially at high temperature and low current. This was attributed to ion desorption and charge redistribution in the porous electrodes. Finally, the reversible heat generation for both electrolytes was larger at the positive than at the negative electrode due to the difference in anion and cation sizes.

Nomenclature

A	Footprint area of the heat flux sensor, cm^2
$C_{diff,m}$	Gravimetric differential capacitance, F/g
$C_{int,m}$	Gravimetric integral capacitance, F/g
D	Diffusion coefficient, m^2/s
I	Current, mA
i	Current density, mA/cm^2
m	Mass loading of active material in electrode, mg
n_c	Cycle number, -
q''	Heat flux, mW/cm^2
\dot{Q}	Heat generation rate, mW
$\bar{\dot{Q}}$	Time-averaged heat generation rate, mW
R	Resistance, Ω
R_s	Internal resistance for entire device, Ω
S	Heat flux sensor sensitivity, $\mu\text{V}/(\text{W}/\text{cm}^2)$
t	Time, s
t_c^-	Time immediately after the beginning of the discharging step, s
t_c^+	Time at the end of the charging step, s
T	Temperature or absolute temperature, $^\circ\text{C}$ or K
ΔV	Voltage difference generated in the heat flux sensor, μV
z_i	Valency, -

Greek symbols

ϵ_r	Dielectric constant, -
ν	Scan rate, mV/s
σ	Ionic conductivity, mS/cm
$\psi_{s,min}, \psi_{s,max}$	Minimum, maximum cell potential, V

$\psi_s(t)$ Cell potential, V

Superscripts and subscripts

c	Refers to charging step
cd	Refers to charging-discharging cycle
d	Refers to discharging step
i	Refers to ion species “i”
J	Refers to Joule heating
T	Refers to entire cell
rev, i	Refers to reversible heat generation
+ or -	Refers to positive or negative electrode

1 Introduction

Electric double layer capacitors (EDLCs) feature large power densities, high cycle efficiency, and long cycle life [1–11]. They have received significant interest for applications requiring charging/discharging at high rates such as the utility grid and regenerative braking in hybrid or electric vehicles [1–11]. EDLCs consist typically of two carbon-based electrodes and a separator immersed in concentrated aqueous, organic, or ionic liquid-based electrolytes [12, 13]. They store electrical energy in the electric double layer (EDL) formed by ions at the porous electrode/electrolyte interface [10–13]. Their energy density E (in J/m²) can be expressed as [1],

$$E = \frac{1}{2} C \Delta\psi_s^2 \quad (1)$$

where C is the specific capacitance of the cell (in F/m²) and $\Delta\psi_s$ is the potential window (in V). Increasing $\Delta\psi_s$ can significantly increase the energy density E . However, $\Delta\psi_s$ is limited by the electrochemical stability of the electrolyte [1]. Similarly, increasing temperature moderately enhances ion transport and increases the capacitance C . However, in high power applications, EDLCs can experience a considerable amount of heat generation resulting in excessively high cell temperature [8, 9, 14, 15]. Elevated temperatures, in turn, can lead to (i) accelerated aging of the device [8, 9, 14–18], (ii) increased self-discharge rate [14, 15, 17], and (iii) thermal decomposition of the electrolyte [17–19].

Ionic liquids (ILs) and their mixtures have been considered as promising electrolytes for EDLCs for their good thermal stability [20–25], wide operating potential windows [23–28], and operation at low temperatures [21, 24, 28, 29]. However, neat ILs typically suffer from low ionic conductivity (~ 1 to 20 mS/cm at room temperature) [20, 22, 30–34] compared with aqueous electrolytes (~ 200 to 800 mS/cm) [33, 34]. Nevertheless, their ionic conductivity increases strongly with increasing temperature [20, 35–38]. Another way to increase the ionic conductivity of ILs is to dilute them in carbonate-based organic solvents such as propylene carbonate (PC) or a mixture of ethylene carbonate (EC)- dimethyl carbonate (DMC) as well as in nitrile-based solvent such as acetonitrile (ACN) [20, 21, 39]. The increase in ionic

conductivity and the associated decrease in viscosity in diluted ILs are due to the reduction in ion pairing via solvation [21]. However, diluted ILs tend to be less electrochemically and thermally stable than their neat IL counterpart [21]. In addition, despite the wide theoretical potential window of ILs, they may react with the carbonaceous electrode surface as a result of catalytic activity [40, 41]. Moreover, elevated temperature can shorten the operating potential window due to solvent decomposition [42].

The present study aims to assess the effect of operating temperature on the instantaneous heat generation rate and the associated electrochemical phenomena taking place in carbon-based EDLCs with either neat IL or diluted IL electrolytes cycled under a large potential window. The cells consisted of two activated carbon electrodes separated by a chemical resistant mesh immersed in either neat N-butyl-N-methylpyrrolidinium bis(trifluoromethane sulfonyl)imide (Pyr₁₄TFSI) or 1 M Pyr₁₄TFSI in PC electrolytes. The instantaneous heat generation rate at each electrode was measured using a recently developed *in operando* isothermal calorimeter [43] at temperatures ranging from 5 to 80 °C under galvanostatic cycling and a potential window $\Delta\psi_s = 2.5$ V. The results were analyzed in terms of reversible and irreversible heat generation rates to provide insight into the physicochemical processes occurring during operation under large potential windows and high temperatures. The result can also be used in the design of thermal management solutions for EDLCs.

2 Background

2.1 Neat and diluted Pyr₁₄TFSI ionic liquid-based electrolytes

Ionic liquid Pyr₁₄TFSI and its mixtures with organic solvents have been used widely as electrolytes in EDLCs due to their exceptional thermal, electrochemical, and cycling stability [26, 31, 44–46]. In fact, the operating potential window of neat Pyr₁₄TFSI can be as high as ~ 3.5 V in the temperature range of 20 to 60 °C [29] compared with ≤ 3 V for organic electrolytes (e.g., ACN) and ~ 1 V for aqueous electrolytes [47]. The maximum potential windows of Pyr₁₄TFSI mixtures in PC or ACN were recommended to be up to 3.5

V at 20 °C [29]. In addition, Pyr₁₄TFSI-based electrolytes show larger power and/or energy densities and better capacitance retention compared to the widely used organic electrolyte tetraethylammonium tetrafluoroborate (TEABF₄) in PC or ACN [26, 48]. Furthermore, leakage current was about three times smaller in activated carbon (AC)-based EDLCs with Pyr₁₄TFSI, neat or diluted in PC, than with TEABF₄ in PC [49]. Indeed, the ionic conductivity of neat Pyr₁₄TFSI is as low as ~ 2.0 mS/cm at 20 °C [50, 51]. However, it depends strongly on temperature and increases to ~ 7.0 mS/cm at 60 °C [45, 52]. In addition, the ionic conductivity of 1 M Pyr₁₄TFSI in PC increased to 10.3 mS/cm at 25 °C [26].

2.2 Experimental calorimetry

2.2.1 Calorimeter device

Few experimental studies have investigated heat generation in EDLCs [43, 53, 54]. Dandeville et al. [53] measured time-dependent temperature evolution in two-electrode cells under galvanostatic cycling in a custom-made isothermal calorimeter. The heat generation rate in the entire cell was calculated by deconvoluting the measured time-dependent cell temperature during cycling [53]. Moreover, the heat generation rate in an AC-based EDLC cell electrode was assumed to be equally divided between the two electrodes [53]. In addition, heat generation was decomposed into (i) irreversible heat generation due to Joule heating and (ii) reversible heat generation caused by EDL formation [53].

More recently, Munteshari et al. [43, 54] developed an *in operando* isothermal calorimeter with integrated thermoelectric heat flux sensors to measure the instantaneous irreversible and reversible heat generation rates at each electrode of an EDLC cell. The authors investigated EDLC cells consisting of two identical AC-based electrodes immersed in aqueous or organic liquid electrolytes under constant current cycling I with potential window ≤ 1.0 V and at constant temperature of 20 °C [43, 54]. The irreversible heat generation rate at each electrode was found to be proportional to I^2 under constant current cycling. The total irreversible heat generation in the cell was in excellent agreement with Joule heating ex-

pressed as $\bar{Q}_J = R_s I^2$ where R_s is the internal resistance of the device measured from IR drop and found to be independent of current I [43]. The reversible heat generation rate at the positive electrode was (i) exothermic during charging due to ion adsorption and (ii) endothermic during discharging due to ion desorption, as predicted theoretically [55, 56]. However, at the negative electrode, the reversible heat generation rate was first endothermic and then exothermic during charging [43]. This was attributed to the presence of negatively charged functional groups associated with carboxymethyl cellulose (CMC) binder forming at the negative electrode and responsible for the overscreening effect [54]. In fact, the hydroxyl ($-\text{OH}$) and carboxymethyl ($-\text{CH}_2\text{COONa}$) functional groups of the CMC binder dissociate in 1 M LiPF_6 in EC:DMC organic electrolyte forming negatively charged functional groups ($-\text{O}^-$) and ($-\text{CH}_2\text{COO}^-$) that electrostatically attracted cations (e.g., Li^+), creating overscreening of the electrode surface [54, 57]. In order to charge-balance the inner Helmholtz layer in the electrolyte, an additional layer of anions (e.g., PF_6^-) was required [54, 57]. Thus, the negative electrode containing such functional groups was first charged by desorption of these sub-layer anions (endothermic) followed by cation adsorption (exothermic) [54, 58].

2.2.2 Effect of potential window

As previously discussed, the operating potential window is an essential parameter for improving the specific energy of EDLCs. However, the operating potential window may be limited by the electrochemical stability window (ESW) of the electrolyte at a given temperature. Leyva-Garcia et al. [40] investigated the effect of potential window on the electrochemical performance of porous activated carbon (AC) electrodes with (i) neat $\text{Pyr}_{14}\text{TFSI}$ or (ii) 1 M $\text{Pyr}_{14}\text{TFSI}$ in PC electrolytes at 20 °C. The authors observed a redox peak in the CV curves at the negative electrode in 1 M $\text{Pyr}_{14}\text{TFSI}$ in PC electrolyte whereas no redox peak was observed in neat $\text{Pyr}_{14}\text{TFSI}$. They attributed this redox peak to PC solvent decomposition at the negative electrode under large potential [40]. Indeed, under large potential windows, PC decomposes (i) at the cathode to produce propane and hydrogen gases due to PC reduction or (ii) at the anode to produce carbon dioxide, propylene oxide, and other byproducts due

to PC oxidation [40, 59, 60].

Moreover, Borenstein et al. [41] reported that a significant amount of FSI⁻ anions intercalated in the positive electrode of an AC-based EDLC with neat Pyr₁₄FSI ionic liquid electrolyte after 3,000 galvanostatic cycles at $\Delta\psi_s = 3.4$ V [41]. This finding was confirmed by scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDX) measurements.

More recently, Munteshari et al. [61] studied the effects of potential window ranging from 1 to 4 V on the heat generation rate in cells consisting of two identical porous AC electrodes with either neat Pyr₁₄TFSI or 1 M Pyr₁₄TFSI in PC electrolytes using *in operando* isothermal calorimeter at 20 °C. For devices with neat Pyr₁₄TFSI electrolyte, an endothermic dip appeared in the instantaneous heat generation rate at the positive electrode for cell potential window of 4.0 V as a result of TFSI⁻ intercalation, as confirmed by EDX spectroscopy [61]. On the other hand, for devices with 1 M Pyr₁₄TFSI in PC electrolyte, an endothermic dip appeared in the instantaneous heat generation rate at the negative electrode starting from cell potential window of 3.0 V as a result of PC decomposition [61]. In addition, the irreversible and reversible heat generation rates at both electrodes increased with increasing potential window for given current in both neat and diluted Pyr₁₄TFSI electrolytes [61]. For 1 M Pyr₁₄TFSI in PC electrolyte, the irreversible heat generation rate increased sharply as the potential window increased from 3.0 V to 3.5 V due to PC decomposition at potential window of 3.5 V [61]. Furthermore, unlike previous studies [43, 54] with cell potential window $\Delta\psi_s \leq 1$ V, the total irreversible heat generation rate of the entire cell exceeded Joule heating for $\Delta\psi_s > 1$ V in both neat and diluted Pyr₁₄TFSI electrolytes [61]. This additional irreversible heat generation rate was attributed to the heat generation associated with charge redistribution in the porous carbon electrode and identified as the leakage current dissipated through the pore resistance [61].

2.2.3 Effect of temperature

Numerous studies have investigated the effect of temperature on the performance of EDLCs with various electrolytes [16,18,19,42,62–71]. Electrochemical measurement methods such as galvanostatic charge-discharge cycling (GCD), cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) were performed within the temperature range of -40 to 100 °C on (i) test cells in three-electrode setup [67] and two-electrode cells [19, 62, 64, 71] and on (ii) commercial EDLC devices and module [16, 42, 62, 63, 65, 66]. The specific capacitance was found to increase with increasing temperature as a result of increasing ion mobility [19, 62, 66, 67, 72]. For the same reason, the cell internal resistance R_s decreased with increasing temperature in organic [16, 19, 66] as well as in ILs [62, 73] electrolytes. However, increasing the operating temperature can have a negative effect on the self-discharge rate of EDLCs [14, 15, 17]. In fact, at high temperatures, ions feature higher desorption rates leading to device self-discharge [16, 71, 74]. Moreover, high operating temperatures and/or high applied voltages can lead to accelerated aging of EDLCs due to thermal and electrochemical degradation of the electrolyte and/or of the electrode materials [18, 42, 75]. First, for temperatures larger than the onset of decomposition temperature, electrolytes may decompose to produce gases such as carbon monoxide (CO), hydrogen (H_2), and other organic byproducts, as previously discussed [75]. These gases can lead to pressure rise inside the cell leading potentially to explosions [76]. The gases generated can also block access to the pores in the electrodes to the liquid electrolyte, leading to an increase in cell resistance and a decrease in the device capacitance [42, 75]. High temperatures can also accelerate decomposition reactions in the electrolyte and/or in the electrode by oxidation/reduction reactions producing solid byproducts [77]. These byproducts can attach onto the electrode/electrolyte interface thus reducing the electrode active surface area [77].

Most recently, we investigated the effect of operating temperature on irreversible and reversible heat generation rates in a full-cell device consisting of two identical porous AC electrodes with 1 M Pyr₁₄TFSI in PC electrolyte cycled with a potential window of 1 V [73]. The instantaneous heat generation rate at each electrode was measured at temperatures

ranging from 20 to 60 °C [73] using an *in operando* isothermal calorimeter [43]. The measurements were similar at both electrodes and proportional to I^2 . Their sum was equal to Joule heating given by $\bar{Q}_J(T) = R_s(T)I^2$ where $R_s(T)$ is the internal resistance of the device measured at temperature T and I is the imposed current. The internal resistance $R_s(T)$ and thus $\bar{Q}_J(T)$ decreased with increasing temperature due to the increasing electrolyte ionic conductivity [73]. However, the reversible heat generation rate was found to be independent of temperature for the potential window of 1 V considered [73].

Overall, previous calorimetric studies have investigated the instantaneous heat generation rate in EDLCs (i) with aqueous or organic electrolytes for potential window $\Delta\psi_s \leq 1.0$ V at 20 °C [43], (ii) with neat Pyr₁₄TFSI or 1 M Pyr₁₄TFSI in PC for potential window varying from 1.0 V to 4.0 V at 20 °C [61], and (iii) with 1 M Pyr₁₄TFSI in PC for potential window of 1.0 V and temperature varying from 20 to 60 °C [73]. The present study aims to assess the effect of temperature on reversible and irreversible heat generation rates in EDLC with IL-based electrolyte under galvanostatic cycling. Here, a potential window of 2.5 V was chosen as a stable potential window for both neat Pyr₁₄TFSI and 1 M Pyr₁₄TFSI in PC electrolytes at 20 °C. The operating temperature was varied between 5 and 80 °C to assess its effect on the heat generation rate. The results can also be used to design thermal management strategies for EDLCs and to determine the operating limits of the devices.

3 Materials and Methods

3.1 Electrode and device fabrication

Activated carbon slurries were prepared by mixing (i) activated carbon (YP-50F, Kuraray Chemical), (ii) TX-100 surfactant (DOW Chemical), (iii) carboxymethyl cellulose (CMC, DOW Chemical) used as a thickening agent/binder, and (iv) styrene-butadiene rubber (SBR, MTI Corp.) as a binder, in DI water in an 80:5:1.5:13.5 weight ratio. The slurry was drop-casted onto carbon-coated aluminum current collector sheets (MTI Corp.) with 1×1 cm² footprint area. The current collectors were previously treated by oxygen plasma to enhance

their hydrophilicity and ensure uniform spreading of the slurry. The mass loading on each electrode was 2.5 mg of slurry (2.0 mg of AC) corresponding to an electrode thickness of about 60 μm . The electrodes were dried in a vacuum oven at 120 $^{\circ}\text{C}$ for 24 h before being assembled into full-cell devices in a glove box under argon (Ar) atmosphere (< 1 ppm $\text{H}_2\text{O}/\text{O}_2$).

The EDLC devices consisted of two identical activated carbon electrodes separated by a 1 mm-thick chemical-resistant polypropylene mesh serving as a separator and as thermal insulator. The devices were assembled using either (i) neat $\text{Pyr}_{14}\text{TFSI}$ (Device 1) or (ii) 1 M $\text{Pyr}_{14}\text{TFSI}$ diluted in PC electrolyte (Device 2). The concentration of 1 M $\text{Pyr}_{14}\text{TFSI}$ in PC corresponds to the maximum ionic conductivity (~ 8.3 mS/cm) and the lowest viscosity (~ 5 mPa·s) at 20 $^{\circ}\text{C}$ [78]. Finally, the device was assembled and placed in the calorimeter compartment inside a glove box under Ar atmosphere before being taken out for isothermal calorimetric measurements at temperatures ranging from 5 to 80 $^{\circ}\text{C}$. The isothermal calorimeter was described in detail in Ref. [43].

3.2 Device characterization

First, linear sweep voltammetry (LSV) was employed to determine the electrochemical stability window (ESW) of the electrolytes with either (i) neat $\text{Pyr}_{14}\text{TFSI}$ or (ii) 1 M $\text{Pyr}_{14}\text{TFSI}$ in PC incorporated in a two-terminal stainless steel coin cell (MTI Corp). Each coin cell, consisted of two AC-based electrodes (previously described) with a diameter of 9.5 mm (3/8") separated by a Whatman glass microfiber D (Sigma-Aldrich). The coin cells were pressed to a pressure of ~ 6 MPa inside of an argon-rich glovebox. LSV measurements were performed at slow sweep rate of 0.1 mV/s at temperatures 20 $^{\circ}\text{C}$, 40 $^{\circ}\text{C}$, and 80 $^{\circ}\text{C}$.

Second, cyclic voltammetry (CV) measurements were performed on Devices 1 and 2 inside the isothermal calorimeter at scan rate ν ranging from 5 to 30 mV/s at temperatures ranging from 5 to 80 $^{\circ}\text{C}$. The device's gravimetric integral capacitance $C_{int,m}$ (in F/g) was evaluated from the CV curves as a function of scan rate ν according to [79],

$$C_{int,m}(\nu) = \frac{1}{m(\psi_{s,max} - \psi_{s,min})} \oint \frac{I(\psi_s)}{2\nu} d\psi_s. \quad (2)$$

Here, m is the total mass loading of AC in both electrodes ($m = 4.0$ mg) while $I(\psi_s)$ is the current measured at cell potential ψ_s . A cell potential window between $\psi_{s,min} = 0$ V and $\psi_{s,max} = 2.5$ V was selected because it fell within the ESW of both electrolytes investigated at room temperature [61].

Third, galvanostatic cycling combined with calorimetric measurements were performed on the devices at constant current I ranging from 1 to 5 mA at temperatures between 5 and 80 °C. For a given temperature, fifteen consecutive cycles were performed for each value of current I to guarantee that oscillatory steady state had been reached. In addition, the gravimetric differential capacitance $C_{diff,m}$ (in F/g) was estimated according to [79],

$$C_{diff,m}(I) = \frac{I}{m|d\psi_s/dt|} \quad (3)$$

where $|d\psi_s/dt|$ was estimated at the end of the discharging or charging step for each cycle at constant current I .

Furthermore, the internal resistance R_s was calculated from the IR drop observed at the charging/discharging transitions under galvanostatic cycling according to [80–83],

$$R_s(I) = \frac{\psi_s(t_c^+) - \psi_s(t_c^-)}{2I} \quad (4)$$

where $\psi_s(t_c^+)$ and $\psi_s(t_c^-)$ denote the potentials across the cell at the end of the charging step and immediately after the beginning of the discharging step, respectively. The IR drop, $\psi_s(t_c^+) - \psi_s(t_c^-)$, was obtained by estimating the cell potential $\psi_s(t_c^-)$ 10 ms after the beginning of the discharging step (i.e., $t_c^+ - t_c^- = 10$ ms), as suggested for supercapacitors by Zhao et al. [81] and successfully used in our previous studies [43, 54, 73].

3.3 Isothermal Calorimeter

The instantaneous heat generation rate at each electrode in Devices 1 and 2 was measured under galvanostatic cycling at constant temperatures ranging from 5 to 80 °C. The instantaneous heat generation rate $\dot{Q}_i(t)$ (in mW) at electrode “ i ” was found by measuring the heat transfer rate $q_i''(t)$ through the thermoelectric heat flux sensor and in thermal contact

with the current collector such that [43],

$$\dot{Q}_i(t) = q_i''(t)A_i = \frac{\Delta V_i(t)}{S_i}A_i \quad \text{with } i = + \text{ or } - \quad (5)$$

where $\Delta V_i(t)$ refers to the instantaneous voltage difference measured within each thermoelectric heat flux sensor in thermal contact with electrode “ i ”. Here, subscript “ i ” refers to either the positive “+” or negative “−” electrode. In addition, S_i denotes the temperature-dependent sensitivity of the heat flux sensor provided by the manufacturer (in $\mu\text{V}/(\text{W}/\text{m}^2)$) and A_i refers to the footprint area of the electrode (in cm^2). Then, the instantaneous total heat generation rate in the entire device (denoted by subscript “ T ”) can be written as $\dot{Q}_T(t) = \dot{Q}_+(t) + \dot{Q}_-(t)$.

Moreover, the instantaneous heat generation rate $\dot{Q}_i(t)$ in each electrode can be decomposed as the sum of the reversible $\dot{Q}_{rev,i}(t)$ and irreversible $\dot{Q}_{irr,i}(t)$ heat generation rates, i.e., $\dot{Q}_i(t) = \dot{Q}_{rev,i}(t) + \dot{Q}_{irr,i}(t)$ [43, 54]. Furthermore, by definition, time-averaging of the reversible heat generation rate $\dot{Q}_{rev,i}(t)$ at electrode “ i ” over a complete charging-discharging cycle yields $\bar{\dot{Q}}_{rev,i} = 0$. Thus, the time-averaged heat generation rate of $\dot{Q}_i(t)$ over a charging-discharging cycle period t_{cd} is equal to the time-averaged irreversible heat generation rate $\bar{\dot{Q}}_{irr,i}$ at electrode “ i ”, i.e. [43, 54],

$$\bar{\dot{Q}}_{irr,i} = \frac{1}{t_{cd}} \int_{(n_c-1)t_{cd}}^{n_c t_{cd}} \dot{Q}_i(t) dt \quad \text{with } i = + \text{ or } - . \quad (6)$$

Here, n_c refers to the cycle number chosen to be large enough for $\dot{Q}_i(t)$ to have reached oscillatory steady state.

Finally, in order to compare the reversible heat generation rate at each electrode, the instantaneous reversible heat generation rate $\dot{Q}_{rev,i}(t)$ was time-averaged only over a charging period t_c according to [43, 54],

$$\bar{\dot{Q}}_{rev,i}^c = \frac{1}{t_c} \int_{(n_c-1)t_{cd}}^{(n_c-1)t_{cd}+t_c} \dot{Q}_{rev,i}(t) dt \quad \text{with } i = T, +, \text{ or } - . \quad (7)$$

4 Results and discussion

4.1 Combined thermal and electrochemical stabilities

Figure S1 plots the linear sweep voltammograms (LSVs) for coin cells with the same AC electrodes as those used for calorimetric measurement with either neat Pyr₁₄TFSI or 1 M Pyr₁₄TFSI in PC electrolyte at scan rate of 0.1 mV/s and temperatures of 20 °C, 40 °C, and 80 °C. The current density $i(\psi_s)$ was defined as the ratio of the measured current response $I(\psi_s)$ during increasing coin cell potential ψ_s over the footprint area of the AC-based electrode in the coin cell, i.e., $i(\psi_s) = I(\psi_s)/A$ with $A = 0.7 \text{ cm}^2$. The ESW depends on the choice of the cutoff current density beyond which the electrolyte is considered unstable. The cutoff current density typically ranges between 10 $\mu\text{A}/\text{cm}^2$ and 1 mA/cm^2 [84]. Figure S1 indicates that the ESW of the neat Pyr₁₄TFSI electrolyte decreased with increasing temperature from above 5.5 V at 20 °C, to 4.6 V at 40 °C, and down to 3.7 V at 80 °C, based on the cutoff current density of 0.5 mA/cm^2 suggested in Refs [84–86].

Moreover, the ESW of the 1 M Pyr₁₄TFSI in PC electrolyte was smaller than that of neat Pyr₁₄TFSI for a given temperature due to the lower electrochemical stability of PC. In addition, the ESW decreased with increasing temperature from 4.2 V at 20 °C, to 3.7 V at 40 °C, and 3.3 V at 80 °C. Note that, partial decomposition of some electrolyte components may start below the reported ESW.

4.2 Cyclic voltammetry and gravimetric integral capacitance

Figures 1(a) and 1(b) show the CV curves measured for Device 1 with neat Pyr₁₄TFSI ionic liquid electrolyte at different temperatures between 5 and 80 °C for scan rate (a) $\nu = 5 \text{ mV/s}$ and (b) $\nu = 30 \text{ mV/s}$, respectively. The CV curves at both scan rates featured leaf-like shape at low temperatures ($\leq 20 \text{ °C}$) and became larger and more rectangular with increasing temperature. These observations can be attributed to the increase in the ionic conductivity and to decreasing viscosity of neat IL with increasing temperature [45, 52]. However, at $T = 80 \text{ °C}$, small and broad peaks were observed around $\psi_s \sim 1.0 - 2.0 \text{ V}$ for

both positive and negative sweeps. This may be attributed to reversible faradaic reactions involving electron transfer across the double layer, as observed in carbon-based SWNT at 100 °C [19] and graphene nanosheet at 60 °C in IL-based electrolytes [67].

Similarly, Figures 1(c) and 1(d) show the CV curves measured for Device 2 with 1 M Pyr₁₄TFSI in PC electrolyte at different temperatures from 5 to 80 °C for scan rate (c) $\nu = 5$ mV/s and (d) $\nu = 30$ mV/s, respectively. Here, the CV curves were nearly rectangular at both low and high scan rates and did not change significantly with temperature, including at or below 20 °C. However, for slow charging at scan rate $\nu = 5$ mV/s, all curves featured a peak at the end of the charging step near $\psi_{s,max} = 2.5$ V that became more prominent as temperature increased, suggesting more ion storage due to increased ionic conductivity and accessibility in porous electrode [87] but also parasitic redox reactions at higher potential [88]. For faster charging at scan rate $\nu = 30$ mV/s, this change in current response peak with temperature was small due to ion transport limitation within shorter charging time and/or slow redox reactions.

Furthermore, for a given scan rate ν and temperature T , Device 2 featured current $I(t)$ two to eight times larger than that in Device 1 owing to better ion mobility when Pyr₁₄TFSI is dissolved in PC. Moreover, the area enclosed by the CV curves of Device 1 expanded significantly with increasing temperature. By contrast, those of Device 2 almost collapsed on top of each other except near $\psi_{s,min}$ and $\psi_{s,max}$. In other words, the increase in temperature contributed greatly to improving the performance of Device 1 while it had a modest effect on that of Device 2. This was due to the fact that neat Pyr₁₄TFSI features ionic conductivity and viscosity that depend strongly on temperature [45, 52], unlike Pyr₁₄TFSI in PC.

Figures 2(a) and 2(b) plot the gravimetric integral capacitance $C_{int,m}$ [Equation (2)] as a function of scan rate ν for temperatures T ranging from 5 to 80 °C for Devices 1 and 2, respectively. Figure 2 indicates that, for a given temperature, the gravimetric integral capacitance $C_{int,m}$ decreased with increasing scan rate ν , as typically observed in various EDLCs [43, 89–91] and attributed to ion-diffusion limitation in porous electrodes at high

scan rates [92]. In addition, the capacitance $C_{int,m}$ of Device 2 was about two to five times larger than that of Device 1 for any given scan rate ν and temperature T . This was likely due to the fact that the dielectric constant ϵ_r of PC was much larger than that of Pyr₁₄TFSI. For example, $\epsilon_r(\text{PC}) \approx 65$ [93,94] while $\epsilon_r(\text{Pyr}_{14}\text{TFSI}) \approx 11.7$ to 14.7 at $25\text{ }^\circ\text{C}$ [95–97]. Similarly, the viscosity of 1 M Pyr₁₄TFSI in PC was much smaller than that of neat Pyr₁₄TFSI leading to better wetting of the porous AC electrodes [67]. Moreover, Figure 2(a) establishes that the capacitance of Device 1 increased significantly with increasing temperature from $\sim 4\text{ F/g}$ at $5\text{ }^\circ\text{C}$ to $\sim 21\text{ F/g}$ at $80\text{ }^\circ\text{C}$ due to the increasing ion mobility of the neat IL with increasing temperature. On the other hand, $C_{int,m}$ of Device 2 increased slightly from $\sim 25\text{ F/g}$ at $5\text{ }^\circ\text{C}$ to $\sim 32\text{ F/g}$ at $60\text{ }^\circ\text{C}$. Interestingly, performance of Device 2 started degrading at $80\text{ }^\circ\text{C}$ and high scan rates.

4.3 Galvanostatic cycling

Figure 3 plots the internal resistance R_s obtained from the IR drop [Equation (4)] observed in the galvanostatic charge-discharge curves (see Figure S2 in Supplementary Materials) as a function of temperature T ranging from 5 to $80\text{ }^\circ\text{C}$ for (a) Device 1 and (b) Device 2 for imposed current I ranging from 1 to 5 mA . Figure 3(a) establishes that the internal resistance R_s of Device 1 with neat Pyr₁₄TFSI electrolyte (i) was independent of the imposed current I at any given temperature and (ii) decreased significantly with increasing temperature from $R_s = 213 \pm 6\text{ }\Omega$ at $5\text{ }^\circ\text{C}$ to $R_s = 22 \pm 5\text{ }\Omega$ at $80\text{ }^\circ\text{C}$. This observation was due mainly to the significant increase in ionic conductivity of neat Pyr₁₄TFSI with temperature [45,52]. Similarly, Figure 3(b) indicates that the internal resistance R_s of Device 2 with 1 M Pyr₁₄TFSI in PC electrolyte was nearly independent of the imposed current I and decreased with increasing temperature T . In fact, the internal resistance R_s of Device 2 decreased from around $R_s = 47 \pm 3\text{ }\Omega$ at $5\text{ }^\circ\text{C}$ to $R_s = 16 \pm 5\text{ }\Omega$ at $60\text{ }^\circ\text{C}$ and was about two to four times smaller than that of Device 1 at any temperature up to $60\text{ }^\circ\text{C}$. Interestingly, the internal resistance R_s of Device 2 was larger at $80\text{ }^\circ\text{C}$ than at $40\text{ }^\circ\text{C}$ and $60\text{ }^\circ\text{C}$ and depended on the imposed current I . This was due to PC decomposition at high temperatures and

large potential windows. In fact, neat PC can lose about 10% of its initial mass within 4 h at 60 °C due to PC reduction at the negative electrode forming gaseous propane and/or hydrogen [59, 99]. Note, however, that the rate of mass loss was smaller when mixed with ILs [59, 99]. Regardless, PC degradation impeded access of the liquid electrolyte to the pores in the porous electrode resulting in large internal resistance [59, 100]. Such increase in internal resistance with increasing temperature is responsible for thermal runaway [101].

Figure 4 shows the gravimetric differential capacitance $C_{diff,m}$ calculated from galvanostatic charge-discharge cycles [Equation (3)] as a function of cycle number n_c under different current I ranging from 1 to 5 mA for (a) Device 1 and (b) Device 2 at temperature T ranging between 5 and 80 °C. First, Figure 4 indicates that $C_{diff,m}$ decreased with increasing current I in both devices. This could be due to ion diffusion limitation through the porous electrode under high current and fast charging. In addition, for any imposed current I in both devices, $C_{diff,m}$ increased with increasing temperature, except for Device 2 beyond $T = 60$ °C. However, $C_{diff,m}$ of Device 1 was more sensitive to the temperature than that of Device 2. For example, in Device 1, $C_{diff,m}$ increased from 3.4 F/g at 20 °C to 16.1 F/g at 60 °C during discharging at $I = 4$ mA. By contrast, in Device 2, $C_{diff,m}$ increased only slightly from 27.4 F/g at 20 °C to 29.4 F/g at 60 °C also at $I = 4$ mA. Furthermore, $C_{diff,m}$ in both devices was slightly larger during charging than during discharging for any imposed current I and temperature T . This difference increased for smaller currents and higher temperatures. This could be attributed to self-discharge caused by (i) higher ion desorption rate at the electrode/electrolyte interface at high temperature and (ii) longer charging-discharging time t_{cd} at low current. Similar results were observed in devices composed of activated carbon electrodes with 1 M TEABF₄ or 1 M EMIBF₄ in ACN electrolytes [71]. Interestingly, $C_{diff,m}$ of Device 2 at $T = 80$ °C featured unusual fluctuations. This is consistent with the previous explanation that gaseous and/or solid byproducts generated during PC decomposition impeded electrolyte from entering porous electrodes.

4.4 Instantaneous heat generation rates

Figure 5 shows the instantaneous heat generation rates (a) $\dot{Q}_+(t)$ at the positive electrode and (b) $\dot{Q}_-(t)$ at the negative electrode for Device 1 with neat Pyr₁₄TFSI electrolyte as functions of dimensionless time t/t_{cd} for different temperatures ranging between 5 and 80 °C during four consecutive galvanostatic cycles under constant current $I = 4$ mA. Similarly, Figures 5(c) and 5(d) show $\dot{Q}_+(t)$ and $\dot{Q}_-(t)$ for Device 2 with 1 M Pyr₁₄TFSI in PC electrolyte, respectively. Note that, for Device 1, the imposed current I was limited to 2 mA at 5 °C due to an excessively large resistance and IR-drop and thus short charging-discharging time t_{cd} . For both devices, Figure 5 indicates that the heat generation rate measurements were repeatable cycle after cycle for all temperatures considered. Note that the heat generation rate due to Joule heating – often considered as the only source of heat generation in EDLCs [9,15,17] – is constant over time under constant current cycling. Instead, experimental measurements in Figure 5 featured strong temporal oscillations due to additional heat generation processes including reversible processes such as ion adsorption/desorption and solvation/desolvation.

Figures 5(a) and 5(b) indicate that $\dot{Q}_+(t)$ and $\dot{Q}_-(t)$ at the positive and negative electrodes of Device 1 had similar magnitude for all temperatures, except for $T = 80$ °C when $\dot{Q}_+(t)$ was larger than $\dot{Q}_-(t)$. By contrast, in Device 2, the magnitude of $\dot{Q}_+(t)$ was consistently larger than that of $\dot{Q}_-(t)$ at any given temperature. This difference became larger with increasing temperature. Moreover, Figure 5 indicates that $\dot{Q}_+(t)$ and $\dot{Q}_-(t)$ decreased with increasing temperature in Devices 1 and 2 for temperatures up to 60 °C. However, in both devices, the amplitude of the oscillations in $\dot{Q}_+(t)$ and $\dot{Q}_-(t)$ increased with increasing temperature. In Device 2 at 80 °C, both $\dot{Q}_+(t)$ and $\dot{Q}_-(t)$ increased due to the overall increase in internal resistance as a result of PC decomposition [Figure 3(b)].

Furthermore, the instantaneous heat generation rate $\dot{Q}_+(t)$ at the positive electrode in both devices was strictly (i) exothermic during charging due to ion adsorption and (ii) endothermic during discharging due to ion desorption. This was consistent with results obtained from numerical simulations [55,56] and from previous experimental studies on AC-based EDLCs with aqueous, organic, or IL-based electrolytes [43,54,61,73]. On the other

hand, the instantaneous heat generation rate $\dot{Q}_-(t)$ at the negative electrode of both Devices 1 and 2 featured an endothermic dip at the beginning of the charging step whose magnitude increased with increasing temperature. This dip was more significant in Device 2 than in Device 1. Indeed, for Device 1 with neat Pyr₁₄TFSI, a small endothermic dip can be observed at $T \geq 40$ °C for potential window of 2.5 V. A similar endothermic dip was also observed at $T = 20$ °C albeit for larger potential window of 3.5 V and 4 V in similar devices with neat Pyr₁₄TFSI electrolyte [61]. This dip was attributed to the overscreening effect at the beginning of the charging step in presence of CMC binder at the negative AC-electrode with neat Pyr₁₄TFSI electrolyte, as explained previously [54, 61]. Similarly, the fact that the endothermic dip in $\dot{Q}_-(t)$ during charging was larger in Device 2 than in Device 1 could be due not only to the overscreening effect but also to the complete or partial endothermic desolvation of Pyr₁₄⁺ cations of their PC solvation shell as they enter the AC nanopores to form an EDL [11, 34, 102, 103].

Finally, the endothermic dip at the negative electrode of Device 2 became noticeably larger with increasing temperature as a result of increasing PC decomposition caused by endothermic PC reduction reaction [61]. Note that, this dip dominated at the beginning of the charging step due to the competing and sharply increasing exothermic heat generation rate associated with cation adsorption throughout the charging step [61].

4.5 Time-averaged irreversible heat generation rates

Figures 6 and 7 plot the time-averaged irreversible heat generation rates (a) $\bar{\dot{Q}}_{irr,+}$ at the positive electrode, (b) $\bar{\dot{Q}}_{irr,-}$ at the negative electrode, (c) $\bar{\dot{Q}}_{irr,T}$ in the entire cell, and (d) the ratio $\bar{\dot{Q}}_{irr,T}/\bar{\dot{Q}}_J$ of total irreversible heat generation rate to Joule heating as functions of I^2 with imposed current I ranging from 1 to 5 mA and temperature T varying between 5 and 80 °C for Device 1 and Device 2, respectively. The error bars correspond to two standard deviation or 95% confidence interval estimated by evaluating $\bar{\dot{Q}}_{irr,i}$ over five consecutive galvanostatic cycles. In addition, Joule heating was estimated as

$$\bar{\dot{Q}}_J = \bar{R}_s(T)I^2 \quad (8)$$

where $\bar{R}_s(T)$ is the average internal resistance reported in Figure 3, except for Device 2 at 80 °C when variations in $R_s(T)$ with imposed current I were accounted for.

Figures 6 and 7 indicate that $\bar{Q}_{irr,+}$ and $\bar{Q}_{irr,-}$ were fairly similar in each device and for any given temperature. This was attributed to the fact that (i) the positive and negative electrodes were synthesized in the same manner and should be nearly identical and (ii) the diffusion coefficients of Pyr_{14}^+ cations and TFSI^- anions were similar in each electrolyte considered [37, 52, 104, 105]. In fact, the ratio of the diffusion coefficients of Pyr_{14}^+ to that of TFSI^- in neat $\text{Pyr}_{14}\text{TFSI}$, i.e., D_+/D_- was reported to be equal to 1.2 at 20 °C and 1.1 at 40 °C [104] and approaching 1.0 as the temperature increases [37]. Similarly, in Device 2 (Figure 7), $D_+ \approx D_-$ in 1 M of $\text{Pyr}_{14}\text{TFSI}$ dissolved in PC at 20 °C [52, 105]. Therefore, the ionic conductivity of the electrolyte in each half cell were similar at all temperatures in each device. The slight differences between $\bar{Q}_{irr,+}$ and $\bar{Q}_{irr,-}$ could be due to differences in the electrode mass loading. In addition, the irreversible heat generation rates $\bar{Q}_{irr,+}$ and $\bar{Q}_{irr,-}$ in Device 2 were typically smaller than those in Device 1 due, in part, to its smaller internal resistance R_s (Figure 3).

Moreover, Figure 6 establishes that the time-averaged irreversible heat generation rates $\bar{Q}_{irr,+}$ and $\bar{Q}_{irr,-}$ at the positive and negative half-cells as well as $\bar{Q}_{irr,T}$ in the entire Device 1 decreased significantly with increasing temperature from 5 to 80 °C. This was due, in part, to the fact that the ionic conductivity of neat $\text{Pyr}_{14}\text{TFSI}$ and the wettability of the electrodes increased sharply with increasing temperature. By contrast, Figure 7 establishes that $\bar{Q}_{irr,+}$, $\bar{Q}_{irr,-}$, and $\bar{Q}_{irr,T}$ in Device 2 decreased slightly between 5 and 20 °C and were nearly independent of temperature between 20 to 60 °C for any given current. These observations are surprising given the decrease in internal resistance $\bar{R}_s(T)$ of Device 2 with increasing temperature from 5 to 60 °C [Figure 3(b)]. It suggested that Joule heating was not the only source of irreversible heat generation. However, $\bar{Q}_{irr,+}$, $\bar{Q}_{irr,-}$, and $\bar{Q}_{irr,T}$ increased significantly at 80 °C in Device 2 due to the partial PC decomposition resulting in electrode pore blockage [42, 75] and increasing cell resistance [Figure 3(b)].

Furthermore, $\bar{Q}_{irr,+}$, $\bar{Q}_{irr,-}$, and $\bar{Q}_{irr,T}$ in EDLCs with aqueous and organic electrolytes

at 20 °C [43, 54] and in IL-based electrolyte between 20 to 60 °C [73] all for cell potential window $\Delta\psi_s \leq 1$ V were linearly proportional to I^2 . In fact, the total heat generation rate $\bar{Q}_{irr,T}$ was equal to Joule heating, i.e., $\bar{Q}_J = R_s I^2$. By contrast, $\bar{Q}_{irr,+}$, $\bar{Q}_{irr,-}$, and $\bar{Q}_{irr,T}$ in both Devices 1 and 2 with $\Delta\psi_s = 2.5$ V did not vary linearly with I^2 , as indicated by power law fit. In fact, the total irreversible heat generation rate $\bar{Q}_{irr,T}$ in both Devices 1 and 2 exceeded Joule heating \bar{Q}_J for any temperatures between 5 and 80 °C, i.e., $\bar{Q}_{irr,T}/\bar{Q}_J > 1$. The ratio $\bar{Q}_{irr,T}/\bar{Q}_J$ increased with increasing temperature and decreasing current in both Devices 1 and 2. Similar results were also observed in similar devices cycled at 20 °C under large potential windows $\Delta\psi_s$ up to 4 V [61]. This can be attributed to a combination of phenomena namely (i) the charge redistribution in porous electrodes caused by higher ions desorption rate with increasing temperature and modeled as the leakage current flowing through the pore resistance [14, 16, 61, 71, 74] and (ii) the longer charging-discharging time t_{cd} at low current (see Figure S3 in Supplementary Materials). In fact, the pore resistance is responsible for EDLC self-discharge and increased with increasing potential window [14, 61, 107, 108].

4.6 Reversible heat generation rates

As previously discussed, the instantaneous irreversible heat generation rate $\dot{Q}_{irr,i}(t)$ cannot be solely attributed to Joule heating and may vary with time. Thus, the instantaneous reversible heat generation rate $\dot{Q}_{rev,i}(t) = \dot{Q}_i(t) - \dot{Q}_{irr,i}(t)$ cannot be estimated from our measurements. Instead, Figure 8 shows the time-averaged reversible heat generation rates during a charging step [Equation (7)] (a,c) $\bar{Q}_{rev,+}^c$ at the positive electrode and (b,d) $\bar{Q}_{rev,-}^c$ at the negative electrode as functions of current I for (a,b) Device 1 and (c,d) Device 2, respectively. Here also, the current I ranged from 1 to 5 mA and the temperature T from 5 to 80 °C and the error bars correspond to 95% confidence interval estimated by evaluating $\bar{Q}_{rev,i}^c$ over five cycles. Figure 8 indicates that, in both Devices 1 and 2, $\bar{Q}_{rev,+}^c$ was systematically larger than $\bar{Q}_{rev,-}^c$. This could be attributed to the fact that TFSI⁻ anions are smaller (~ 0.7 nm) than Pyr₁₄⁺ cations (~ 1.1 nm). In fact, d'Entremont et al. [56] established theoretically that

adsorption of smaller ions at a given electrode resulted not only in larger integral capacitance but also in larger reversible heat generation rate. Thus, TFSI⁻ adsorption at the positive electrode during charging caused more reversible heat generation than Pyr₁₄⁺ adsorption at the negative electrode in Device 1 with neat Pyr₁₄TFSI. Similar arguments apply to Device 2 where solvated PC-Pyr₁₄⁺ ions were significantly larger than TFSI⁻ ions in the 1 M Pyr₁₄TFSI in PC electrolyte [56].

Moreover, for any given current and temperature, $\bar{Q}_{rev,+}^c$ was typically larger in Device 2 than in Device 1 due to the fact that the capacitance of Device 2 was significantly larger than that of Device 1 (Figures 2 and 4). By contrast, $\bar{Q}_{rev,-}^c$ in Device 2 was smaller than in Device 1 as solvated PC-Pyr₁₄⁺ cations were larger compared to non-solvated Pyr₁₄⁺ cations in neat IL.

Figures 8(a) and 8(b) also establish that, for a given current in Device 1, $\bar{Q}_{rev,+}^c$ increased with increasing temperature whereas $\bar{Q}_{rev,-}^c$ generally did not change significantly with temperature. This could be due to the endothermic dip previously observed in $\dot{Q}_-(t)$ at the negative electrode and associated with overscreening effect, ion desolvation, and/or PC decomposition. Indeed, the magnitude of this endothermic dip increased with increasing temperature and compensate the rise in reversible heat generation caused by increasing capacitance.

Furthermore, in Device 1 with neat Pyr₁₄TFSI [Figures 8(a) and 8(b)], both $\bar{Q}_{rev,+}^c$ and $\bar{Q}_{rev,-}^c$ increased linearly with imposed current I for all temperatures considered. This was consistent with results from numerical simulations of EDLCs [55]. Similar observations were also made in previous experimental studies for EDLC cells consisting of AC-electrodes with organic or aqueous electrolytes for potential window $\Delta\psi_s \leq 1$ V [43, 54] and with neat or diluted Pyr₁₄TFSI electrolyte for different potential windows between 1 V to 4 V at 20 °C [61]. Similarly, in Device 2 with 1 M Pyr₁₄TFSI diluted in PC [Figures 8(c) and 8(d)], $\bar{Q}_{rev,+}^c$ and $\bar{Q}_{rev,-}^c$ increased fairly linearly with imposed current I except for temperatures $T = 60$ and 80 °C. This was due to the fact that the endothermic dip in the instantaneous heat generation rate at the negative electrode [Figure 5(d)] attributed to overscreening effect

and/or desolvation of Pyr_{14}^+ from PC solvent shell and PC decomposition became significant at 60 and 80 °C.

5 Conclusion

This study reported the irreversible and reversible heat generation rates in two sets of AC-based EDLC devices with either (i) neat $\text{Pyr}_{14}\text{TFSI}$ or (ii) 1 M $\text{Pyr}_{14}\text{TFSI}$ in PC electrolytes. The measurements were performed in an isothermal *in operando* calorimeter under galvanostatic cycling with potential window of 2.5 V and temperatures ranging from 5 to 80 °C. The instantaneous heat generation rate at each electrode was measured under galvanostatic cycling at temperatures between 5 and 80 °C for a potential window of 2.5 V. First, the instantaneous heat generation rate was similar at each electrode in neat IL. By contrast, it was smaller at the negative electrode than at the positive electrode in devices with diluted IL in PC. Large oscillations in the instantaneous heat generation rate were observed due to reversible processes such as ion adsorption/desorption and ion solvation/desolvation. In addition, endothermic dips appeared and grew with increasing temperature above 60 °C at the negative electrode at the beginning of the charging step. They were attributed to (i) overscreening effects in both electrolytes as well as to (ii) desolvation of Pyr_{14}^+ cations and (iii) partial decomposition of PC in diluted IL electrolyte. Moreover, the irreversible heat generation rate in both devices decreased with increasing temperature due to the significant increase in the electrolyte ionic conductivity, particularly for the device with neat $\text{Pyr}_{14}\text{TFSI}$ electrolyte. The irreversible heat generation rates in the device with 1 M $\text{Pyr}_{14}\text{TFSI}$ in PC increased sharply at 80 °C as a result of PC decomposition. In addition, the total irreversible heat generation rate in each device exceeded Joule heating. This was attributed to additional irreversible heat generation caused by charge redistribution in the porous electrode and increasing leakage current due to ion desorption with increasing temperature. Second, in both EDLC devices, the time-averaged reversible heat generation rate over the charging step increased with increasing temperature and was larger at the positive than at the

negative electrode due to the better accessibility of smaller TFSI⁻ anions into subnanoscale pores compared with larger Pyr₁₄⁺ cations. Furthermore, the time-averaged reversible heat generation rate during charging at both electrodes increased linearly with imposed current except in the device with IL diluted in PC above 60 °C.

Acknowledgment

This work was supported as part of the Center for Synthetic Control Across Length-scales for Advancing Rechargeables (SCALAR), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award # DE-SC0019381.

References

- [1] B. E. Conway, *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications*, Kluwer Academic/Plenum Publishers, New York, NY, 1999.
- [2] J. B. Goodenough, H. D. Abruna, and M. V. Buchanan, “Basic Research Needs for Electrical Energy Storage: Report of the Basic Energy Sciences Workshop for Electrical Energy Storage”, Tech. Rep. DOI 10.2172/935429, U.S. Department of Energy, 2007.
- [3] A. Burke, “R&D considerations for the performance and application of electrochemical capacitors”, *Electrochimica Acta*, vol. 53, no. 3, pp. 1083–1091, 2007.
- [4] M. Winter and R. J. Brodd, “What are batteries, fuel cells, and supercapacitors?”, *Chemical Reviews*, vol. 104, no. 10, pp. 4245–4270, 2004.
- [5] L. Maharjan, S. Inoue, and H. Akagi, “A transformerless energy storage system based on a cascade multilevel PWM converter with star configuration”, *IEEE Transactions on Industry Applications*, vol. 44, no. 5, pp. 1621–1630, 2008.
- [6] A. Burke, “Ultracapacitors: why, how, and where is the technology”, *Journal of Power Sources*, vol. 91, no. 1, pp. 37–50, 2000.
- [7] M. D. Stoller, S. Park, Y. Zhu, J. An, and R. S. Ruoff, “Graphene-based ultracapacitors”, *Nano Letters*, vol. 8, no. 10, pp. 3498–3502, 2008.
- [8] J. R. Miller, “Electrochemical capacitor thermal management issues at high-rate cycling”, *Electrochimica Acta*, vol. 52, no. 4, pp. 1703–1708, 2006.
- [9] P. Guillemet, Y. Scudeller, and T. Brousse, “Multi-level reduced-order thermal modeling of electrochemical capacitors”, *Journal of Power Sources*, vol. 157, no. 1, pp. 630–640, 2006.
- [10] P. Simon and Y. Gogotsi, “Materials for electrochemical capacitors”, *Nature Materials*, vol. 7, no. 11, pp. 845–854, 2008.

- [11] F. Béguin, V. Presser, A. Balducci, and E. Frackowiak, “Carbons and electrolytes for advanced supercapacitors”, *Advanced Materials*, vol. 26, no. 14, pp. 2219–2251, 2014.
- [12] L. L. Zhang, Y. Gu, and X. Zhao, “Advanced porous carbon electrodes for electrochemical capacitors”, *Journal of Materials Chemistry A*, vol. 1, no. 33, pp. 9395–9408, 2013.
- [13] F. Stoeckli and T. A. Centeno, “Optimization of the characterization of porous carbons for supercapacitors”, *Journal of Materials Chemistry A*, vol. 1, no. 23, pp. 6865–6873, 2013.
- [14] J. Schiffer, D. Linzen, and D. U. Sauer, “Heat generation in double layer capacitors”, *Journal of Power Sources*, vol. 160, no. 1, pp. 765–772, 2006.
- [15] H. Gualous, H. Louahlia-Gualous, R. Gallay, and A. Miraoui, “Supercapacitor thermal modeling and characterization in transient state for industrial applications”, *IEEE Transactions on Industry Applications*, vol. 45, no. 3, pp. 1035–1044, 2009.
- [16] R. Kötz, M. Hahn, and R. Gallay, “Temperature behavior and impedance fundamentals of supercapacitors”, *Journal of Power Sources*, vol. 154, no. 2, pp. 550–555, 2006.
- [17] M. Al Sakka, H. Gualous, J. Van Mierlo, and H. Culcu, “Thermal modeling and heat management of supercapacitor modules for vehicle applications”, *Journal of Power Sources*, vol. 194, no. 2, pp. 581–587, 2009.
- [18] O. Bohlen, J. Kowal, and D. U. Sauer, “Ageing behaviour of electrochemical double layer capacitors: Part I. experimental study and ageing model”, *Journal of Power Sources*, vol. 172, no. 1, pp. 468–475, 2007.
- [19] C. Masarapu, H. F. Zeng, K. H. Hung, and B. Wei, “Effect of temperature on the capacitance of carbon nanotube supercapacitors”, *ACS Nano*, vol. 3, no. 8, pp. 2199–2206, 2009.

- [20] M. Galiński, A. Lewandowski, and I. Stepniak, “Ionic liquids as electrolytes”, *Electrochimica Acta*, vol. 51, no. 26, pp. 5567–5580, 2006.
- [21] V. Ruiz, T. Huynh, S. R. Sivakkumar, and A. G. Pandolfo, “Ionic liquid–solvent mixtures as supercapacitor electrolytes for extreme temperature operation”, *RSC Advances*, vol. 2, no. 13, pp. 5591–5598, 2012.
- [22] C. Chiappe and D. Pieraccini, “Ionic liquids: solvent properties and organic reactivity”, *Journal of Physical Organic Chemistry*, vol. 18, no. 4, pp. 275–297, 2005.
- [23] C. Maton, N. De Vos, and C. V. Stevens, “Ionic liquid thermal stabilities: decomposition mechanisms and analysis tools”, *Chemical Society Reviews*, vol. 42, no. 13, pp. 5963–5977, 2013.
- [24] M. Salanne, “Chapter 2: Ionic Liquids for Supercapacitor Applications”, in *Ionic Liquids II*, B. Kirchner and E. Perlt, Eds., pp. 29–53. Springer International Publishing, Cham, Switzerland, 2018.
- [25] R. Hagiwara and J. S. Lee, “Ionic liquids for electrochemical devices”, *Electrochemistry*, vol. 75, no. 1, pp. 23–34, 2007.
- [26] A. Krause and A. Balducci, “High voltage electrochemical double layer capacitor containing mixtures of ionic liquids and organic carbonate as electrolytes”, *Electrochemistry Communications*, vol. 13, no. 8, pp. 814–817, 2011.
- [27] S. Pohlmann and A. Balducci, “A new conducting salt for high voltage propylene carbonate-based electrochemical double layer capacitors”, *Electrochimica Acta*, vol. 110, pp. 221–227, 2013.
- [28] R. Lin, P.-L. Taberna, S. Fantini, V. Presser, C. R. Pérez, F. Malbosc, N. L. Rupesinghe, K. B. K. Teo, Y. Gogotsi, and P. Simon, “Capacitive energy storage from –50 to 100 °C using an ionic liquid electrolyte”, *The Journal of Physical Chemistry Letters*, vol. 2, no. 19, pp. 2396–2401, 2011.

- [29] A. Balducci, “Electrolytes for high voltage electrochemical double layer capacitors: A perspective article”, *Journal of Power Sources*, vol. 326, pp. 534–540, 2016.
- [30] W. Xu and C. A. Angell, “Solvent-free electrolytes with aqueous solution-like conductivities”, *Science*, vol. 302, no. 5644, pp. 422–425, 2003.
- [31] S. Pohlmann, B. Lobato, T. A. Centeno, and A. Balducci, “The influence of pore size and surface area of activated carbons on the performance of ionic liquid based supercapacitors”, *Physical Chemistry Chemical Physics*, vol. 15, no. 40, pp. 17287–17294, 2013.
- [32] G. Xiong, A. Kundu, and T. S. Fisher, *Thermal Effects in Supercapacitors*, Springer, 2015.
- [33] A. Lewandowski, A. Olejniczak, M. Galinski, and I. Stepniak, “Performance of carbon–carbon supercapacitors based on organic, aqueous and ionic liquid electrolytes”, *Journal of Power Sources*, vol. 195, no. 17, pp. 5814–5819, 2010.
- [34] M. V. Fedorov and A. A. Kornyshev, “Ionic liquids at electrified interfaces”, *Chemical Reviews*, vol. 114, no. 5, pp. 2978–3036, 2014.
- [35] A. Balducci, F. Soavi, and M. Mastragostino, “The use of ionic liquids as solvent-free green electrolytes for hybrid supercapacitors”, *Applied Physics A*, vol. 82, no. 4, pp. 627–632, 2006.
- [36] C. Arbizzani, G. Gabrielli, and M. Mastragostino, “Thermal stability and flammability of electrolytes for lithium-ion batteries”, *Journal of Power Sources*, vol. 196, no. 10, pp. 4801–4805, 2011.
- [37] J. Reiter, S. Jeremias, E. Paillard, M. Winter, and S. Passerini, “Fluorosulfonyl-(trifluoromethanesulfonyl)imide ionic liquids with enhanced asymmetry”, *Physical Chemistry Chemical Physics*, vol. 15, no. 7, pp. 2565–2571, 2013.

- [38] S. Jeremias, M. Kunze, S. Passerini, and M. Schoonhoff, “Polymerizable ionic liquid with state of the art transport properties”, *The Journal of Physical Chemistry B*, vol. 117, no. 36, pp. 10596–10602, 2013.
- [39] K. Hayamizu, Y. Aihara, H. Nakagawa, T. Nukuda, and W. S. Price, “Ionic conduction and ion diffusion in binary room-temperature ionic liquids composed of [emim][BF₄] and LiBF₄”, *The Journal of Physical Chemistry B*, vol. 108, no. 50, pp. 19527–19532, 2004.
- [40] S. Leyva-García, D. Lozano-Castelló, E. Morallón, T. Vogl, C. Schütter, S. Passerini, A. Balducci, and D. Cazorla-Amorós, “Electrochemical performance of a superporous activated carbon in ionic liquid-based electrolytes”, *Journal of Power Sources*, vol. 336, pp. 419–426, 2016.
- [41] A. Borenstein, R. Attias, O. Hanna, S. Luski, R. B. Kaner, and D. Aurbach, “A surprising failure mechanism in symmetric supercapacitors at high voltages”, *Chem-ElectroChem*, vol. 4, no. 10, pp. 2660–2668, 2017.
- [42] A. Hammar, P. Venet, R. Lallemand, G. Coquery, and G. Rojat, “Study of accelerated aging of supercapacitors for transport applications”, *IEEE Transactions on Industrial Electronics*, vol. 57, no. 12, pp. 3972–3979, 2010.
- [43] O. Munteshari, J. Lau, A. Krishnan, B. Dunn, and L. Pilon, “Isothermal calorimeter for measurements of time-dependent heat generation rate in individual supercapacitor electrodes”, *Journal of Power Sources*, vol. 374, pp. 257–268, 2018.
- [44] C. Arbizzani, M. Biso, D. Cericola, M. Lazzari, F. Soavi, and M. Mastragostino, “Safe, high-energy supercapacitors based on solvent-free ionic liquid electrolytes”, *Journal of Power Sources*, vol. 185, no. 2, pp. 1575–1579, 2008.
- [45] S. Pohlmann, T. Olyschläger, P. Goodrich, J. A. Vicente, J. Jacquemin, and A. Balducci, “Azepanium-based ionic liquids as green electrolytes for high voltage supercapacitors”, *Journal of Power Sources*, vol. 273, pp. 931–936, 2015.

- [46] A. Balducci, W. A. Henderson, M. Mastragostino, S. Passerini, P. Simon, and F. Soavi, “Cycling stability of a hybrid activated carbon//poly (3-methylthiophene) supercapacitor with N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ionic liquid as electrolyte”, *Electrochimica Acta*, vol. 50, no. 11, pp. 2233–2237, 2005.
- [47] S. Zhang, S. Brahim, and S. Maat, “High-voltage operation of binder-free CNT supercapacitors using ionic liquid electrolytes”, *Journal of Materials Research*, vol. 33, no. 9, pp. 1179–1188, 2018.
- [48] A. Brandt and A. Balducci, “Theoretical and practical energy limitations of organic and ionic liquid-based electrolytes for high voltage electrochemical double layer capacitors”, *Journal of Power Sources*, vol. 250, pp. 343–351, 2014.
- [49] F. Soavi, C. Arbizzani, and M. Mastragostino, “Leakage currents and self-discharge of ionic liquid-based supercapacitors”, *Journal of Applied Electrochemistry*, vol. 44, no. 4, pp. 491–496, 2014.
- [50] P. Johansson, L. E. Fast, A. Matic, G. B. Appetecchi, and S. Passerini, “The conductivity of pyrrolidinium and sulfonylimide-based ionic liquids: A combined experimental and computational study”, *Journal of Power Sources*, vol. 195, no. 7, pp. 2074–2076, 2010.
- [51] M. Nádherná, J. Reiter, J. Moškon, and R. Dominko, “Lithium bis(fluorosulfonyl)imide–PYR₁₄TFSI ionic liquid electrolyte compatible with graphite”, *Journal of Power Sources*, vol. 196, no. 18, pp. 7700–7706, 2011.
- [52] A. Balducci, R. Dugas, P.-L. Taberna, P. Simon, D. Plee, M. Mastragostino, and S. Passerini, “High temperature carbon–carbon supercapacitor using ionic liquid as electrolyte”, *Journal of Power Sources*, vol. 165, no. 2, pp. 922–927, 2007.
- [53] Y. Dandeville, P. Guillemet, Y. Scudeller, O. Crosnier, L. Athouel, and T. Brousse, “Measuring time-dependent heat profiles of aqueous electrochemical capacitors under cycling”, *Thermochimica Acta*, vol. 526, no. 1-2, pp. 1–8, 2011.

- [54] O. Munteshari, J. Lau, D. S. Ashby, B. Dunn, and L. Pilon, “Effects of constituent materials on heat generation in individual EDLC electrodes”, *Journal of The Electrochemical Society*, vol. 165, no. 7, pp. A1547–A1557, 2018.
- [55] A. L. d’Entremont and L. Pilon, “First-principles thermal modeling of electric double layer capacitors under constant-current cycling”, *Journal of Power Sources*, vol. 246, pp. 887–898, 2014.
- [56] A. L. d’Entremont and L. Pilon, “Thermal effects of asymmetric electrolytes in electric double layer capacitors”, *Journal of Power Sources*, vol. 273, pp. 196–209, 2015.
- [57] M. Z. Bazant, B. D. Storey, and A. A. Kornyshev, “Double layer in ionic liquids: Overscreening versus crowding”, *Physical Review Letters*, vol. 106, no. 4, pp. 046102, 2011.
- [58] M. D. Levi, N. Levy, S. Sigalov, G. Salitra, D. Aurbach, and J. Maier, “Electrochemical quartz crystal microbalance (EQCM) studies of ions and solvents insertion into highly porous activated carbons”, *Journal of the American Chemical Society*, vol. 132, no. 38, pp. 13220–13222, 2010.
- [59] A. Brandt, C. Ramirez-Castro, M. Anouti, and A. Balducci, “An investigation about the use of mixtures of sulfonium-based ionic liquids and propylene carbonate as electrolytes for supercapacitors”, *Journal of Materials Chemistry A*, vol. 1, no. 40, pp. 12669–12678, 2013.
- [60] M. Hahn, A. Würsig, R. Gallay, P. Novák, and R. Kötz, “Gas evolution in activated carbon/propylene carbonate based double-layer capacitors”, *Electrochemistry Communications*, vol. 7, no. 9, pp. 925–930, 2005.
- [61] O. Munteshari, A. Borenstein, R. H. DeBlock, J. Lau, G. Whang, Y. Zhou, A. Likitchatchawankun, R. Kaner, B. Dunn, and L. Pilon, “In operando calorimetric measurements for activated carbon electrodes in neat or diluted ionic liquid electrolytes under large potential windows”, *ChemSusChem*, vol. 13, pp. 1–15, 2020.

- [62] S. I. Fletcher, F. B. Sillars, R. C. Carter, A. J. Cruden, M. Mirzaeian, N. E. Hudson, J. A. Parkinson, and P. J. Hall, “The effects of temperature on the performance of electrochemical double layer capacitors”, *Journal of Power Sources*, vol. 195, no. 21, pp. 7484–7488, 2010.
- [63] H. Michel, “Temperature and dynamics problems of ultracapacitors in stationary and mobile applications”, *Journal of Power Sources*, vol. 154, no. 2, pp. 556–560, 2006.
- [64] M. Arulepp, L. Permann, J. Leis, A. Perkson, K. Rumma, A. Jänes, and E. Lust, “Influence of the solvent properties on the characteristics of a double layer capacitor”, *Journal of Power Sources*, vol. 133, no. 2, pp. 320–328, 2004.
- [65] P. Kreczanik, P. Venet, A. Hijazi, and G. Clerc, “Study of supercapacitor aging and lifetime estimation according to voltage, temperature, and RMS current”, *IEEE Transactions on Industrial Electronics*, vol. 61, no. 9, pp. 4895–4902, 2014.
- [66] P. Liu, M. Verbrugge, and S. Soukiazian, “Influence of temperature and electrolyte on the performance of activated-carbon supercapacitors”, *Journal of Power Sources*, vol. 156, no. 2, pp. 712–718, 2006.
- [67] W. Liu, X. Yan, J. Lang, and Q. Xue, “Effects of concentration and temperature of EMIMBF₄/acetonitrile electrolyte on the supercapacitive behavior of graphene nanosheets”, *Journal of Materials Chemistry*, vol. 22, no. 18, pp. 8853–8861, 2012.
- [68] W. Li, K. Xu, L. An, F. Jiang, X. Zhou, J. Yang, Z. Chen, R. Zou, and J. Hu, “Effect of temperature on the performance of ultrafine MnO₂ nanobelt supercapacitors”, *Journal of Materials Chemistry A*, vol. 2, no. 5, pp. 1443–1447, 2014.
- [69] J.-G. Wang, Y. Yang, Z.-H. Huang, and F. Kang, “Effect of temperature on the pseudocapacitive behavior of freestanding MnO₂@ carbon nanofibers composites electrodes in mild electrolyte”, *Journal of Power Sources*, vol. 224, pp. 86–92, 2013.

- [70] C. Yuan, X. Zhang, Q. Wu, and B. Gao, “Effect of temperature on the hybrid supercapacitor based on NiO and activated carbon with alkaline polymer gel electrolyte”, *Solid State Ionics*, vol. 177, no. 13, pp. 1237–1242, 2006.
- [71] S. Park, S.-W. Kang, and K. Kim, “Competition between ionic adsorption and desorption on electrochemical double layer capacitor electrodes in acetonitrile solutions at different currents and temperatures”, *Journal of Power Sources*, vol. 372, pp. 8–15, 2017.
- [72] B. Xu, F. Wu, R. Chen, G. Cao, S. Chen, and Y. Yang, “Mesoporous activated carbon fiber as electrode material for high-performance electrochemical double layer capacitors with ionic liquid electrolyte”, *Journal of Power Sources*, vol. 195, no. 7, pp. 2118–2124, 2010.
- [73] A. Likitchatchawankun, G. Whang, J. Lau, O. Munteshari, B. Dunn, and L. Pilon, “Effect of temperature on irreversible and reversible heat generation rates in ionic liquid-based electric double layer capacitors”, *Electrochimica Acta*, vol. 338, pp. 135802, 2020.
- [74] M. Ayadi, A. Eddahech, O. Briat, and J.-M. Vinassa, “Voltage and temperature impacts on leakage current in calendar ageing of supercapacitors”, in *Proceedings of the 4th International Conference on Power Engineering, Energy and Electrical Drives*, May 13–17, 2013; Istanbul, Turkey, IEEE, pp. 1466–1470, 2013.
- [75] T. Umemura, Y. Mizutani, T. Okamoto, T. Taguchi, K. Nakajima, and K. Tanaka, “Life expectancy and degradation behavior of electric double layer capacitor part I”, in *Proceedings of the 7th International Conference on Properties and Applications of Dielectric Materials*, Jun 1–5, 2003; Nagoya, Japan, IEEE, vol. 3, pp. 944–948, 2003.
- [76] M. Hahn, R. Kötz, R. Gallay, and A. Siggel, “Pressure evolution in propylene carbonate based electrochemical double layer capacitors”, *Electrochimica Acta*, vol. 52, no. 4, pp. 1709–1712, 2006.

- [77] A. M. Bittner, M. Zhu, Y. Yang, H. F. Waibel, M. Konuma, U. Starke, and C. J. Weber, “Ageing of electrochemical double layer capacitors”, *Journal of Power Sources*, vol. 203, pp. 262–273, 2012.
- [78] S. Pohlmann, T. Olyschläger, P. Goodrich, J. A. Vicente, J. Jacquemin, and A. Balducci, “Mixtures of azepanium based ionic liquids and propylene carbonate as high voltage electrolytes for supercapacitors”, *Electrochimica Acta*, vol. 153, pp. 426–432, 2015.
- [79] H. Wang and L. Pilon, “Reply to comments on “Intrinsic limitations of impedance measurements in determining electric double layer capacitances” by H. Wang and L. Pilon [Electrochimica Acta 63 (2012) 55]”, *Electrochimica Acta*, vol. 76, pp. 529–531, 2012.
- [80] A. Burke and M. Miller, “Testing of electrochemical capacitors: Capacitance, resistance, energy density, and power capability”, *Electrochimica Acta*, vol. 55, no. 25, pp. 7538–7548, 2010.
- [81] S. Zhao, F. Wu, L. Yang, L. Gao, and A. F. Burke, “A measurement method for determination of DC internal resistance of batteries and supercapacitors”, *Electrochemistry Communications*, vol. 12, no. 2, pp. 242–245, 2010.
- [82] M. D. Stoller and R. S. Ruoff, “Best practice methods for determining an electrode material’s performance for ultracapacitors”, *Energy & Environmental Science*, vol. 3, no. 9, pp. 1294–1301, 2010.
- [83] B.-A. Mei, O. Munteshari, J. Lau, B. Dunn, and L. Pilon, “Physical interpretations of Nyquist plots for EDLC electrodes and devices”, *The Journal of Physical Chemistry C*, vol. 122, no. 1, pp. 194–206, 2017.
- [84] K. Xu, S. P. Ding, and T. R. Jow, “Toward reliable values of electrochemical stability limits for electrolytes”, *Journal of The Electrochemical Society*, vol. 146, no. 11, pp. 4172, 1999.

- [85] M. Morita, M. Goto, and Y. Matsuda, “Ethylene carbonate-based organic electrolytes for electric double layer capacitors”, *Journal of Applied Electrochemistry*, vol. 22, no. 10, pp. 901–908, 1992.
- [86] M. Ishikawa, M. Ihara, M. Morita, and Y. Matsuda, “Electric double layer capacitors with new gel electrolytes”, *Electrochimica Acta*, vol. 40, no. 13-14, pp. 2217–2222, 1995.
- [87] C. Yin, X. Liu, J. Wei, R. Tan, J. Zhou, M. Ouyang, H. Wang, S. J. Cooper, B. Wu, C. George, and Q. Wang, “All-in-Gel design for supercapacitors towards solid-state energy devices with thermal and mechanical compliance”, *Journal of Materials Chemistry A*, vol. 7, no. 15, pp. 8826–8831, 2019.
- [88] Y. Cheng, H. Zhang, S. Lu, C. V. Varanasi, and J. Liu, “Flexible asymmetric supercapacitors with high energy and high power density in aqueous electrolytes”, *Nanoscale*, vol. 5, no. 3, pp. 1067–1073, 2013.
- [89] C. Kim, “Electrochemical characterization of electrospun activated carbon nanofibres as an electrode in supercapacitors”, *Journal of Power Sources*, vol. 142, no. 1-2, pp. 382–388, 2005.
- [90] Y. Gao, Y. S. Zhou, M. Qian, X. N. He, J. Redepenning, P. Goodman, H. M. Li, L. Jiang, and Y. F. Lu, “Chemical activation of carbon nano-onions for high-rate supercapacitor electrodes”, *Carbon*, vol. 51, pp. 52–58, 2013.
- [91] S. R. C. Vivekchand, C. S. Rout, K. S. Subrahmanyam, A. Govindaraj, and C. N. R. Rao, “Graphene-based electrochemical supercapacitors”, *Journal of Chemical Sciences*, vol. 120, no. 1, pp. 9–13, 2008.
- [92] H. Wang and L. Pilon, “Physical interpretation of cyclic voltammetry for measuring electric double layer capacitances”, *Electrochimica Acta*, vol. 64, pp. 130–139, 2012.

- [93] R. Payne and I. E. Theodorou, “Dielectric properties and relaxation in ethylene carbonate and propylene carbonate”, *The Journal of Physical Chemistry*, vol. 76, no. 20, pp. 2892–2900, 1972.
- [94] J. Barthel, R. Neueder, and H. Roch, “Density, relative permittivity, and viscosity of propylene carbonate + dimethoxyethane mixtures from 25 °C to 125 °C”, *Journal of Chemical & Engineering Data*, vol. 45, no. 6, pp. 1007–1011, 2000.
- [95] I. Krossing, J. M. Slattery, C. Daguenet, P. J. Dyson, A. Oleinikova, and H. Weingärtner, “Why are ionic liquids liquid? A simple explanation based on lattice and solvation energies”, *Journal of the American Chemical Society*, vol. 128, no. 41, pp. 13427–13434, 2006.
- [96] H. Weingärtner, P. Sasisanker, C. Daguenet, P. J. Dyson, I. Krossing, J. M. Slattery, and T. Schubert, “The dielectric response of room-temperature ionic liquids: effect of cation variation”, *The Journal of Physical Chemistry B*, vol. 111, no. 18, pp. 4775–4780, 2007.
- [97] M.-M. Huang, Y. Jiang, P. Sasisanker, G. W. Driver, and H. Weingaärtner, “Static relative dielectric permittivities of ionic liquids at 25 °C”, *Journal of Chemical & Engineering Data*, vol. 56, no. 4, pp. 1494–1499, 2011.
- [98] A. Likitchatchawankun, A. Kundu, O. Munteshari, T. S. Fisher, and L. Pilon, “Heat generation in all-solid-state supercapacitors with graphene electrodes and gel electrolytes”, *Electrochimica Acta*, vol. 303, pp. 341–353, 2019.
- [99] A. B. McEwen, S. F. McDevitt, and V. R. Koch, “Nonaqueous electrolytes for electrochemical capacitors: imidazolium cations and inorganic fluorides with organic carbonates”, *Journal of The Electrochemical Society*, vol. 144, no. 4, pp. L84, 1997.
- [100] K. Xu, “Nonaqueous liquid electrolytes for lithium-based rechargeable batteries”, *Chemical Reviews*, vol. 104, no. 10, pp. 4303–4418, 2004.

- [101] Q. Wang, P. Ping, X. Zhao, G. Chu, J. Sun, and C. Chen, “Thermal runaway caused fire and explosion of lithium ion battery”, *Journal of Power Sources*, vol. 208, pp. 210–224, 2012.
- [102] J. Chmiola, C. Largeot, P.-L. Taberna, P. Simon, and Y. Gogotsi, “Desolvation of ions in subnanometer pores and its effect on capacitance and double-layer theory”, *Angewandte Chemie International Edition*, vol. 47, no. 18, pp. 3392–3395, 2008.
- [103] X. Baokou and M. Anouti, “Physical properties of a new deep eutectic solvent based on a sulfonium ionic liquid as a suitable electrolyte for electric double-layer capacitors”, *The Journal of Physical Chemistry C*, vol. 119, no. 2, pp. 970–979, 2015.
- [104] M. Kunze, S. Jeong, G. B. Appetecchi, M. Schönhof, M. Winter, and S. Passerini, “Mixtures of ionic liquids for low temperature electrolytes”, *Electrochimica Acta*, vol. 82, pp. 69–74, 2012.
- [105] S. Pohlmann, R.-S. Kühnel, T. A. Centeno, and A. Balducci, “The influence of anion–cation combinations on the physicochemical properties of advanced electrolytes for supercapacitors and the capacitance of activated carbons”, *ChemElectroChem*, vol. 1, no. 8, pp. 1301–1311, 2014.
- [106] R.-S. Kühnel, N. Böckenfeld, S. Passerini, M. Winter, and A. Balducci, “Mixtures of ionic liquid and organic carbonate as electrolyte with improved safety and performance for rechargeable lithium batteries”, *Electrochimica Acta*, vol. 56, no. 11, pp. 4092–4099, 2011.
- [107] J. Black and H. A. Andreas, “Effects of charge redistribution on self-discharge of electrochemical capacitors”, *Electrochimica Acta*, vol. 54, no. 13, pp. 3568–3574, 2009.
- [108] G. Madabattula and S. Kumar, “Insights into charge-redistribution in double layer capacitors”, *Journal of The Electrochemical Society*, vol. 165, no. 3, pp. A636–A649, 2018.

List of Figures

- 1 Cyclic voltammograms of (a) Device 1 with neat Pyr₁₄TFSI at $\nu = 5$ mV/s and (b) at $\nu = 30$ mV/s and (c) Device 2 with 1 M Pyr₁₄TFSI in PC at $\nu = 5$ mV/s and (d) at $\nu = 30$ mV/s at temperature T ranging from 5 to 80 °C. The potential window ranged between $\psi_{s,min} = 0$ V and $\psi_{s,max} = 2.5$ V. 41
- 2 Gravimetric integral capacitance $C_{int,m}$ [Equation (2)] of (a) Device 1 with neat Pyr₁₄TFSI and (b) Device 2 with 1 M Pyr₁₄TFSI in PC electrolytes obtained from the CV curves shown in Figure 1 for temperature T ranging from 5 to 80 °C and scan rate ν between 5 and 30 mV/s. 42
- 3 Internal resistance R_s [Equation(4)] as a function of temperature T ranging from 5 to 80 °C for (a) Device 1 with neat Pyr₁₄TFSI and (b) Device 2 with 1 M Pyr₁₄TFSI in PC for imposed current I ranging from 1 to 5 mA. 43
- 4 Gravimetric differential capacitance $C_{diff,m}$ of (a) Device 1 with neat Pyr₁₄TFSI and (b) Device 2 with 1 M Pyr₁₄TFSI in PC as a function of cycle number n_c during charging and discharging steps at constant current I between 1 and 5 mA and at temperature T ranging from 5 to 80 °C. 44
- 5 Instantaneous heat generation rates as functions of dimensionless time t/t_{cd} for Device 1 with neat Pyr₁₄TFSI electrolyte (a) $\dot{Q}_+(t)$ at the positive and (b) $\dot{Q}_-(t)$ at negative electrodes and for Device 2 with 1 M Pyr₁₄TFSI in PC electrolyte (c) $\dot{Q}_+(t)$ at the positive and (d) $\dot{Q}_-(t)$ at negative electrodes for temperatures between 5 and 80 °C during four consecutive galvanostatic cycles under constant current $I = 4$ mA. 45
- 6 Time-averaged irreversible heat generation rates (a) $\bar{Q}_{irr,+}$ at the positive electrode, (b) $\bar{Q}_{irr,-}$ at the negative electrode, (c) $\bar{Q}_{irr,T}$ in the entire cell, and (d) $\bar{Q}_{irr,T}/\bar{Q}_J$ the ratio of total irreversible heat generation rate to Joule heating as functions of I^2 with imposed current I ranging from 1 to 5 mA for Device 1 with neat Pyr₁₄TFSI electrolyte. 46

7	Time-averaged irreversible heat generation rates (a) $\bar{\dot{Q}}_{irr,+}$ at the positive electrode, (b) $\bar{\dot{Q}}_{irr,-}$ at the negative electrode, (c) $\bar{\dot{Q}}_{irr,T}$ in the entire cell, and (d) $\bar{\dot{Q}}_{irr,T}/\bar{\dot{Q}}_J$ the ratio of total irreversible heat generation rate to Joule heating as functions of I^2 with imposed current I ranging from 1 to 5 mA for Device 2 with 1 M Pyr ₁₄ TFSI in PC electrolyte.	47
8	Time-averaged reversible heat generation rates during the charging step as functions of imposed current I ranging between 1 and 5 mA for Device 1 with neat Pyr ₁₄ TFSI electrolyte (a) $\bar{\dot{Q}}_{rev,+}^c$ at the positive and (b) $\bar{\dot{Q}}_{rev,-}^c$ at negative electrodes and for Device 2 with 1 M Pyr ₁₄ TFSI in PC electrolyte (c) $\bar{\dot{Q}}_{rev,+}^c$ at the positive and (d) $\bar{\dot{Q}}_{rev,-}^c$ at negative electrodes for temperatures between 5 and 80 °C.	48

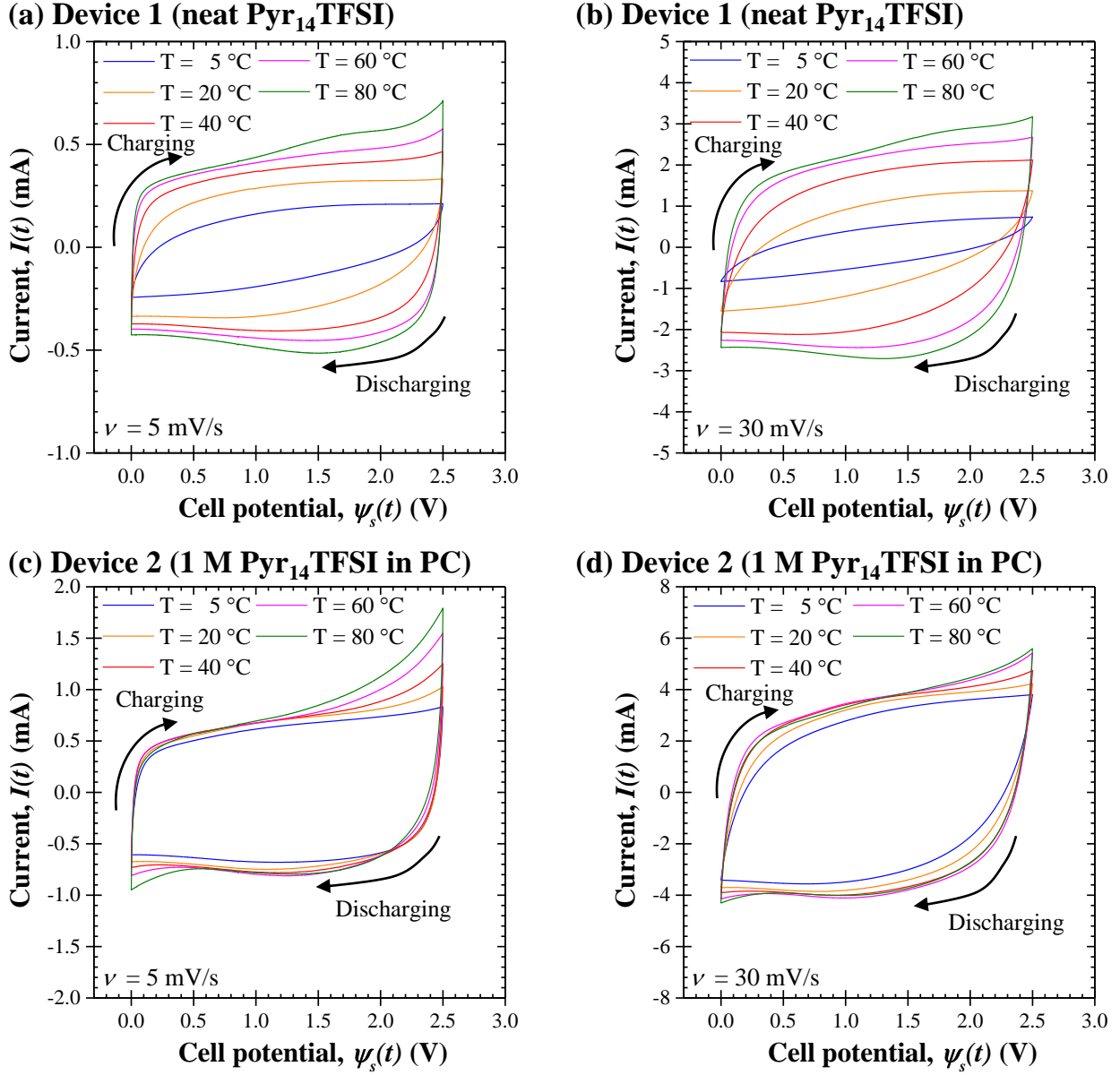
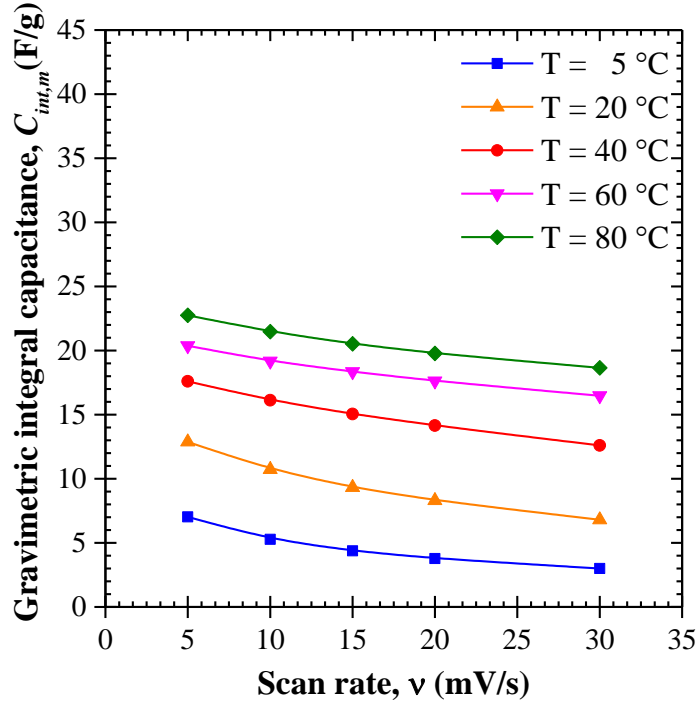


Figure 1: Cyclic voltammograms of (a) Device 1 with neat Pyr₁₄TFSI at $\nu = 5$ mV/s and (b) at $\nu = 30$ mV/s and (c) Device 2 with 1 M Pyr₁₄TFSI in PC at $\nu = 5$ mV/s and (d) at $\nu = 30$ mV/s at temperature T ranging from 5 to 80 °C. The potential window ranged between $\psi_{s,min} = 0$ V and $\psi_{s,max} = 2.5$ V.

(a) Device 1 (neat Pyr₁₄TFSI)



(b) Device 2 (1 M Pyr₁₄TFSI in PC)

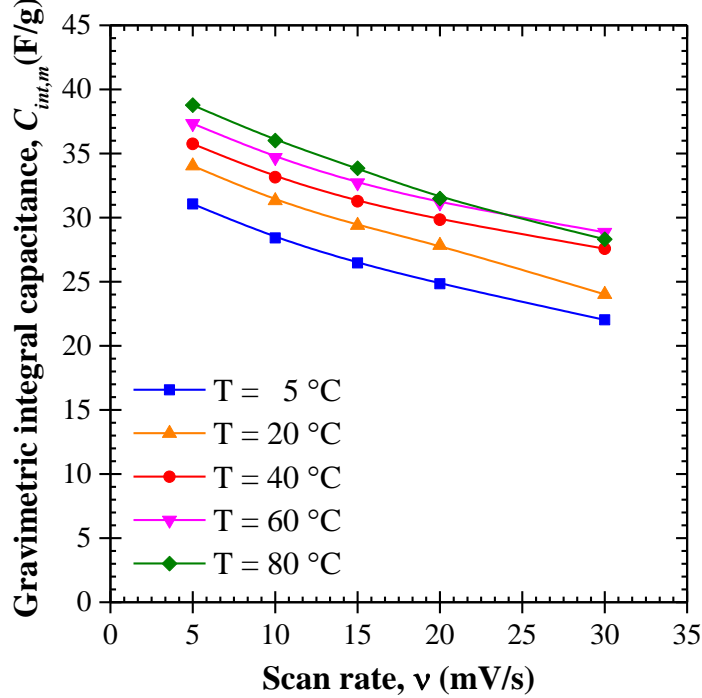
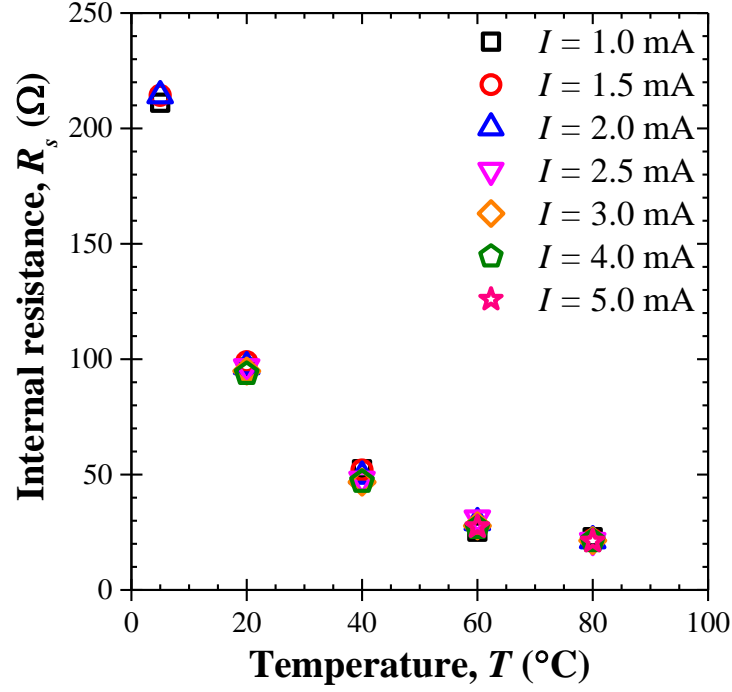


Figure 2: Gravimetric integral capacitance $C_{int,m}$ [Equation (2)] of (a) Device 1 with neat Pyr₁₄TFSI and (b) Device 2 with 1 M Pyr₁₄TFSI in PC electrolytes obtained from the CV curves shown in Figure 1 for temperature T ranging from 5 to 80 °C and scan rate ν between 5 and 30 mV/s.

(a) Device 1 (neat Pyr₁₄TFSI)



(b) Device 2 (1 M Pyr₁₄TFSI in PC)

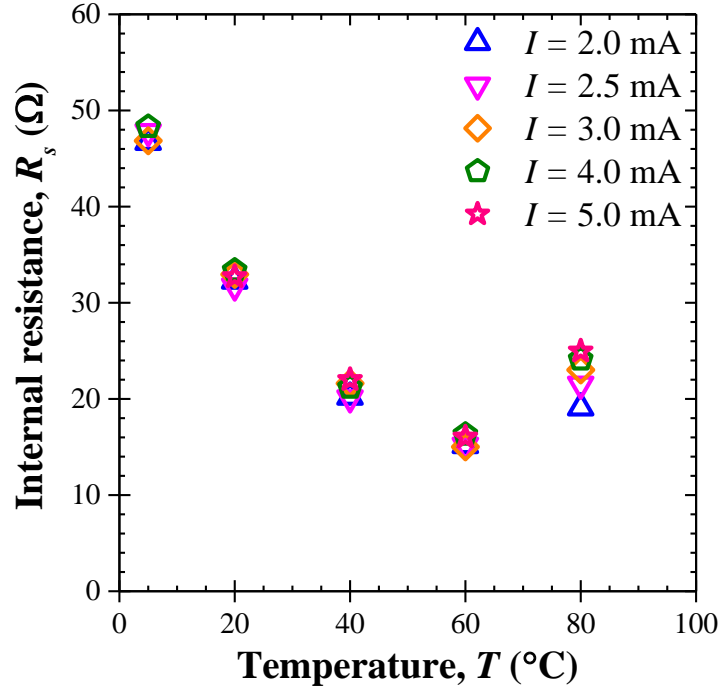
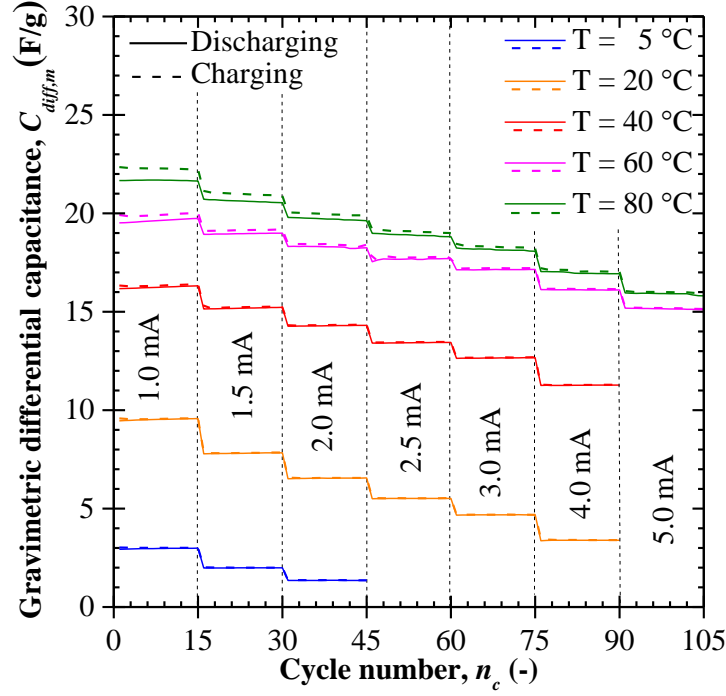


Figure 3: Internal resistance R_s [Equation(4)] as a function of temperature T ranging from 5 to 80 °C for (a) Device 1 with neat Pyr₁₄TFSI and (b) Device 2 with 1 M Pyr₁₄TFSI in PC for imposed current I ranging from 1 to 5 mA.

(a) Device 1 (neat Pyr₁₄TFSI)



(b) Device 2 (1 M Pyr₁₄TFSI in PC)

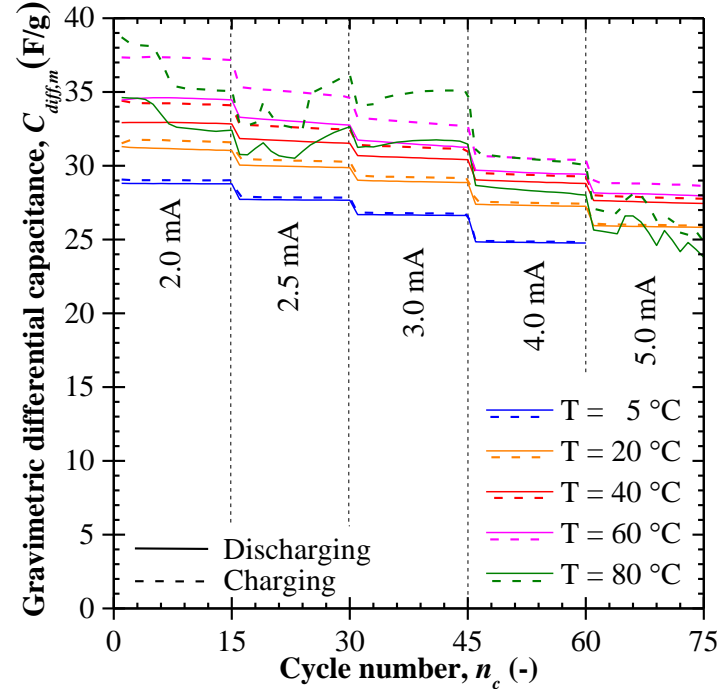


Figure 4: Gravimetric differential capacitance $C_{diff,m}$ of (a) Device 1 with neat Pyr₁₄TFSI and (b) Device 2 with 1 M Pyr₁₄TFSI in PC as a function of cycle number n_c during charging and discharging steps at constant current I between 1 and 5 mA and at temperature T ranging from 5 to 80 °C.

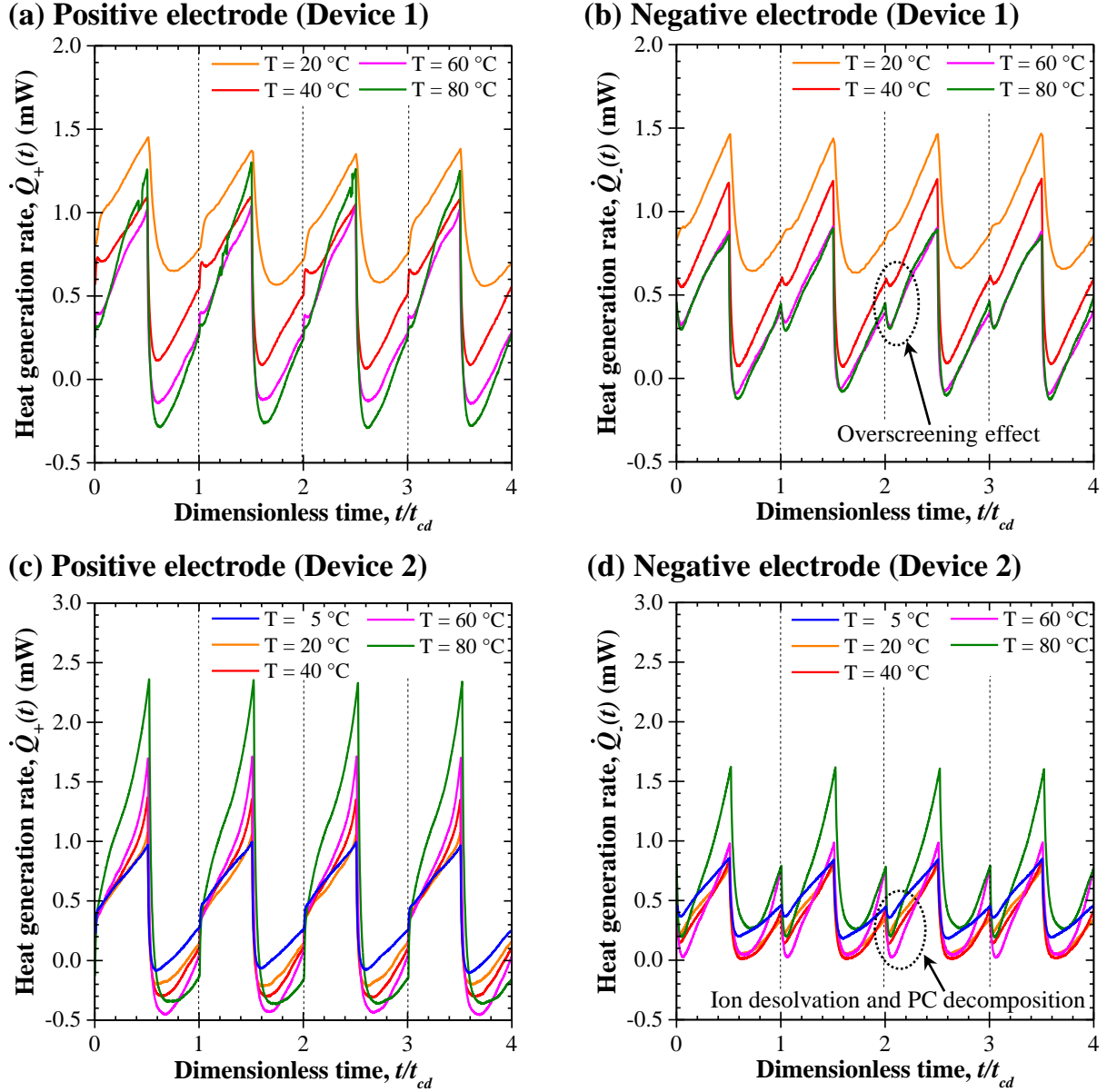


Figure 5: Instantaneous heat generation rates as functions of dimensionless time t/t_{cd} for Device 1 with neat Pyr₁₄TFSI electrolyte (a) $\dot{Q}_+(t)$ at the positive and (b) $\dot{Q}_-(t)$ at negative electrodes and for Device 2 with 1 M Pyr₁₄TFSI in PC electrolyte (c) $\dot{Q}_+(t)$ at the positive and (d) $\dot{Q}_-(t)$ at negative electrodes for temperatures between 5 and 80 °C during four consecutive galvanostatic cycles under constant current $I = 4$ mA.

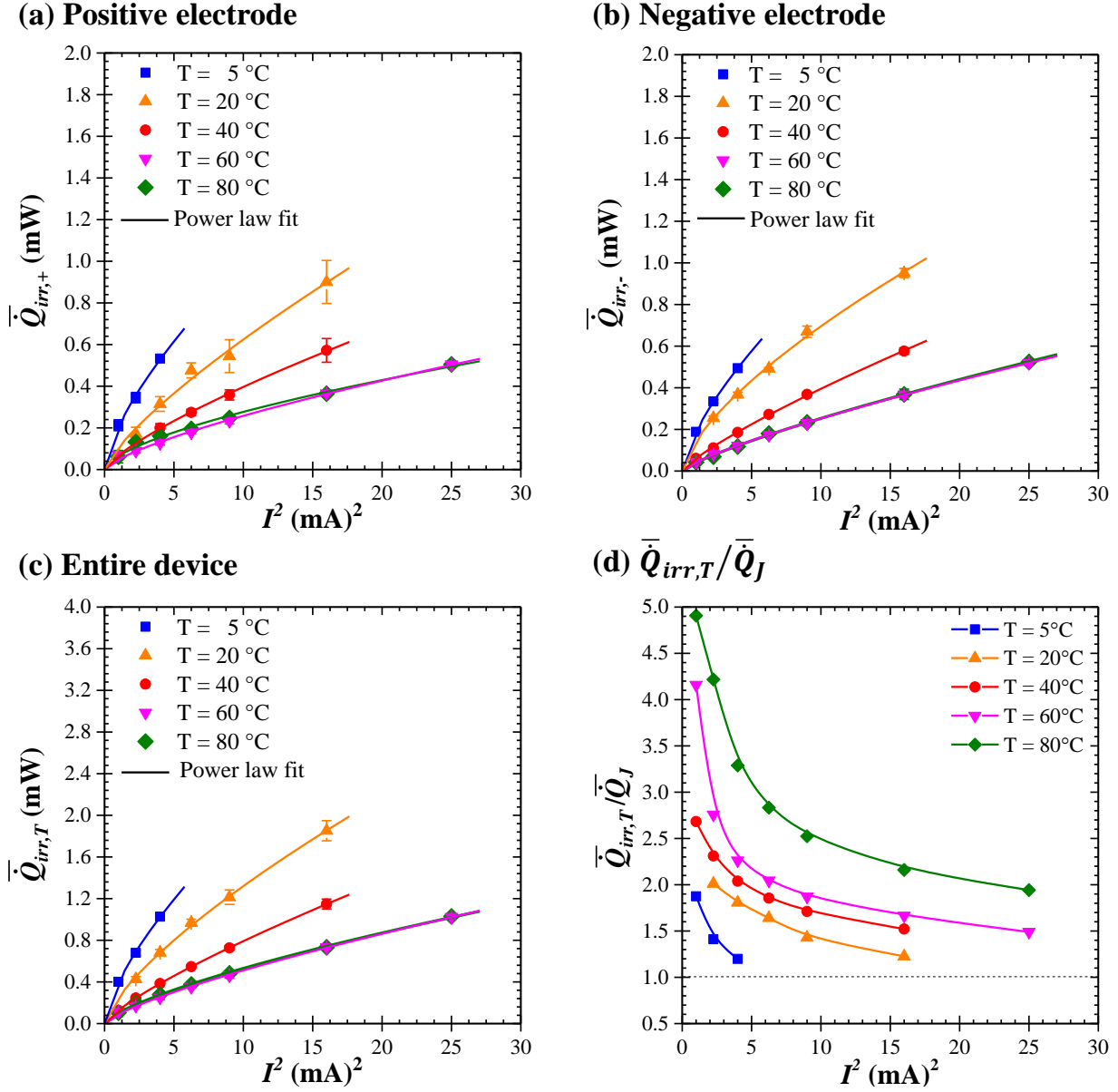


Figure 6: Time-averaged irreversible heat generation rates (a) $\bar{Q}_{irr,+}$ at the positive electrode, (b) $\bar{Q}_{irr,-}$ at the negative electrode, (c) $\bar{Q}_{irr,T}$ in the entire cell, and (d) $\bar{Q}_{irr,T}/\bar{Q}_J$ the ratio of total irreversible heat generation rate to Joule heating as functions of I^2 with imposed current I ranging from 1 to 5 mA for Device 1 with neat Pyr₁₄TFSI electrolyte.

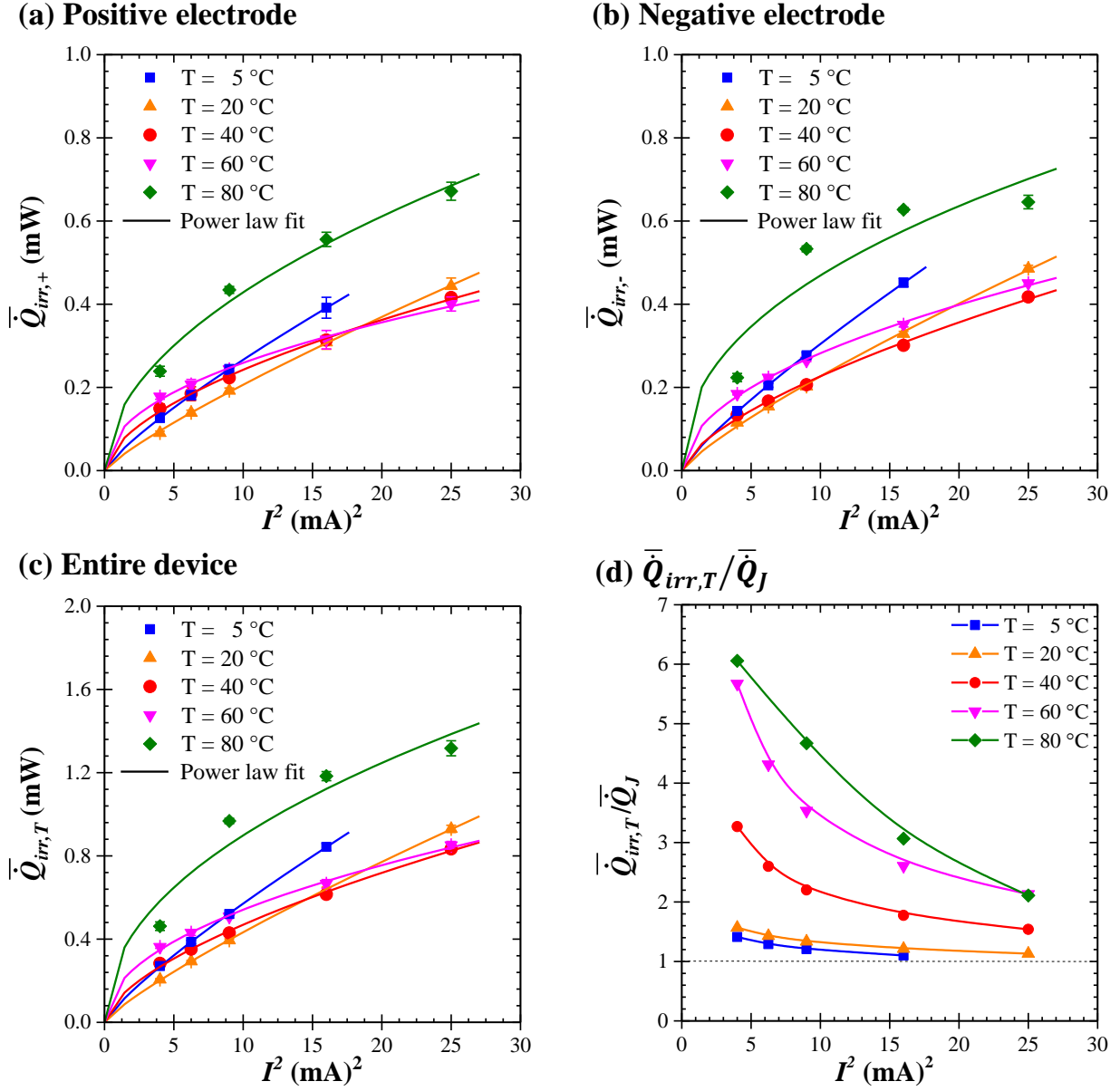
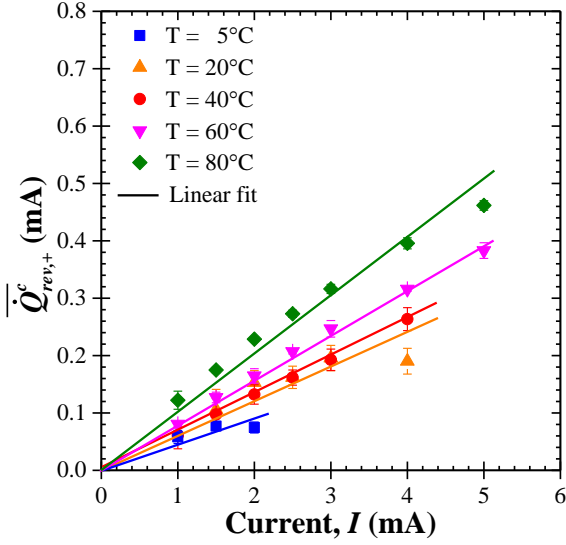
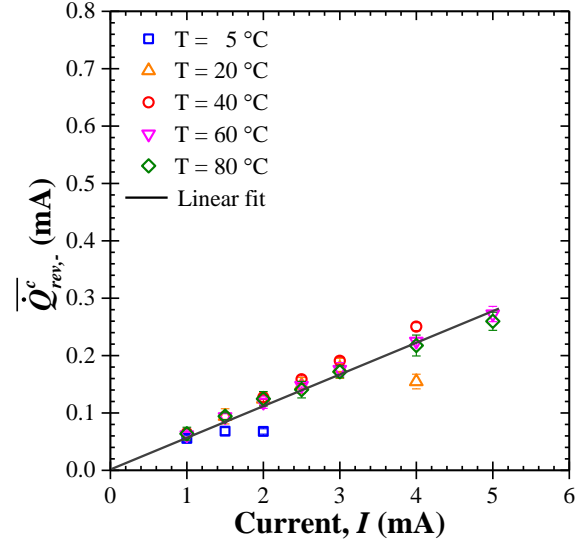


Figure 7: Time-averaged irreversible heat generation rates (a) $\bar{\dot{Q}}_{irr,+}$ at the positive electrode, (b) $\bar{\dot{Q}}_{irr,-}$ at the negative electrode, (c) $\bar{\dot{Q}}_{irr,T}$ in the entire cell, and (d) $\bar{\dot{Q}}_{irr,T}/\bar{\dot{Q}}_J$ the ratio of total irreversible heat generation rate to Joule heating as functions of I^2 with imposed current I ranging from 1 to 5 mA for Device 2 with 1 M Pyr₁₄TFSI in PC electrolyte.

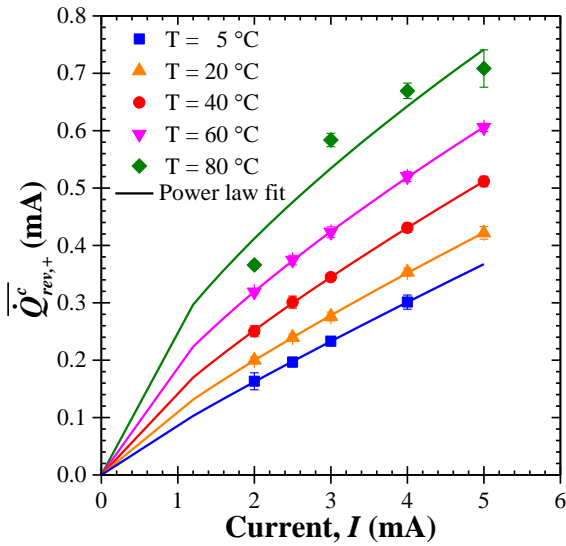
(a) Positive electrode (Device 1)



(b) Negative electrode (Device 1)



(c) Positive electrode (Device 2)



(d) Negative electrode (Device 2)

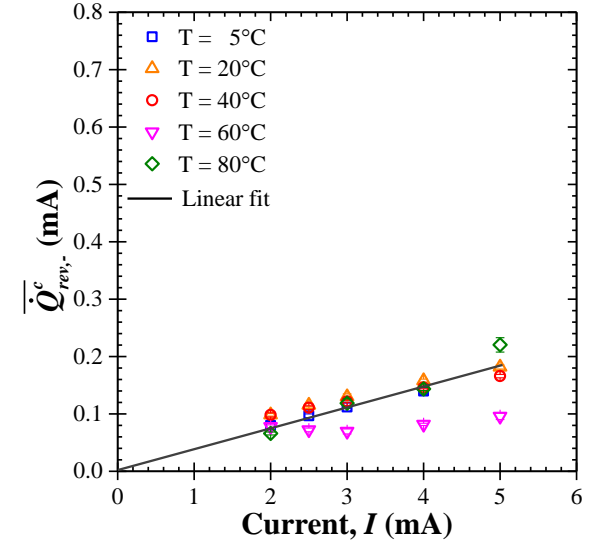


Figure 8: Time-averaged reversible heat generation rates during the charging step as functions of imposed current I ranging between 1 and 5 mA for Device 1 with neat Pyr₁₄TFSI electrolyte (a) $\bar{\dot{Q}}_{rev,+}^c$ at the positive and (b) $\bar{\dot{Q}}_{rev,-}^c$ at negative electrodes and for Device 2 with 1 M Pyr₁₄TFSI in PC electrolyte (c) $\bar{\dot{Q}}_{rev,+}^c$ at the positive and (d) $\bar{\dot{Q}}_{rev,-}^c$ at negative electrodes for temperatures between 5 and 80 °C.