



Open Archive TOULOUSE Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible.

This is an author-deposited version published in : <http://oatao.univ-toulouse.fr/>
Eprints ID : 8687

To link to this article : DOI:10.1021/jz201065t
URL : <http://dx.doi.org/10.1021/jz201065t>

To cite this version : Lin, Rongying and Taberna, Pierre-Louis and Fantini, Sébastien and Presser, Volker and Pérez, Carlos R. and Malbosc, François and Rupesinghe, Nalin L. and Teo, Kenneth B. K. and Gogotsi, Yury and Simon, Patrice. *Capacitive energy storage from -50 to 100 °C using an ionic liquid electrolyte*. (2011) *The Journal of Physical Chemistry Letters*, vol. 2 (n° 19). pp. 2396-2401. ISSN 1948-7185

Any correspondence concerning this service should be sent to the repository administrator: staff-oatao@listes-diff.inp-toulouse.fr

Capacitive Energy Storage from -50 to 100 °C Using an Ionic Liquid Electrolyte

Rongying Lin,^{†,‡} Pierre-Louis Taberna,[†] Sébastien Fantini,[‡] Volker Presser,[§] Carlos R. Pérez,[§] François Malbosc,[‡] Nalin L. Rupesinghe,^{||} Kenneth B. K. Teo,^{||} Yury Gogotsi,[§] and Patrice Simon^{*,†}

[†]Université Paul Sabatier, Toulouse Cedex, France;

[‡]SOLVIONIC Company, Toulouse, France;

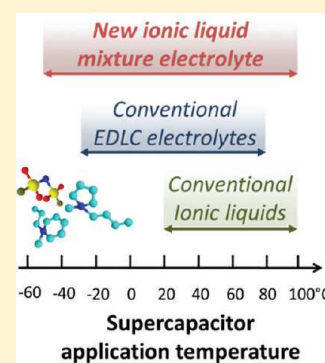
[§]Department of Materials Science and Engineering & A.J. Drexel Nanotechnology Institute, Drexel University, Philadelphia, PA 19104, United States

^{||}AIXTRON, Cambridge, U.K.

S Supporting Information

ABSTRACT: Relying on redox reactions, most batteries are limited in their ability to operate at very low or very high temperatures. While performance of electrochemical capacitors is less dependent on the temperature, present-day devices still cannot cover the entire range needed for automotive and electronics applications under a variety of environmental conditions. We show that the right combination of the exohedral nanostructured carbon (nanotubes and onions) electrode and a eutectic mixture of ionic liquids can dramatically extend the temperature range of electrical energy storage, thus defying the conventional wisdom that ionic liquids can only be used as electrolytes above room temperature. We demonstrate electrical double layer capacitors able to operate from -50 to 100 °C over a wide voltage window (up to 3.7 V) and at very high charge/discharge rates of up to 20 V/s.

SECTION: Energy Conversion and Storage



Electrochemical energy storage (EES) devices are at the center of attention to address one of today's major technological and societal challenges: sustainable energy solutions. EES devices enable operation of hybrid and electric vehicles and broad implementation of renewable energy sources (solar, wind, and tidal power). Over the past decade, EES systems have seen tremendous improvements in performance; however, all current technologies are limited to a rather narrow range of operation temperatures.

EES systems are traditionally divided into energy devices (batteries) and power devices (electrochemical capacitors: ECs). There have been several breakthroughs and significant improvements in the battery area during the past years, mainly associated with the development of Li-ion batteries.¹ However, the development of high voltage cathodes for batteries with extended operational range from low (below -20 °C) to high (beyond 70 °C) temperatures is still hampered by electrolyte stability.^{1–3} While batteries are characterized by charge/discharge times ranging from minutes to hours, ECs are high-power devices (~ 10 kW/kg) with medium energy density (~ 5 Wh/kg), which can be fully charged or discharged in a few seconds.⁴ While not limited to that application, ECs complement or replace batteries wherever high power densities are needed for short times (e.g., starting a car or truck engine).⁵ ECs can be divided into two groups: electrochemical double layer capacitors (EDLCs) and pseudocapacitors,⁶ with the latter benefiting from a combination

of electrostatic and Faradic (surface) processes involved in the charge storage mechanism.^{7,8}

EDLCs, also called supercapacitors or ultracapacitors, store energy electrostatically through ion adsorption from an electrolyte on the surface of charged high surface area carbon electrodes, by charging the so-called double layer capacitance.^{6,9} This charge storage mechanism explains the key features of EDLCs: outstanding cycle life (no redox reaction), high power density (fast surface storage), and identical charging and discharging rates (reversible ion ad-/desorption). As is true for the entirety of EES technologies, ECs have seen great improvements in performance, which were facilitated by recent discoveries such as the ion desolvation and capacitance increase in subnanometer pores,¹² the evidence of the influence of the nanostructure of oxides on the pseudocapacitive behavior¹⁰ and the measurement of ion fluxes in micropores with in situ electrochemical techniques.¹¹

With a large number of carbon nanomaterials already under investigation, the discovery of graphene has stipulated tremendous research effort, and Miller's group reported high power performance for thin graphene layers explained by the high

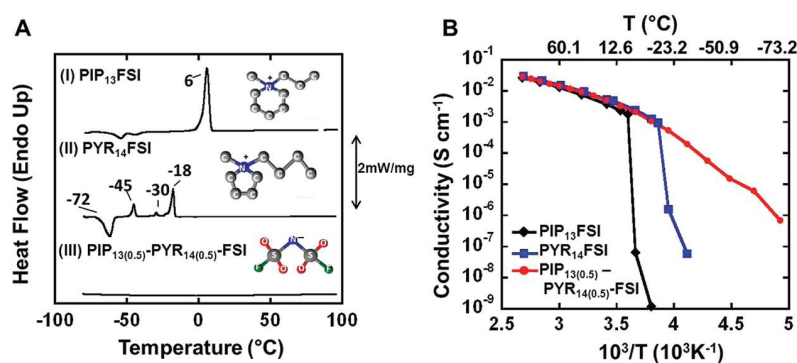


Figure 1. Characteristics of the ILs. (A) DSC profiles of (I) PIP₁₃FSI, (II) PYR₁₄FSI and (III) (PIP₁₃FSI)_{0.5}(PYR₁₄FSI)_{0.5} mixture, and their chemical structures. (B) Change of the conductivity versus the inverse temperature for PIP₁₃FSI, PYR₁₄FSI and (PIP₁₃FSI)_{0.5}(PYR₁₄FSI)_{0.5} IL mixture.

conductivity and highly accessible surface area.¹² Zhu et al. reported the remarkable power and energy density of thin film electrodes made from activated graphene with a >3000 m²/g specific surface area.¹³ Tailoring the carbon structure, specific surface area, pore size, and pore size distribution is important for improving EC performance, and examples include composites of carbon nanotubes (CNTs) and activated carbon,¹⁴ self-assembled CNT on graphene,¹⁵ or activated cup-stacked CNT electrodes.¹⁶ However, device performance is not solely determined by the electrode material but by the behavior and properties of the electrical double layer, and, thus, it is the electrode–electrolyte combination^{17,18} that finally defines cycle lifetime, capacitance, usable voltage window, and charge/discharge rate.

Conventional electrolytes used in ECs contain a mixture of solvent and salt, the latter usually being composed of ammonium cations and fluorinated anions, such as tetraethylammonium tetrafluoroborate (TEA-BF₄), for use over a ~2.7 V window. Without the need of a solid–electrolyte interphase at EDLC electrodes, unlike in Li-ion batteries, acetonitrile (AN) can be used as electrolyte solvent, thus enabling operation temperatures as low as -40 °C. However, the boiling point of AN (80 °C) limits the maximum operation temperature to about 70 °C. AN is also toxic and has a low flash point (~5 °C) that leads to safety concerns to the point that some countries, such as Japan, do not allow use of AN in ECs. Replacement of AN with propylene carbonate (PC) shifts the operating temperature to the -25 to 70 °C range, with a limited power performance because of a lower ionic conductivity of PC-based electrolytes versus AN-based systems.

Extending the temperature range for batteries or ECs is of great importance since this could solve the problem of the operation in severe conditions required for automotive, aerospace, solar/wind energy, and power electronics applications. Because of the limited possibility of reaching temperatures below -30 °C for batteries due to the Faradic charge storage mechanism, ECs became attractive candidates for low-temperature applications, such as, starting truck or locomotive engines in winter, electrical energy storage from solar panels, or back-up power supplies that operate outside climate-controlled spaces.¹⁹ Operation temperatures below -60 °C have been reported by using carbon electrodes in AN/TEA-BF₄ mixed with various proportions of cosolvents with low boiling point such as methyl formate, methyl acetate, or 1,3-dioxolane.²⁰ However, the addition of low boiling point cosolvents to AN limits the upper temperature boundary of these electrolytes to approximately

50 °C, while the safety concerns linked with the use of AN are still present. Consequently, such devices cannot be used in summer time in hot climates or in an engine compartment of cars and trucks.

Safe operation at elevated temperatures may be achieved by using solvent-free ionic liquids (ILs) in EES systems.³ Having a melting point below 20 °C, room-temperature ionic liquids (RTILs) have attracted much interest in the past decade since they have negligible vapor pressure, are nonflammable, and are stable in an electrochemical potential window larger than 3 V.^{3,21} However, RTILs suffer from a low ionic conductivity (few mS/cm at room temperature versus tens of mS/cm for conventional organic electrolytes),²² high viscosity and a melting point usually greater than 0 °C. These features make ILs attractive for high temperature ($T > 50$ °C) use, with an improved voltage window leading to a higher energy density ($E \approx V^2$).^{23–26} However, the low ionic mobility in these ILs effectively prevents the use of such electrolytes especially below 0 °C, and most of the current literature reports IL and RTIL performance at temperatures greater than or equal to 60 °C.^{3,25,27} Recently, room temperature use of an IL electrolyte was demonstrated in combination with activated carbon,²⁸ CNTs,²⁹ and with a graphene electrode,¹³ but there are no reports on use of an RTIL as EC electrolyte that could operate at low (<-30 °C) and high (>50 °C) temperature.

In this paper, we report on achieving a dramatic expansion of the operation temperature range for supercapacitor electrodes utilizing an IL mixture with a low melting point (lower than its constituents) combined with exohedral carbon nanomaterials. By using CNTs and onion-like carbon (OLC), we illustrate concepts and discuss approaches to designing next-generation supercapacitors with improved temperature range and a widened voltage window.

An eutectic mixture (1:1 by weight or molar ratio) of *N*-methyl-*N*-propylpiperidinium bis(fluorosulfonyl)imide (PIP₁₃FSI) and *N*-butyl-*N*-methylpyrrolidinium bis(fluorosulfonyl)imide (PYR₁₄FSI) was used as the electrolyte. Individually, these ILs show melting points of 6 °C (PIP₁₃FSI) and -18 °C (PYR₁₄FSI) (Figure 1A). The latter is consistent with already reported data.³⁰ The DSC curve of the mixture displays no peaks between -80 and 100 °C excluding the presence of first- or second-order phase transitions in this temperature range. Mixing PIP₁₃FSI with PYR₁₄FSI resulted in an IL with two different cationic species and only one anion (namely, (PIP₁₃FSI)_{0.5}(PYR₁₄FSI)_{0.5}), and having a liquid range lowered to -80 °C, which was the lowest measurable value with our apparatus. This confirms previously published studies on mixtures with common cations and anions

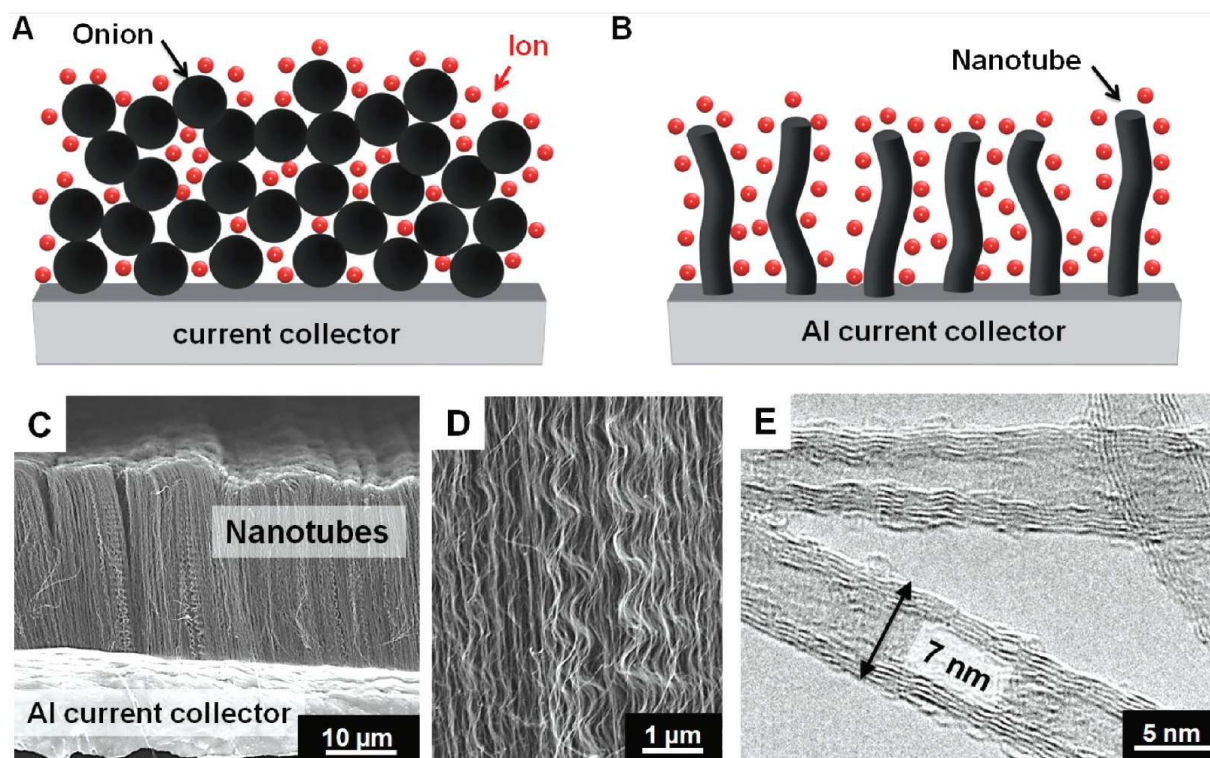


Figure 2. High-surface area exohedral electrode materials that only adsorb ions on their outer surface. (A) Schematic of a carbon onion electrode. (B) Schematic of a CNT electrode. (C) Scanning electron microscopy (SEM) image of the CNT electrode. (D) SEM image of CNT brush. (E) Transmission electron microscopy (TEM) image of individual CNTs.

that show that the crystallization process is mainly influenced by the anions.^{30,31} Our results demonstrate that selection of a proper combination of cations with the same anion prevents an ordered arrangement and crystallization, thereby inhibiting the formation of a lattice. The liquid state of the mixture can then be maintained several tens of degrees lower compared to ILs taken individually. Both ILs of this study have the same anion (FSI), same molecular weight, and same number of atoms of the same nature, and the only difference is their cation molecular structure, based on a five-member or six-member heterocycle, respectively, for pyrrolidinium and piperidinium (Figure 1A). We note that a similar behavior is observed for other cationic mixtures of ILs (Figure S1, Supporting Information).

Figure 1B depicts the Arrhenius plots of the PIP₁₃FSI, the PYR₁₄FSI, and the 1:1 IL mixture. Conductivity values of 28.9 mS/cm and 4.9 mS/cm were measured at 100 and 20 °C, respectively, for the mixture. The temperature dependence of the mixture follows the Arrhenius behavior down to -70 °C. This clearly shows the extended temperature range of ionic conductivity of the (PIP₁₃FSI)_{0.5}(PYR₁₄FSI)_{0.5} mixture compared to the single constituents, thus enabling its use at temperatures as low as -50 °C; however, devices operating at such low temperatures are expected to suffer from a reduced rate capability, whereas normal device operation will remain unaffected.

Using this eutectic IL mixture as the electrolyte in a supercapacitor cell assembled using a conventional high surface area porous activated carbon (1700 m²/g) as active material (see Figure S2, Supporting Information), resulted in very poor electrochemical performance below 0 °C, and the cyclic voltammograms (CVs) showed highly resistive behavior resulting from

poor accessibility of carbon pores to the ions. Figure S2 provides evidence that the electrode structure must be tailored to match the electrolyte if capacitive performance at low temperatures is required. To address ion transport limitations in nanometer pores of activated carbons, we used exohedral carbons, namely OLCs and multiwall nanotubes.³² Their external surface is fully ion accessible and exohedral carbon nanomaterials can therefore overcome ion transfer limitations and, depending on size and curvature, provide a way to increase the capacitance per unit of surface area.³³ Thus, the formation of the electrical double layer occurs exclusively on the outer surface of carbon nanoparticles and ion adsorption/desorption replaces ion transport into internal pore of carbon particles as the rate controlling mechanism (Figure 2A,B).

Vertically aligned carbon nanotube arrays (VA-CNT) were grown directly on aluminum foils via plasma-enhanced chemical vapor deposition (PECVD) in a cold wall reactor (AIXTRON Black Magic, see Supporting Information). This technique allows preparing supercapacitor electrodes in one step, since the supporting thin Al foil (10 μm) can be used directly as a current collector in a supercapacitor cell. Low-temperature CVD synthesis allows CNT growth directly on Al, which is a major advantage when considering that other technologies require high temperatures and limit the substrate choice to much heavier metals such as Ti, Ni, or steel, which also have lower electrical conductivity and narrower voltage stability windows.³⁴⁻³⁶ The resulting CNT density allows easy electrolyte access (Figure 2C), and obtained CNT films were homogeneous in thickness and tube density with the average intertube distance varying between tens and hundreds of nanometers (Figure 2D), as is typical for

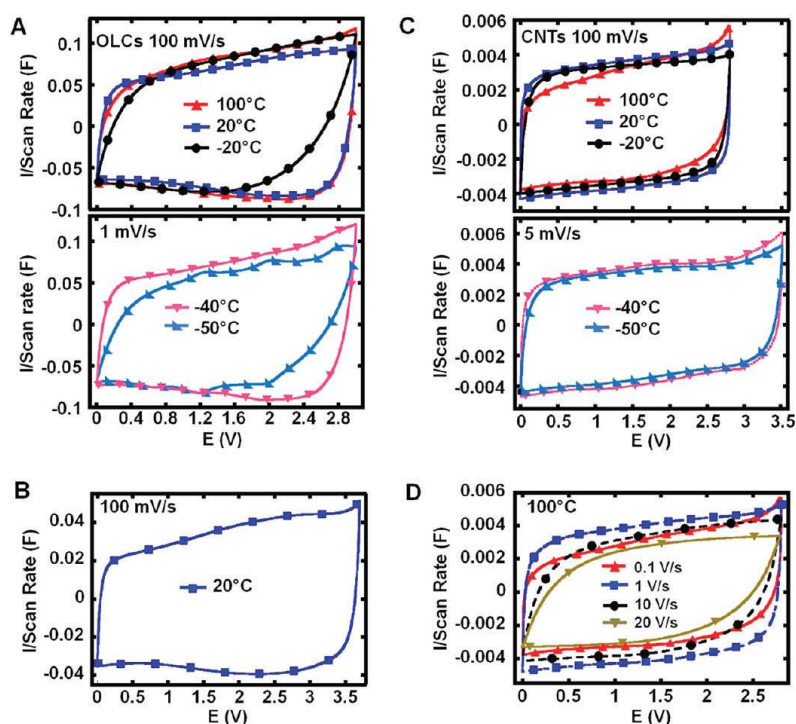


Figure 3. Cyclic voltammetry data. (A) CVs at temperatures from -40 to 100 °C for OLCs recorded at 100 and 1 mV/s, (B) CV at 20 °C and 100 mV/s for OLCs; OLC weight in panel B is 2.2 mg/cm². OLCs in the IL mixture show a large cell voltage of 3.7 V at room temperature. (C) CVs at temperatures from -50 to 100 °C at 100 mV/s for CNTs, and (D) CVs of CNTs at 100 °C and scan rates from 100 mV/s to 20 V/s.

such grown nanotubes.³⁷ The CNT diameters ranged between 5 and 10 nm with 4 – 7 carbon walls (Figure 2E). While there was a small residual amount of the iron catalyst (<0.5 wt% and <0.05 wt% respectively vs carbon and Al substrate weight), no binder or additive was required in manufacturing these electrodes. Such binder-free electrodes, with improved contact between the active material and the Al current collector, have a lower equivalent series resistance (ESR) and can be used at higher rates compared to binder-containing pressed powder electrodes.^{38,39} Carbon onions can be visualized as multishell fullerenes with concentric graphitic shells and the OLC electrodes consist of agglomerated nonporous particles (~ 5 nm) with a specific surface area of approximately 500 m²/g. Their synthesis⁴⁰ and use in supercapacitors at up to 100 V/s charge/discharge rates⁴¹ have been reported elsewhere. To obtain mechanically stable electrodes with ~ 200 μ m thickness, OLC was mixed with 5 wt % polytetrafluoroethylene (PTFE)³² and OLC loading was 5.5 mg/cm² (unless another weight is specified). CNT electrodes of 1.1 cm² were cut from AIXTRON electrodes. Both types of materials were tested in Swagelock cells⁴² using two layers of a 25 μ m thick porous alumina separator.

Electrochemical characterization of OLCs and VA-CNTs has been performed in a two-electrode setup. The CVs of OLC electrodes (Figure 3A) in the IL mixture exhibit a pure capacitive behavior as can be seen from the close-to-rectangular shape of the CV, where the Y-axes are expressed as F. However, more important is the large usable temperature range between -50 and 100 °C in which capacitive behavior is observed, with a maximum voltage up to 3 V. While the scan rate and, therefore, the power handling ability at very low temperature are reduced, it clearly defies the conventional wisdom stating that IL electrolytes cannot operate at all under such conditions. A 150 °C

temperature window for this IL mixture is far beyond the 100 °C temperature window for PC-based supercapacitors (-30 to 70 °C).

Besides varying scan rate ability as a function of the temperature, the usable voltage window is also sensitive to temperature. Higher temperatures, such as 100 °C (Figure 3A) limit the usable voltage range to 3 V, whereas room temperature operation enables a broader potential window of 3.7 V; that is, 1 V higher than used in current supercapacitors based on organic electrolytes. Since the energy density E is proportional to V^2 , ($E = 1/2 CV^2$, where C is capacitance), it is twice that of the organic electrolyte. For the OLC electrodes, when employing PC instead of the IL mixture, a maximum voltage window is 2.5 V at 100 °C and 3.2 V at room temperature, with a limited capacitive behavior and a modest capacitance at -40 °C (Figure S3).

Figure 3C shows CVs of VA-CNT electrodes. Thanks to the large intertube distance that enhances the electrochemical accessibility of the CNT surface to the ions, a low temperature of -50 °C could be reached while maintaining the capacitive behavior at faster potential scan rates (5 mV/s) than OLC electrodes. VA-CNT electrodes showed less dependence of the capacitance on the operation temperature, but the usable voltage window (2.8 V at 100 °C) was narrower, probably as a result of impurities (catalyst residue). At 100 °C, the capacitive behavior of VA-CNT electrodes was almost independent of the charge/discharge rate up to 20 V/s, thus demonstrating high power capabilities of this system (Figure 3D). Although shifted to higher resistance, the Nyquist plot of the VA-CNT cell recorded at -50 °C in the IL mixture shows remarkable capacitive behavior as can be seen from the sharp increase of the imaginary part at low frequency⁴³ (Figure S4A). The capacitance change with the potential scan rate was found to be remarkably stable,

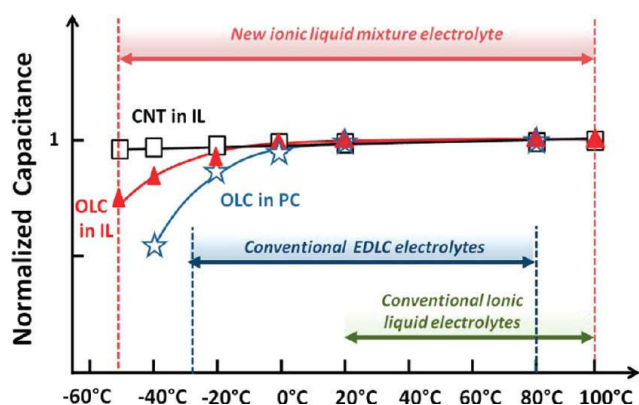


Figure 4. Normalized capacitance ($C/C_{20\text{ }^\circ\text{C}}$) for the OLC and VA-CNT electrodes in $(\text{PIP}_{13}\text{FSI})_{0.5}(\text{PYR}_{14}\text{FSI})_{0.5}$ IL mixture and PC + 1 M TEA-BF₄ electrolytes. Capacitances were calculated at 100 mV/s, except for the $-50\text{ }^\circ\text{C}$ (1 mV/s) and $-40\text{ }^\circ\text{C}$ (5 mV/s) experiments. This plot shows that the use of the IL mixture extends the temperature range for supercapacitors into the -50 to $100\text{ }^\circ\text{C}$ range while conventional electrolytes using PC as solvent are limited to the -30 to $80\text{ }^\circ\text{C}$ range. $C_{20\text{ }^\circ\text{C}}$ was 80 mF and 4 mF, respectively, for OLC and VA-CNT cells. All cells were cycled from 0 up to 2.8 V

with 60% of the low scan-rate capacitance being still delivered at 20 V/s (Figure S4B).

Figure 4 shows the change of capacitance versus the temperature for OLC and VA-CNT electrodes, calculated from cycling up to 2.8 V. When using 1 M TEA-BF₄ in PC as electrolyte with OLC electrodes, the temperature range was limited to $110\text{ }^\circ\text{C}$ (-30 to $80\text{ }^\circ\text{C}$) because of the capacitance drop at low temperatures and electrolyte oxidation at high temperature for cell voltage beyond 2.5 V, in agreement with commercial supercapacitors. The use of the $(\text{PIP}_{13}\text{FSI})_{0.5}(\text{PYR}_{14}\text{FSI})_{0.5}$ mixture in conjunction with OLC and VA-CNT electrodes extends the temperature range on both the low and high temperature sides. Such a wide temperature window of $150\text{ }^\circ\text{C}$ around room temperature has, to the best of our knowledge, never before been reported—especially not for IL-based ECs. Moreover, VA-CNT electrodes in a eutectic IL mixture show improved power performance in the same temperature range of -50 to $100\text{ }^\circ\text{C}$, thanks to the large accessible surface area, the binder-free electrode setup, and the improved carbon–metal interface as a result of the CVD process.

Although using a nonoptimized IL/carbon interface, these results show that a proper design of the carbon electrode structure in conjunction with an electrolyte formulation offers an opportunity for expanding the operation range of EES devices and adapting them for applications under extreme climatic conditions. Now that the long-held restriction of the ILs to energy storage applications above the room temperature has been lifted, the door is open for research that will optimize the carbon accessible surface area (e.g., by using activated graphene,¹³ debundled single-walled nanotubes,⁴⁴ or mesoporous templated carbons⁴⁵), the electrolyte viscosity and conductivity, pushing the temperature limits further, increasing the capacitance and energy density, and extending the applications of supercapacitors and accelerating the transition to “electrical economy” and wider use of renewable energy.

■ ASSOCIATED CONTENT

Supporting Information. Experimental procedures and additional results are included in the Supporting Information.

This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: simon@chimie.ups-tlse.fr.

Author Contributions

R.L. performed IL synthesis at Solvionic. R.L., P.L.T., and P.S. were involved in electrodes processing, cell assembly, electrochemical characterizations and conductivity measurements at different temperatures. VA-CNTs were made at Aixtron Laboratories by N.L.R. and K.B.K.T. Y.G. was involved in onion-like carbon synthesis and characterization. P.S., R.L., Y.G., C.R.P., and V.P. jointly wrote the paper.

■ ACKNOWLEDGMENT

R.L. was supported by a Ph.D. grant from Solvionic. Y.G. and C.R.P. were supported by the U.S. National Science Foundation under the International Collaborations in Chemistry Grant No. 0924570. V.P. acknowledges the financial support from the Alexander von Humboldt Foundation. P.S. and Y.G. would like to thank the Partner University Fund (PUF) for funding their collaborative efforts. N.L.R. and K.B.K.T. acknowledge funding from the EC project TECHNO-TUBES. The authors thank Jean-Francois Meunier (LCC laboratory) for his assistance with DSC measurements, John McDonough (Drexel University) for help with the synthesis of onion-like carbon, Dr. Junjie Niu (Drexel University) for TEM imaging, and Prof. A. Kornyshev (Imperial College) for helpful discussions on ionic liquids.

■ REFERENCES

- (1) Armand, M.; Tarascon, J. M. Building Better Batteries. *Nature* **2008**, *451*, 652–657.
- (2) Hung, K.; Masarapu, C.; Ko, T.; Wei, B. Wide-Temperature Range Operation Supercapacitors from Nanostructured Activated Carbon Fabric. *J. Power Sources* **2009**, *193*, 944–949.
- (3) Armand, M.; Endres, F.; MacFarlane, D. R.; Ohno, H.; Scrosati, B. Ionic-Liquid Materials for the Electrochemical Challenges of the Future. *Nat. Mater.* **2009**, *8*, 621–629.
- (4) Miller, J. R.; Simon, P. Materials Science - Electrochemical Capacitors for Energy Management. *Science* **2008**, *321*, 651–652.
- (5) Miller, J. M. Energy Storage System Technology Challenges Facing Strong Hybrid, Plug-in and Battery Electric Vehicles. *Vehicle Power Propul. Conf., 2009. VPPC '09. IEEE* **2009**, 4–10.
- (6) Conway, B. E. *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications*; Kluwer Academic/Plenum Publishing: New York, 1999.
- (7) Trasatti, S. Physical Electrochemistry of Ceramic Oxides. *Electrochim. Acta* **1991**, *36*, 225–241.
- (8) Ardizzone, S.; Fregonara, G.; Trasatti, S. “Inner” and “Outer” Active Surface of RuO₂ Electrodes. *Electrochim. Acta* **1990**, *35*, 263–267.
- (9) Simon, P.; Gogotsi, Y. Materials for Electrochemical Capacitors. *Nat. Mater.* **2008**, *7*, 845–854.
- (10) Brezesinski, T.; Wang, J.; Tolbert, S. H.; Dunn, B. Ordered Mesoporous α -MoO₃ with Iso-oriented Nanocrystalline Walls for Thin-Film Pseudocapacitors. *Nat. Mater.* **2010**, *9*, 146–151.
- (11) Levi, M. D.; Salitra, G.; Levy, N.; Aurbach, D.; Maier, J. Application of a Quartz-Crystal Microbalance to Measure Ionic Fluxes in Microporous Carbons for Energy Storage. *Nat. Mater.* **2009**, *8*, 872–875.
- (12) Miller, J. R.; Outlaw, R. A.; Holloway, B. C. Graphene Double-Layer Capacitor with ac Line-Filtering Performance. *Science* **2010**, *329*, 1637–1639.

- (13) Zhu, Y.; Murali, S.; Stoller, M. D.; Ganesh, K. J.; Cai, W.; Ferreira, P. J.; Pirkle, A.; Wallace, R. M.; Cychosz, K. A.; Thommes, M.; et al. Carbon-Based Supercapacitors Produced by Activation of Graphene. *Science* **2011**, *24*, 1537–1541.
- (14) Lu, W.; Hartman, R.; Qu, L.; Dai, L. Nanocomposite Electrodes for High-Performance Supercapacitors. *J. Phys. Chem. Lett.* **2011**, *2*, 655–660.
- (15) Yu, D.; Dai, L. Self-Assembled Graphene/Carbon Nanotube Hybrid Films for Supercapacitors. *J. Phys. Chem. Lett.* **2009**, *1*, 467–470.
- (16) Jang, I. Y.; Ogata, H.; Park, K. C.; Lee, S. H.; Park, J. S.; Jung, Y. C.; Kim, Y. J.; Kim, Y. A.; Endo, M. Exposed Edge Planes of Cup-Stacked Carbon Nanotubes for an Electrochemical Capacitor. *J. Phys. Chem. Lett.* **2010**, *1*, 2099–2103.
- (17) Dash, R.; Chmiola, J.; Yushin, G.; Gogotsi, Y.; Laudisio, G.; Singer, J.; Fischer, J.; Kucheyev, S. Titanium Carbide Derived Nanoporous Carbon for Energy-Related Applications. *Carbon* **2006**, *44*, 2489–2497.
- (18) Dzubiella, J.; Hansen, J. P. Electric-Field-Controlled Water and Ion Permeation of a Hydrophobic Nanopore. *J. Chem. Phys.* **2005**, *122*, 234706–234714.
- (19) Miller, J. R.; Burke, A. F. Electrochemical Capacitors: Challenges and Opportunities for Real-World Applications. *Interface* **2008**, *17*, 53–57.
- (20) Brandon, E.; Smart, M.; West, W. Low-Temperature Supercapacitors. *NASA Tech Briefs* **2008**, *32*, 32.
- (21) Torimoto, T.; Tsuda, T.; Okazaki, K.-i.; Kuwabata, S. New Frontiers in Materials Science Opened by Ionic Liquids. *Adv. Mater.* **2010**, *22*, 1196–1221.
- (22) Galinski, M.; Lewandowski, A.; Stepniak, I. Ionic Liquids As Electrolytes. *Electrochim. Acta* **2006**, *51*, 5567–5580.
- (23) Burke, A. Ultracapacitors: Why, How, and Where Is the Technology. *J. Power Sources* **2000**, *91*, 37–50.
- (24) Lazzari, M.; Mastragostino, M.; Pandolfo, A. G.; Ruiz, V.; Soavi, F. Role of Carbon Porosity and Ion Size in the Development of Ionic Liquid Based Supercapacitors. *J. Electrochem. Soc.* **2011**, *158*, A22–A25.
- (25) Arbizzani, C.; Biso, M.; Cericola, D.; Lazzari, M.; Soavi, F.; Mastragostino, M. Safe, High-Energy Supercapacitors Based on Solvent-Free Ionic Liquid Electrolytes. *J. Power Sources* **2008**, *185*, 1575–1579.
- (26) Balducci, A.; Dugas, R.; Taberna, P. L.; Simon, P.; Plée, D.; Mastragostino, M.; Passerini, S. High Temperature Carbon–Carbon Supercapacitor Using Ionic Liquid as Electrolyte. *J. Power Sources* **2007**, *165*, 922–927.
- (27) Lockett, V.; Sedev, R.; Ralston, J.; Horne, M.; Rodopoulos, T. Differential Capacitance of the Electrical Double Layer in Imidazolium-Based Ionic Liquids: Influence of Potential, Cation Size, and Temperature. *J. Phys. Chem. C* **2008**, *112*, 7486–7495.
- (28) Wei, D.; Ng, T. W. Application of Novel Room Temperature Ionic Liquids in Flexible Supercapacitors. *Electrochem. Commun.* **2009**, *11*, 1996–1999.
- (29) Lu, W.; Qu, L.; Henry, K.; Dai, L. High Performance Electrochemical Capacitors from Aligned Carbon Nanotube Electrodes and Ionic Liquid Electrolytes. *J. Power Sources* **2009**, *189*, 1270–1277.
- (30) Kunze, M.; Jeong, S.; Paillard, E.; Winter, M.; Passerini, S. Melting Behavior of Pyrrolidinium-Based Ionic Liquids and Their Binary Mixtures. *J. Phys. Chem. C* **2010**, *114*, 12364–12369.
- (31) Kunze, M.; Montanino, M.; Appetecchi, G. B.; Jeong, S.; Schönhoff, M.; Winter, M.; Passerini, S. Melting Behavior and Ionic Conductivity in Hydrophobic Ionic Liquids. *J. Phys. Chem. A* **2010**, *114*, 1776–1782.
- (32) Portet, C.; Yushin, G.; Gogotsi, Y. Electrochemical Performance of Carbon Onions, Nanodiamonds, Carbon Black and Multi-walled Nanotubes in Electrical Double Layer Capacitors. *Carbon* **2007**, *45*, 2511–2518.
- (33) Huang, J.; Sumpter, B. G.; Meunier, V.; Gogotsi, Y. G.; Yushin, G.; Portet, C. Curvature Effects in Carbon Nanomaterials: Exohedral versus Endohedral Supercapacitors. *J. Mater. Res.* **2010**, *25*, 1525–1531.
- (34) Gao, L.; Peng, A.; Wang, Z. Y.; Zhang, H.; Shi, Z.; Gu, Z.; Cao, G.; Ding, B. Growth of Aligned Carbon Nanotube Arrays on Metallic Substrate and Its Application to Supercapacitors. *Solid State Commun.* **2008**, *146*, 380–383.
- (35) Fang, W.-C.; Chyan, O.; Sun, C.-L.; Wu, C.-T.; Chen, C.-P.; Chen, K.-H.; Chen, L.-C.; Huang, J.-H. Arrayed CN_x NT-RuO₂ Nanocomposites Directly Grown on Ti-Buffered Si Substrate for Supercapacitor Applications. *Electrochem. Commun.* **2007**, *9*, 239–244.
- (36) Zhang, H.; Cao, G.; Yang, Y.; Gu, Z. Capacitive Performance of an Ultralong Aligned Carbon Nanotube Electrode in an Ionic Liquid at 60 °C. *Carbon* **2008**, *46*, 30–34.
- (37) Wei, S.; Kang, W. P.; Davidson, J. L.; Huang, J. H. Supercapacitive Behavior of CVD Carbon Nanotubes Grown on Ti Coated Si Wafer. *Diamond Relat. Mater.* **2008**, *17*, 906–911.
- (38) Talapatra, S.; Kar, S.; Pal, S. K.; Vajtai, R.; Ci, L.; Victor, P.; Shaijumon, M. M.; Kaur, S.; Nalamasu, O.; Ajayan, P. M. Direct Growth of Aligned Carbon Nanotubes on Bulk Metals. *Nat. Nanotechnol.* **2006**, *1*, 112–116.
- (39) Presser, V.; Heon, M.; Gogotsi, Y. Carbide-Derived Carbons – From Porous Networks to Nanotubes and Graphene. *Adv. Funct. Mater.* **2011**, *21*, 810–833.
- (40) Mykhaylyk, O. O.; Solonin, Y. M.; Batchelder, D. N.; Brydson, R. Transformation of Nanodiamond into Carbon Onions: A Comparative Study by High-Resolution Transmission Electron Microscopy, Electron Energy-Loss Spectroscopy, X-ray Diffraction, Small-Angle X-ray Scattering, and Ultraviolet Raman Spectroscopy. *J. Appl. Phys.* **2005**, *97*, 074302–16.
- (41) Pech, D.; Brunet, M.; Durou, H.; Huang, P.; Mochalin, V.; Gogotsi, Y.; Taberna, P.-L.; Simon, P. Ultrahigh-Power Micrometre-Sized Supercapacitors Based on Onion-Like Carbon. *Nat. Nanotechnol.* **2010**, *5*, 651–654.
- (42) Heon, M.; Lofland, S.; Applegate, J.; Nolte, R.; Cortes, E.; Hettinger, J. D.; Taberna, P.-L.; Simon, P.; Huang, P.; Brunet, M.; Gogotsi, Y. Continuous Carbide-Derived Carbon Films with High Volumetric Capacitance. *Energy Environ. Sci.* **2011**, *4*, 135–138.
- (43) Taberna, P. L.; Simon, P.; Fauvarque, J. F. Electrochemical Characteristics and Impedance Spectroscopy Studies of Carbon–Carbon Supercapacitors. *J. Electrochem. Soc.* **2003**, *150*, A292–A300.
- (44) Izadi-Najafabadi, A.; Yasuda, S.; Kobashi, K.; Yamada, T.; Futaba, D. N.; Hatori, H.; Yumura, M.; Iijima, S.; Hata, K. Extracting the Full Potential of Single-Walled Carbon Nanotubes as Durable Supercapacitor Electrodes Operable at 4 V with High Power and Energy Density. *Adv. Mater.* **2010**, *22*, E235–E241.
- (45) Kyotani, T.; Chmiola, J.; Gogotsi, Y. Carbide Derived Carbon and Templated Carbons. In *Carbon Materials for Electrochemical Energy Storage Systems*; Beguin, F., Frackowiak, E., Eds.; CRC Press/Taylor and Francis: Boca Raton, FL, 2009; pp 77–113.