Low Temperature Double-Layer Capacitors With Improved Energy Density: An Overview of Recent Development Efforts

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Abstract: Electrochemical double-layer capacitors are finding increased use in a wide range of energy storage applications, particularly where high pulse power capabilities are required. Double-layer capacitors store charge at a liquid/solid interface, making them ideal for low temperature power applications, due to the facile kinetic processes associated with the rearrangement of the electrochemical double-layer at these temperatures. Potential low temperature applications include hybrid and electric vehicles, operations in polar regions, high altitude aircraft and aerospace avionics, and distributed environmental and structural health monitoring. State-of-the-art capacitors can typically operate to -40°C, with a subsequent degradation in power performance below room temperature. However, recent efforts focused on advanced electrolyte and electrode systems can enable operation to temperatures as low as -70°C, with capacities similar to room temperature values accompanied by reasonably low equivalent series resistances. This presentation will provide an overview of recent development efforts to extend and improve the wide temperature performance of these devices.

Keywords: Supercapacitors, ultracapacitors, double-layer capacitors, low temperature electrolytes, zeolite templated carbons.

Introduction

Supercapacitors form a class of unique energy storage devices that store charge either purely at an electrochemical double layer (double-layer capacitor), or through partial charge transfer to an electrochemically active electrode (pseudo-capacitor) [1]. The maximum operating voltage is set by the electrochemical window of the electrolyte solvent, and is typically not greater than 2.8V. These designs can also be combined with a battery-like intercalation electrode (such as lithium titanate) to form an asymmetric or hybrid capacitor. Due to the nature of this electrode system, wider operating voltages are possible. Pure double-layer capacitors behave similarly to a traditional electrolytic capacitor with a voltage that varies as a function of state of charge, whereas pseudo-capacitors and hybrid capacitors typically display a more complex, battery-like discharge with a flatter voltage profile vs. discharge time.

Double-layer capacitors are of great interest for power applications due to their high specific energies (5 Wh/kg) relative to electrolytic capacitors, high specific power levels (>1 kW/kg) and long cycle life (up to 10^6 charge/discharge cycles) [1]. A particularly favorable attribute unique to double-layer capacitors is their ability to operate at relatively low temperatures (down to -40°C for commercially available cells). This exceptional performance occurs since charge is stored at a liquid/solid interface, rather than through Faradaic charge transfer as occurs in batteries. The rates of these Faradaic processes can be highly temperature dependent, whereas charging and discharging double-layer capacitors only involves rearrangement of the electrochemical double-layer.

One of the main issues hampering even lower temperature operation is the lack of electrolytes with a suitably wide liquid range. Over the last several years, the Jet Propulsion Laboratory (JPL) has developed electrolytes capable of supporting double-layer capacitor operation to below -70°C [2-5]. Another aspect of designing double-layer capacitors for low temperature operation is optimization of the electrode structure for storing maximum charge and delivering maximum power at these temperatures. JPL electrolytes have been evaluated using advanced zeolite

template carbon (ZTC) electrodes developed at Georgia Tech. Using the low temperature electrolytes in combination with these advanced electrodes, the performance of these materials at -70°C rivals that of commercially available materials and cells at room temperature.

Electrolyte design

Standard double-layer capacitors typically employ an organic electrolyte such as acetonitrile (AN) or propylene carbonate (PC). A quaternary ammonium compound, such as tetraethylammonium tetrafluoroborate (TEATFB), is usually chosen as the electrolyte salt, based on the relatively high solubility in organic solvents and high electrochemically stability. The high melting points of AN (-45°C) and PC (-55°C) preclude their use at very low temperatures. Furthermore, the high viscosity of PC results in poor performance below room temperature, due to an increase in the equivalent series resistance (ESR) of the capacitor. Even AN-based cells display a significant increase in ESR below 0ºC.

Finding a single solvent that meets the requirements of a low temperature double-layer capacitor electrolyte is challenging. Two key solvent parameters influencing the suitability of solvents for low temperature operation are the melting point and the dielectric constant. Ideally, a solvent would possess a melting point well below the lowest desired operating temperature. Furthermore, a high dielectric constant is required to maximize salt solubility (and achieve a high ionic conductivity), which is typically reduced at low temperature relative to room temperature. Fig. 1 depicts the dielectric constant of several solvent systems appropriate for electrochemical cells as a function of the solvent melting point.

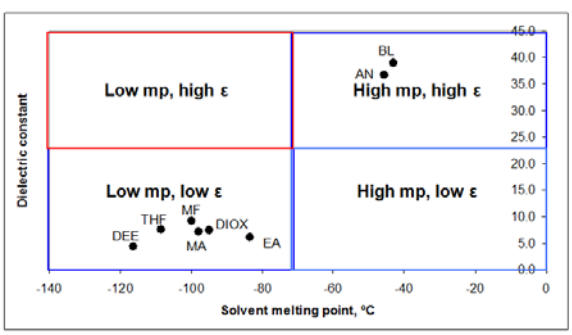

Figure 1. Dielectric constant vs. solvent melting point for candidate electrolyte solvents (AN=acetonitrile; BL=gamma butyrolactone; DEE=diethyl ether; THF=tetrahydrofuran; MF=methyl formate; MA=methyl acetate; DIOX=1,3-dioxolane; EA=ethyl acetate)

The ideal combination of attributes for such a solvent would fall in the upper left quadrant of the plot, wherein the solvent features a low melting point and high dielectric constant. However, most appropriate solvents tend to feature a combination of high melting point/high dielectric constant or low melting point/low dielectric constant, as seen in Fig. 1.

One strategy to address this limitation is to employ solvent blends, starting with the common single solvent electrolyte systems and adding lower melting point co-solvents, to extend the low temperature limits of these electrolytes. To guide the selection of appropriate co-solvents, it is critical to again examine key solvent parameters such as melting point, viscosity and dielectric constant. A few of these parameters are listed in Table 1.

Table 1. Key solvent parameters for representative single solvent and blended solvent systems.

Solvent	Melting Point (°C)	Dielectric Constant (ε)	Viscosity (cP)
Acetonitrile (AN)	-45.7	37.5	0.345
Methyl formate (MF)	-100	8.5	0.319
1,3-dioxolane (DIOX)	-95	7.3	0.6
3:1 AN:DIOX	-67.9	27.1	Not measured
1:1 AN:DIOX	-85.7	19.3	Not measured

A specific example illustrating this strategy of solvent design is illustrated in Fig. 2, where a 1:1 by volume (50:50 vol/vol%) blend of AN and 1,3-dioxolane (DIOX) are mixed. DIOX was chosen for its electrochemical stability, its low melting point and its low viscosity. Fig. 2 depicts heat flow vs. temperature for this solvent blend, as reflected in the differential scanning calorimetry (DSC) thermogram. The DSC data were collected using a sealed pan placed in a flow of argon. The peak occurs at the solvent mixture's melting point.

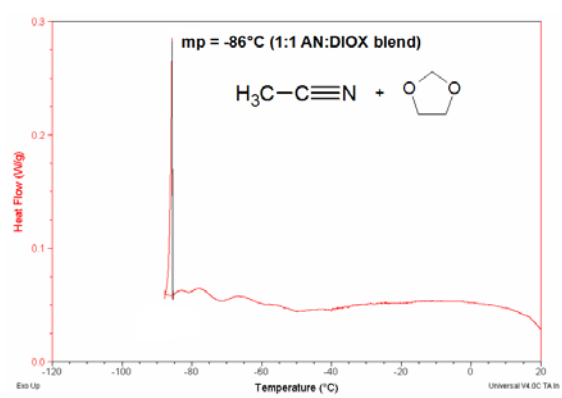

Figure 2. Differential scanning calorimetry (DSC) data for a 1:1 (50:50 vol/vol%) solvent blend of AN and DIOX.

The resulting mixture displays a melting point of -86ºC, 40°C lower than pure AN. As seen in Table 1, there is trade-off in key solvent parameters as the AN/DIOX ratio

is increased. At a higher AN content, the dielectric constant of the blend is higher. Increasing the DIOX content suppresses the melting point to a greater extent, but at the sacrifice of a reduced dielectric constant. In general, selection of the ideal ratio of solvent to co-solvent is guided by the lowest desired operating temperature. Then, the salt concentration must be tuned to achieve full solubility over this temperature range.

Addition of TEATFB results in an electrolyte which still exhibits appreciable conductivity down to -65°C. Electrolyte ionic conductivity data (measured in a standard conductivity cell under argon) as a function of temperature are shown in Fig. 3 for three different 1:1 AN:DIOX electrolyte formulations at three different TEATFB concentrations. Other more complex salts, such as spiro-(1,1')-bipyrrolidinium tetrafluoroborate (SBP-BF_4), were found to yield high conductivity at low temperatures, when used with these modified solvent blends [5].

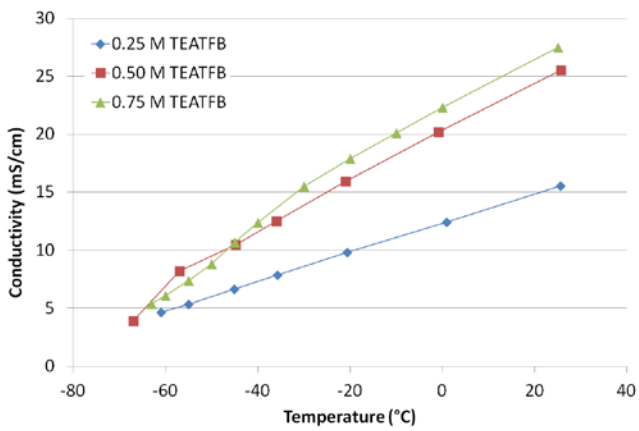

Figure 3. Conductivity of bulk electrolyte samples vs. temperature for three different TEATFB concentrations of 1:1 AN:DIOX.

Cell testing with high surface area carbon electrodes

As indicated earlier, to maximize power delivery of double-layer capacitors at low temperature, it is crucial to maintain a low ESR. To evaluate the ESR of double-layer capacitors using these modified electrolyte systems, coin cells were fabricated and tested using electrochemical impedance spectroscopy (EIS) down to -65°C. The configuration of the coin cells is depicted in Fig. 4. High surface area activated carbon electrodes from Material Methods (PACMM203, ~1300 m^2/g) were typically used in conjunction with a Tonen polyethylene separator. Cell assembly was performed in an inert atmosphere glovebox. Initial direct current charging tests indicated a capacitance of ~0.9 F for these cells, as extracted from the slope of the voltage vs. discharge time curve. EIS data were collected over the frequency range of 100 kHz to 10 mHz using a Princeton Applied Physics VMP2 instrument (using an excitation amplitude of 20 mV). The ESR was determined as the real component of the impedance (where the imaginary component was zero).

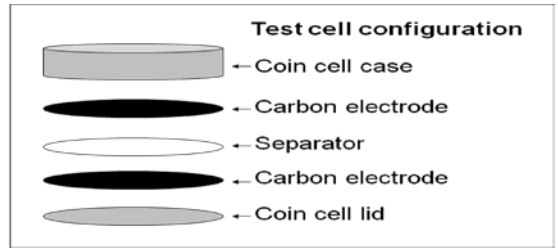

Figure 4. Configuration of coin cells used for evaluating low temperature electrolyte systems.

As seen in Fig. 5, the ESR of 0.250 M and 0.500 M TEATFB in 1:1 AN:DIOX electrolytes is low down to -65°C. The 0.750 M system, however, increases at approximately -35°C. This is due to a reduction in solubility at these temperatures, which causes the salt to precipitate into the pores of the high surface area electrode. Research is ongoing to develop and optimize electrolyte systems which maintain low ESR at higher salt concentrations.

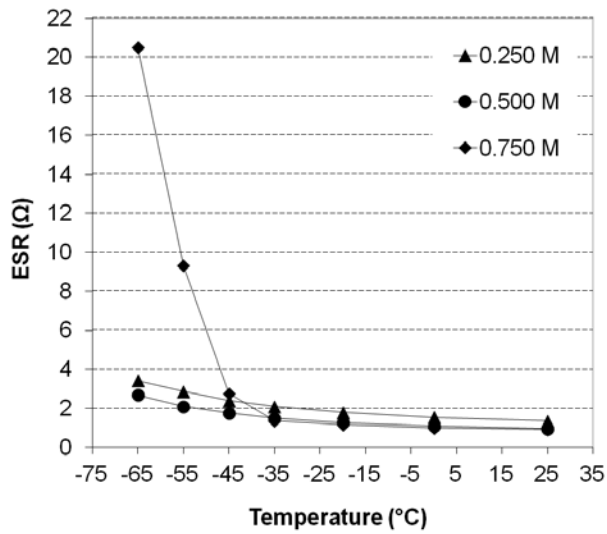

Figure 5. ESR vs. temperature (coin cells) for three different 1:1 AN:DIOX formulations, at three different TEATFB concentrations.

Initial testing of solvents has also been conducted in full scale double-layer capacitor cells. Initial evaluation of an advanced low temperature electrolyte in an MC650P cell using constant current testing at -70°C and three different currents is shown in Fig. 6. These data indicate a very linear voltage vs. discharge time profile and a capacitance of 500 F at this low temperature. Further testing is continuing over a wider range of voltages and cycles.

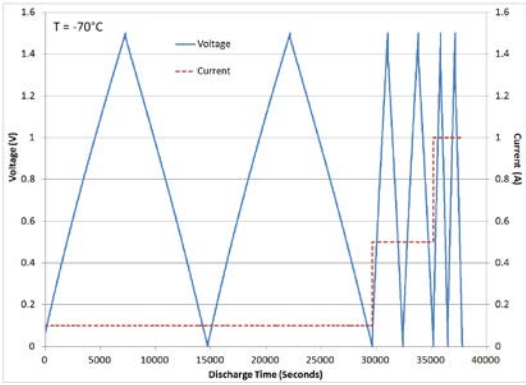

Figure 6. Testing at -70°C for a double-layer capacitor (MC650P cell) using low temperature electrolyte.

Advanced electrode materials

The initial results reported above indicate the great promise double-capacitors have for low temperature operation [2-4]. The focus of these early studies at JPL was to lower the operational temperature of the electrolyte, to depress the melting point of the solution and to ensure adequate solubility of the salt at low temperature. This approach enabled operation to temperatures below -70°C.

The next step in the development of low temperature double-layer capacitors was the optimization of the electrode structure for maximum capacity and power delivery at these temperatures [5]. The prior studies typically utilized high surface area activated carbon/binder electrodes. Recent work by Georgia Tech, however, has shown that micro-porous carbide-derived carbons, such as zeolite-templated carbons (ZTC), provide for not only high surface area, but straight, ordered and interconnected micropores for improved ion transport [6]. An example of one of these ZTC materials is shown in the scanning electron microscopy (SEM) micrograph in Fig. 7.

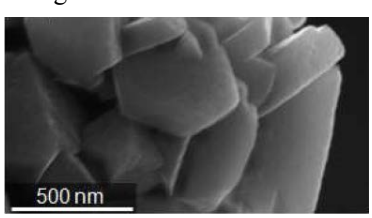

Figure 7. SEM micrograph of ZTC powder electrode material.

These electrode materials were evaluated in test cells using a 0.5 M SBP-BF_4 in 1:1 AN:MF electrolyte. As seen in Fig. 8, a specific capacitance of up to 120 F/g is observed at -60°C. This is higher than the room temperature specific capacitance observed for electrodes used in most commercially available cells (typically 75 F/g).

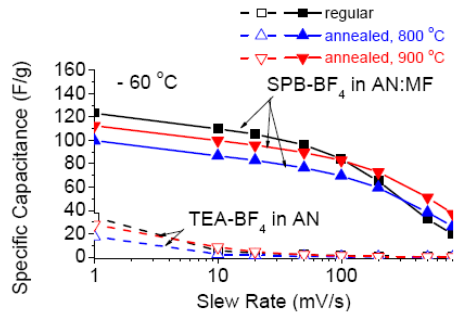

Figure 8. Specific capacitance vs. slew rate for several different ZTC, using low temperature electrolytes.

Conclusions

Through careful design of both the electrolyte and electrodes, the operation of double-layer capacitors has been extended beyond the typical rated limited for commercially available cells of -40°C, to below -70°C. Work is continuing to improve the electrolyte and electrode materials, for maximum power delivery and cycle life.

Acknowledgments

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References

1. B.E. Conway, *Electrochemical Supercapacitors,* Kluwer Academic/Plenum, New York, 1999.
2. Brandon, E.J., West, W.C., Smart, M.C., Whitcanack, L.D. and G.A Plett., "Extending the Low Temperature Operational Limit of Double-layer Capacitors," *J. Power Sources,* Vol. 170, pp.225-232, 2007.
3. West, W.C., Smart, M.C., Brandon, E.J., Whitcanack, L.D. and G.A. Plett, "Double-layer Capacitor Electrolyte Using 1,3-Dioxolane for Low Temperature Operation," *J. Electrochem. Soc.,* Vol. 155, pp. A716-A720, 2008.
4. US Patent 8081418, "Low Temperature Double-Layer Capacitors", Dec 20, 2011.
5. Korneblit, Y., Kajdos, A., West, W.C., Smart, M.C., Brandon, E.J., Kvit, A., Jagiello, J. and G. Yushin, "Electrochemical Studies of Dual-Solvent Supercapacitors involving Microporous Electrodes at Ultra-Low Temperatures," *Adv. Ener. Mater.* online, 2012, doi: 10.1002/adfm.201102573.
6. J. Chmiola, J, Yushin, G., Gogotsi, Y., Portet, C., Simon, P. and P.L. Taberna, "Anomalous Increase in Carbon Capacitance at Pore Sizes Less Than 1 Nanometer," *Science*, Vol. 313, no. 5794, pp. 1760-1763, 2006.