Improved Low Temperature Performance of Supercapacitors

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Supercapacitors bridge the gap between high specific energy batteries and high specific power ceramic and electrolytic capacitors. Double-layer capacitors can provide ~5 Wh/kg and >1 kW/kg over thousands of cycles with little degradation in performance.[1] Recent work has focused on increasing the energy density of supercapacitors, through the incorporation of higher energy density intercalation electrodes (i.e., asymmetric or lithium-ion supercapacitors).

Supercapacitors also offer the capability to charge and discharge at low temperatures. Commercially available supercapacitors are often rated for use to -40°C. Operation beyond this limit is largely limited by the melting point of the acetonitrile or propylene carbonate based electrolytes systems often used.

Recent work at the Jet Propulsion Laboratory (JPL) has demonstrated that double-layer capacitors can be charged and discharged down to -80°C, through the use of activated carbon electrodes and modified acetonitrile electrolyte blends designed for low temperature operation.[2,3] Further increases in capacity can be achieved using these electrolytes in conjunction with zeolite-templated carbon electrodes.[4,5] These electrolyte systems are being adopted in to larger format cells.[6]

Many potential applications of low temperature supercapacitors are mass sensitive, so there is a continuing interest in improving the specific energy of this technology. These applications include space-based avionics systems, more and all electric airplanes and unmanned aerial vehicles, as well as electric and hybrid-electric vehicles. One approach to improving specific energy at the cell level is to couple these modified electrolyte systems with an asymmetric cell configuration. Further progress in reducing equivalent series resistance (ESR) at low temperatures is also desired, to maintain the maximum power delivery capability.

Research at JPL has focused on further reducing the ESR of double-layer capacitors at low temperature using new solvent blends, as well as the improvement of cell specific energy using an asymmetric cell format. These cells feature an activated carbon electrode, combined with a lithium titanate ($Li_4Ti_5O_{12}$) electrode.

In place of the traditional quaternary ammonium salt based electrolytes used in double-layer capacitors, lithium hexafluorophosphate-based systems were used. To enable operation at low temperature, methyl propionate and methyl butyrate were blended with ethylene carbonate/ethyl methyl solvent systems. These blends have been successfully used in lithium ion battery systems,[7-9] and were similarly demonstrated to enable charging and discharging of asymmetric supercapacitor test cells below -40°C.

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1. A. Burke and M. Miller, 21st International Seminar on Double Layer Capacitors and Hybrid Energy Storage Devices, Deerfield Beach, FL, Dec. 5, 2011.
2. E.J. Brandon, W.C. West, M.C. West, L.D. Whitcanack and G.A. Plett, *J. Power Sources*, **170**, 225 (2007).
3. W.C. West, M.C. Smart, E.J. Brandon, L.D. Whitcanack and G.A. Plett, *J. Electrochem. Soc.*, **155**, 716 (2008).
4. Y. Korneblitt, A. Kajdos, W.C. West, M.C. Smart, E.J. Brandon, A. Kvit, J. Jagiello, G. Yushin, *Adv. Ener. Mater.* **22**, 1655 (2012).
5. E.J. Brandon, W.C. West, M.C. Smart, G. Yushin, Y. Korenblit, A. Kajdos, A. Kvit and J. Jagiello, 45th Power Sources Conference, Las Vegas, NV, June 14, 2012.
6. E. Iwama, P.L. Taberna, P. Azais, L. Brégeon P. Simon, *J. Power Sources*, **219**, 235 (2012).
7. M. C. Smart, B. V. Ratnakumar, K. B. Chin, and L. D. Whitcanack, *J. Electrochem. Soc.*, **157 (12)**, A1361-A1374 (2010).
8. M. C. Smart, B. L. Lucht, S. Dalavi, F. C. Krause, and B. V. Ratnakumar, *J. Electrochem. Soc.*, **159 (6)**, A739-A751 (2012).
9. M. C. Smart, B. V. Ratnakumar, M. R. Tomcsi, M. Nagata, V. Visco, and H. Tsukamoto, 2010 Power Sources Conference, Las Vegas, NV, June 16, 2010.