Project title: 
Supercapacitors for Energy Harvesting Applications

Team Members: 
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Statement of the Project Goals:
The primary goal of this project is to develop high energy density supercapacitors enabled by nanomaterials innovation for low power energy harvesting applications. The fabricated capacitors will have low leakage current and self-discharge performance and will be integrated in the Gen I & II testbed demonstrations.

Project’s Role in Support of the Strategic Plan: 
The project has currently led to the development of three different capacitor technologies that have very low leakage performance (100 – 200 nA). Low leakage electrical double layer capacitors fabricated in our lab has been incorporated and tested in Gen I testbed systems by Ben Calhoun’s group in University of Virginia. The capacitors could be charged both externally as well as through the boost converter storing harvested energy from solar. The capacitors demonstrated low leakage and were able to sustain the charge and voltage levels for a long period (~hrs) and worked well at low discharge currents in active/standby modes. We have also reported a 1F lithium ion capacitor capable of operating at 4.0V with leakage current as low as 100 – 200 nA with energy density of 250 J/cc, which was considered very impressive by the industrial board members. The fabricated capacitors have been independently tested by Tyco Inc., an ASSIST member, who have verified low leakage performance and have expressed interest in further exploring the use of these capacitors in their developmental efforts.

Discussion of Fundamental Research, Educational, or Technology Advancement Barriers and the Methodologies Used to Address Them: 
Our electrochemical capacitor research addresses two fundamental problems with electrochemical capacitors that include improving energy density and self-discharge characteristics. Both properties are determined by the nature of electrode materials, interaction at electrode/electrolyte interfaces and electrolyte properties. In previous years, we have shown that development of nanoporous carbon electrode materials with narrow pore size distribution (~ 1 nm) and high purity (< 1 atomic% oxygen) widened the electrochemical window by suppressing solvent decomposition reactions. We demonstrated that it was possible to fabricate double layer capacitors using organic electrolyte (1M tetraethylammonium hexafluorophosphate in propylene carbonate) with cell voltage as high as 3.5V and excellent cyclability [1]. The same carbon electrodes when combined with lithium based electrolytes showed good electrochemical stability upto 4.8V vs Li/Li⁺ [2]. This year, we have addressed the issue of self-discharge, which have three main contributions that include leakage current, solvent decomposition reactions and charge redistribution at porous electrodes. The leakage current and solvent decomposition reactions can be suppressed by designing high purity electrodes and this way, we were able to reduce the leakage current to almost 220 nA as shown in Figure 1.
Addressing the issue of charge redistribution required engineering the porosity of the carbon electrodes. Typical double layer carbon electrodes can have a range of porosity ranging from 0.8 nm to 5 nm. When the carbon electrodes are fully charged, the capacitance is fully realized due to the effective utilization of electrical double layer formed at very small pores (< 1 nm). However, during self-discharge process, there could be charge redistribution due to self-diffusion processes that lead to ion desorption from smaller pores into larger pores leading to loss in capacitance. We suppressed this effect by using carbon materials with narrow pore size distribution centered around 1 nm as electrode materials. Two different nanoporous carbon materials, namely a coconut char derived carbon as well as polyfurfuryl alcohol derived carbon were identified as promising materials to design low leakage capacitors [3]. In the case of lithium ion capacitors, we also came up with a unique design to prelithiate graphite in a controlled manner in order to use it as a negative electrode [3]. The fabricated capacitors showed leakage characteristics which were almost 5 – 10 times lower than current commercial capacitor technologies with similar capacitances making them ideally suitable for low power energy harvesting applications. Capacitors capable of being charged using low currents (5 – 10 µA) and capable of being discharged at higher currents in the order of 1 – 2 mA were fabricated. These capacitors have also been tested by Ben Calhoun’s group at University of Virginia and incorporated in Gen I testbed demonstration. A 1F Lithium ion capacitor operable at 4V with 10% self-discharge over two months, which is quite unprecedented for most electrochemical capacitors was also demonstrated. Our results have also been independently verified by Tyco Inc. In addition to synthesizing novel materials and designing capacitors, we have also developed a physicochemical model that can describe charging and self-discharge characteristics and provide valuable insights into mechanisms that control double layer characteristics, interfacial resistances and parasitic reactions as shown in Figure 2.
Foreign Collaborations: None

Achievements in Year 3 and Previous Years:

Previous years accomplishments: (1) Developed nanomaterials and fabricated high energy density (~250 J/cc) electrochemical capacitors with good cyclability (> 1000 cycles). (2) Three capacitor technologies that include 3.5V organic EDLC, 4.8V Lithium ion capacitor and all solid state ultrahigh power carbon nanotube based capacitor were developed [1-5] (3) Capacitors were capable of lighting an LED for almost an hour [6].

Past year accomplishments:
- Leakage current (~ 100 – 200 nA) was achieved for organic EDLC and Lithium ion capacitor,
- Energy density of 250 J/cc was achieved for lithium ion capacitor
- Lithium ion capacitors charged to 4V demonstrated 10% self-discharge over 2 months
- Organic EDLC have been successfully tested and incorporated for Gen I testbed demonstration
- Low leakage characteristic of Lithium ion capacitor has been verified by Tyco Inc.

Plans for the Next Year:
(1) Reduce the ESR of low leakage capacitors by 1-2 orders of magnitude in order to support wide range of load currents (µA – mA) for testbed demonstrations,
(2) Boost the energy density of electrochemical capacitors to 500 J/cc

Expected Milestones and Deliverables for the Project:
- Develop capacitor technologies with time constant in the range of 1 - 10 s and leakage current < 100 nA and capacitance of 1F.
- Enhance energy density of capacitors to 500 J/cc with target cell capacitance of 150 F/g
- Extend the application of capacitors to testbed demonstrations that include thermoelectric and piezoelectric energy harvesters

Member Company Benefits: Tyco Inc. is interested in testing the developed low leakage lithium ion capacitor technologies for their application.
References: