

Novel development of Li-ion hybrid capacitors through oxygen species manipulation and passivation of surface active sites on carbon-based electrodes for application in electric vehicles

A. Project Overview and Specific Aims

Increased global demands for electric vehicle (EV) production require more efficient, cost effective and environmentally friendly methods of energy storage. The key questions/challenges associated with the scientific problem of long-term EV production needs are the following: What electrode materials offer low cost, sustainable feedstock while providing both power and high energy density capability at low-weight cost? What surface micro and nanostructure will provide the highest resistance-free electrochemical accessibility of the substrate, while simultaneously preventing the breakdown of the electrode upon extensive cycling of the cell?

Carbon nanotube composite Li-ion batteries and carbon powder-based Li-ion capacitors offer improvements in all these areas over costly heavy metal batteries (e.g., LiCoO_2) and pseudocapacitors. However, improvements to carbon electrode materials are needed to achieve the highest possible charge storage, conductivity and working life for both battery and capacitor components. The precise tuning of surface features for both types of electrode components can yield stable working potential windows and achieve power/energy density balance for use as low-weight, hybrid battery-type capacitors, as displayed with the Ragone plot in Figure 1A. Combinations of these electrode types (Figure 1B) are being developed in the form of asymmetric supercapacitors (1–7). Such a cell combines a reversible, faradaic rechargeable battery electrode (e.g., Li-doped graphitic carbon; Figure 1B—negative electrode) with a double-layer, activated carbon (supercapacitor) electrode (Figure 1B—positive electrode). The energy storage devices can theoretically meet the needs of fully electric vehicles that require extended power output for acceleration and high specific energy densities for long periods of travel. Carbon gas-diffusion-electrodes have shown drastic increases in capacity when using surfactants to free -up pore-impeding precipitates that form during charging/discharging (8,9). In a similar manner, the methodology presented illustrates how preliminary degrees of oxidation treatment facilitate charge storage and coordinate surfactant to the most active surface sites—drastically increase the carbon electrode loading capacity as well as the electrochemical accessibility of capacitor-type electrodes.

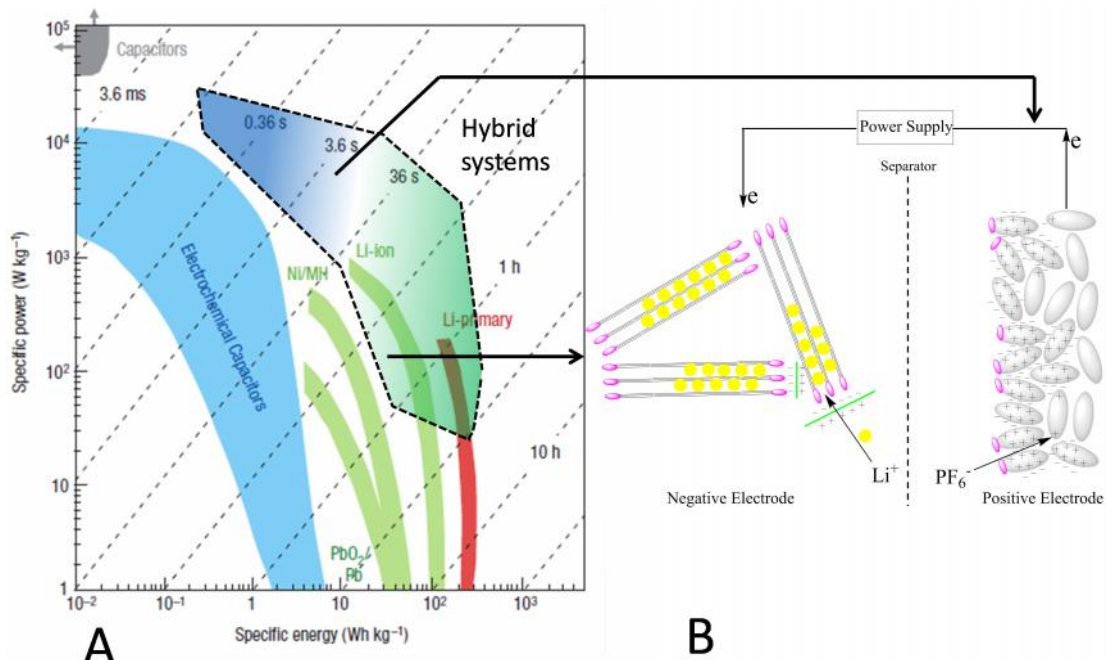


Figure 1. (A) Ragone plot showing specific power vs specific energy. Blue/Green area enclosed by dashed line represents area of electrochemical advancement for hybrid systems proposed. Time constants displayed are obtained by dividing the energy density by the power. Originally adapted from (10). **(B)** Illustration of proposed Li-ion asymmetric supercapacitor during charge cycle. Magenta orbs represent chemically adsorbed surfactant on carbon particle edge sites. Adapted from (1,2)

This proposal outlines techniques into improving the performance of carbon based electrode materials by examining both the effects of carbon surface oxidation and passivation via *in-situ* temperature programmable desorption-mass spectrometry (TPD-MS) and X-ray photoelectron spectroscopy (XPS) and *ex-situ* Diffuse Reflectance Fourier Transform Spectroscopy (DRIFTS). Furthermore, *ex-situ* characterization on surfactant-doped, post-cycled carbon electrodes will allow for re-engineering opportunities of the solid electrolyte interphase (SEI) layer, enabling the maximum capacity of battery electrode components through increasing the electrochemically accessible surface area. In a similar fashion, the oxygen specie manipulation combined with thermal hydrogenation and surfactant passivation techniques can significantly increase both the electrochemical accessibility and improve the degree of graphitization comprising capacitor materials—allowing for tunability of both conductive and electrostatic charge storage ability of capacitor electrodes. In addition, the carbon nanotube oxygen-specie-determined battery electrode will also provide a surface structure that facilitates a more effective dispersion of low-cost oxide materials (e.g., iron-oxide), as well as other increased rate performance cathode materials (e.g., S-F co-doped LiFePO_4) as previously outlined by Ban *et. al.* (11–13) This proposal defines methodology for enabling an increase in the bulk performance of hybrid battery-type capacitor devices in an environmentally-sustainable, cost-effective fashion. The specific aims of this research proposal are as follows:

- **Addition and Characterization of SOGs by TPD-MS, XPS and DRIFTS:**

This aim determines a method of creating a consistent population of surface oxygen groups (SOGs) (14–26). Different carbon powder, granule and nanotube source material combined with several liquid and

gaseous oxidation treatments are used to produce a wide array of SOG species and quantities, resulting in diverse source material for subsequent characterization. Figure 2 displays common SOGs observed on carbon surfaces.

Specifically, these oxidizing agents are known to create consistent Lewis-basic SOGs (20,31–33). Lewis-Basic SOGs (decompose >700C) offer added stability in preserving the original state of its redox sites, in comparison to proton-losing Acidic groups (<700C). The addition of exclusively Basic-type SOGs on the carbon surface is one dominant factor in producing economical, long-lasting battery-type electrodes that can experience a high number of charge and discharge cycles without breaking down due to surface exfoliation. The SOG population as a function of oxidant used and oxidation duration will be quantified using *in-situ* TPD-MS and XPS, as well as *ex-situ* DRIFTS.

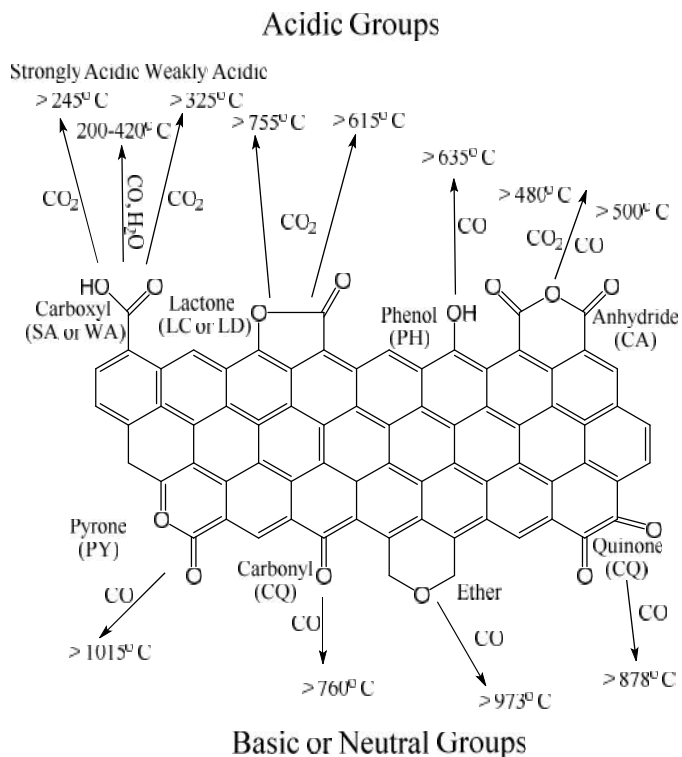


Figure 2. Decomposition products of specific surface oxygen groups as specified by temperature and evolved species (Adapted from REFS (14,15,27–30)).

- **Selective SOG Desorption and Control of ASA through Hydrogen Passivation:**

This aim determines consistent methods for the selective removal of SOGs using TPD. TPD-MS is used to both thermally remove and quantify individual SOGs(14,19,27–30,34–36). Surface oxygen groups on carbon materials decompose into CO₂, CO and H₂O upon heating and are measured by the mass spectrometer. Figure 2 displays various surface oxygen groups with their decomposition temperatures and species. It is well known that CO₂ evolves at low temperatures as a consequence of acidic group decomposition (carboxylic groups, anhydrides and lactones). CO evolves at higher temperatures, originated from the decomposition of acidic, basic and neutral groups (phenols, ethers, quinones, pyrones and carbonyls). H₂O evolves from carboxylic and anhydride functionality at relatively low temperatures. The most reactive active surface area (ASA) created from the removal of SOGs are then neutralized through the application of molecular hydrogen. Controlled application of hydrogen at low range temperatures will allow determination of the overall reactivity of molecular hydrogen with both ASA and remaining SOGs and hone in on appropriate passivation parameters. SOGs are further maintained by neutralizing newly created ASA resulting from incremental SOG removal. In the past, reaction of molecular hydrogen with ASA and SOGs has been characterized with regard to temperature(31,37–42). Figure 3 illustrates a number of the SOGs present on an oxidized carbon surface with respective temperatures of selective desorption, and subsequent Hydrogen passivation of ASA sites. As illustrated, particular SOGs can be eliminated by ramping to their corresponding desorption

temperatures. Upon passivation, the carbon material is further characterized via XPS and DRIFTS. The stable changes in surface composition are quantified.

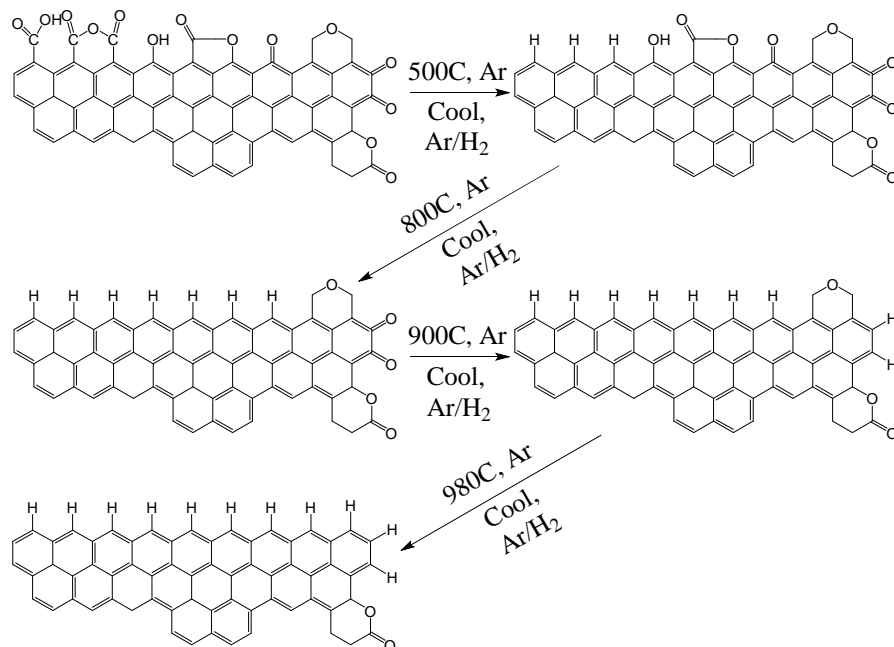


Figure 3. Initial SOG doped carbon surface and examples of its temperature-dependent derivatives. Temperatures shown illustrate groupings of specific SOG removal. Low temperature (<350C) H-passivation of ASA sites occurs upon SOG desorption.

- Low-Cost Oxide Doping, Electrochemical Testing, Surfactant Deposition, Design of Solid Electrolyte Interface and Hybrid Capacitor Assembly:**

This aim incorporates the doping of low-cost oxide materials on the surface-engineered carbons. The electrochemical performance of the chemically engineered electrodes is assessed for improvements in cycle-ability and solid electrolyte interface (SEI) molecular structure. Battery-type nanotube and powder carbon materials engineered with the above described methods are further fused with low-cost, oxide doped materials using a previously established hydrothermal, binder-free methods developed by Ban, *et al* (11–13). Further electrochemical accessibility and charge storage increases are made possible by the use of the implemented Lewis-Basic SOGs as anchoring sites for long-chained perfluorinated surfactant, allowing for a more homogeneous, trace-surface-water-free, more conductive, longer lasting SEI layer (9,8). The electrodes are tested as standard Li-ion coin cells and analyzed for overall cycling performance. Cyclic voltammetry and impedance spectroscopy are performed on battery materials in assessing changes due to surface passivation, doping and SEI alterations. The carbon electrode materials are removed from the coin cells and characterized after cycling to analyze the SEI layer, providing a complete assessment of electrode performance and details allowing for the alteration of the engineering methods described thus far. The high surface area carbon powder that has been partially graphitized (16,43) due to specific SOG incorporation, has been shown to yield favorable changes in specific capacitance and conductive properties (9,43) in cooperation with the anisotropic properties of Lewis-Basic implemented functionality and increased pore access of the surfactant and hydrogen-passivated substrate. The now independently engineered battery and capacitor-type electrode materials can be combined into hybrid Li-ion capacitor cells, using standard hybrid cell assembly (1,5–

7,44). Stable working potential windows will then be finely tuned by readjusting specific surface functionality, the degree of hydrogen passivation, surfactant passivation and oxide doping on the engineered carbon surface layers.

B. Impact

The proposal discussed herein defines a direct strategy and approach towards producing hybrid Li-ion capacitors in a simple, plausible fashion. The work I have contributed thus far into creating techniques for consistent Lewis-Basic SOG implementation, active surface area and SOG passivation as well as enhanced electrochemical accessibility, graphitization character and conductivity is particularly applicable to studies that have been recently published using low-cost, binder-free nanotube/oxide materials. I am completely confident that the combination of low-cost, binder-free materials for use in battery electrodes and the carbon surface engineering methods outlined in the present proposal will no doubt allow for the production of novel hybrid energy storage devices—allowing for significant contribution in the next generation of EV technology and consumer energy storage device production.

C. References

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