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Activated graphene as a cathode material for Li-ion hybrid supercapacitors

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Chemically activated graphene ('activated microwave expanded graphite oxide', a-MEGO) was used as a cathode material for Li-ion hybrid supercapacitors. The performance of a-MEGO was first verified with Li-ion electrolyte in a symmetrical supercapacitor cell. Hybrid supercapacitors were then constructed with a-MEGO as the cathode and with either graphite or $Li_4Ti_5O_{12}$ (LTO) for the anode materials. The results show that the activated graphene material works well in a symmetrical cell with the Li-ion electrolyte with specific capacitances as high as 182 F g^{-1}. In a full a-MEGO/graphite hybrid cell, specific capacitances as high as 266 F g^{-1} for the active materials at operating potentials of 4 V yielded gravimetric energy densities for a packaged cell of 53.2 W h kg^{-1}.

Introduction

Supercapacitors (also referred to as 'ultracapacitors' and 'electric double layer capacitors') and secondary batteries are the two main devices for directly storing electrical energy. Secondary batteries give the highest storage capacity, with lead acid, nickel metal hydride and Li-ion batteries having energy densities ranging from 25 to 150 W h kg^{-1}.[1] However, they have a cycle life limited to approximately 1000 cycles and charge and discharge times of many minutes to hours.

Supercapacitors based on electrochemical double-layer capacitance (EDLC) store and release energy by nanoscopic charge separation at the electrochemical interface between an electrode and an electrolyte.[2] While the capacity of supercapacitors is very high compared to electrostatic and electrolytic capacitors, it is much lower than batteries, with energy densities of 3 to 7 W h kg^{-1}.[1,3] Supercapacitors, however, have life times of 100 000 or more cycles and can be charged and discharged on the order of seconds. Coupling supercapacitors with batteries (or another external power source) is still required for applications that require energy capture and delivery over longer periods of time. Thus, there is a strong interest, *e.g.*, as enunciated by the U.S. Department of Energy, for increasing the energy density of supercapacitors to be closer to the energy density of batteries.[4]

The energy stored in a supercapacitor is proportional to its capacitance and the square of its operating voltage. The operating voltage of supercapacitors in turn is limited by the electrolyte used. The most common electrolyte used today is TEA BF$_4$ in either propylene carbonate or acetonitrile (AN) with operating voltages limited to about 2.7 volts. High voltage ionic liquid electrolytes have also been widely explored but the commercialization of ionic liquid based devices is limited and has yielded only a modest increase in operating voltage.[5] The capacitance of the supercapacitor is primarily a function of the electrode material's surface area (m^2 g^{-1}) and its specific capacitance (μF g^{-1}) when used with various electrolytes. There is thus an interest in developing very high surface area electrode materials that are compatible with organic and ionic liquid electrolytes. Graphene has a theoretical surface area of 2630 m^2 g^{-1}, and various graphene derived materials have been reported for supercapacitor electrodes, specifically: chemically reduced graphene oxide,[6] graphene oxide thermally reduced in propylene carbonate,[7] and microwave exfoliated graphite oxide.[8] We recently reported on a novel carbon produced by the chemical activation of graphene.[9] This activated graphene material yields excellent surface area and performance with a measured specific capacitance of 154 F g^{-1} with commercial organic electrolytes.

Hybrid supercapacitors combine the rapid charge/discharge and long cycle life of the electrochemical double layer capacitor with the higher charge storage capacity inherent to Li-ion batteries.[10] These cells combine a Li-ion battery anode (graphite or LTO), a supercapacitor cathode (typically activated carbon), and Li-ion battery electrolyte. The hybrid configuration increases the energy storage capacity three ways: 1) higher operating voltages (commercial cells now available that are rated at 3.8 volts),[11] 2) the capacity of the graphite anode material is up to five times higher than the activated carbon it replaces, and 3) the specific capacitance of the activated carbon cathode is often higher when used with Li-ion battery electrolytes.

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While the measured energy densities for the hybrid cell are almost twice those of symmetrical supercapacitors,[11] the energy density is still constrained by the activated carbon cathode. In this study, the activated carbon cathode material in a Li-ion hybrid supercapacitor is replaced with a novel, high surface area chemically activated graphene based material (a-MEGO) and its performance is measured.

Experimental

Electrode materials and measurement methods

The preparation and activation of graphene has been previously described.[8,9] Briefly, graphite oxide (GO) cake was synthesized from purified natural graphite (SP-1, Bay Carbon, MI) by the Hummers method.[12] Microwave exfoliated graphite oxide (MEGO) was prepared by irradiating the GO in a microwave oven (GE) in ambient conditions at 700 W for 1 min. Upon microwave irradiation, the very large volumetric expansion of the GO cake yields a black and fluffy MEGO powder. The as-prepared MEGO powder was then dispersed and soaked in aqueous KOH solution (with a KOH/MEGO mass ratio of 7) for 20 h, followed by filtration and drying, to form the MEGO/KOH mixture for chemical activation. The MEGO/KOH mixture was then put in a tube furnace under flowing argon at a pressure of about 400 Torr, and heated at 800 °C for one hour. Activation with KOH transforms MEGO into a carbon material consisting of a continuous network of pores of extremely small sizes ranging from <1 nm to 10 nm and a very high specific surface area of 3100 $m^2 g^{-1}$ as measured by N_2 BET adsorption. Supercapacitor electrodes prepared with the activated MEGO (a-MEGO) have yielded excellent performance with organic electrolytes with a measured specific capacitance of 154 F g^{-1}.[9]

The a-MEGO powder was mixed with 5% binder (PVDF, Aldrich), rolled into thin sheets and punched into 1 cm diameter electrodes. For anode materials, a slightly different procedure was used. Spherodized natural graphite (SLC1520P, Superior Graphite) was mixed with 10% conductive carbon (Super P, Timcal) along with 5% PVDF and N-methyl-2-pyrrolidone (NMP), mixed into a paste, and pressed onto a stainless steel mesh (500 mesh, McMaster Carr) collector. LTO spinel nano-powder (Aldrich) was mixed with 10% conductive carbon, 5% PVDF, and NMP, and dropped onto 25 μm thick copper foil (99.8% pure, Alfa Aesar) to form the electrode/collector assembly.

Best practice methods were used for measuring the performance of the supercapacitor electrodes.[13] For a-MEGO symmetrical cell testing, a two-electrode test cell assembly was constructed of two current collectors, two a-MEGO electrodes, and a porous separator (Celgard 3501). The collector material is from Intelicoat Technologies–a 0.5 mil (~12 microns) aluminum foil with conducting carbon coating. The cell assembly was supported in a test fixture consisting of two stainless steel plates fastened together using threaded bolts. Spacers (PET, McMaster Carr) were placed between the SS plates to electrically isolate the plates, provide a hermetic seal, and maintain a consistent, even pressure on the cell. Hybrid cells utilized the same fixture with the battery anode/collector assembly substituted for one of the a-MEGO supercapacitor electrodes and collectors. For half-cell graphite and LTO anode testing, 2032 coin-type cells were used with

lithium foil (Aldrich) as the counter electrode. All cells were assembled in a glove box in argon with less than 1ppm oxygen and H_2O. 1 M $LiPF_6$ in EC/DEC 1:1 by volume (supplied by Novolyte) electrolyte was used for all cells.

Cyclic voltammogram (CV) curves, electrical impedance spectroscopy (EIS), and galvanostatic charge/discharge (CC) testing was done with an Eco Chemie Autolab PGSTAT100 potentiostat equipped with the FRA2 frequency response analyzer module and GPES/FRA software. EIS was done using a sinusoidal signal with mean voltage typically set to open circuit potentials with an amplitude of 10 mV over a frequency range of 500 000 Hz to 0.01 Hz. Specific capacitance reported is the capacitance for the carbon material of one electrode (specific capacitance = capacitance of single electrode/weight active material of a single electrode), as per the normal convention. Because the hybrid cell anode and cathode electrode masses were not always the same, the average of the two electrode masses was used. Capacitance as determined from galvanostatic charge/discharge was measured using $C = I/(dV/dt)$ with dV/dt calculated from the slope of the discharge curves. For half-cell tests, the cells were discharged and charged galvanostatically with voltage windows specific to the materials using a LAND battery tester (LAND Company, China). Equivalent series resistance (ESR) was calculated using the IR drop at the beginning of the discharge portion of the galvanostatic charge/discharge curves.

Symmetrical and hybrid cell testing

Before assembling a hybrid cell with a-MEGO, its performance with Li-ion based electrolyte was first determined. A symmetrical cell was assembled with two equal sized a-MEGO electrodes and the Novolyte electrolyte. Fig. 1 shows a CV scanned at 40 mV s^{-1}, and Fig. 2 shows a CC plot at a current density of 1.1 A g^{-1}. As previously stated, one of the ways that capacity is enhanced with a hybrid is the higher specific capacitance often observed when using the Li-ion electrolyte specific to batteries. The specific capacitance of a-MEGO in the Li-ion electrolyte ranged from 165 to 182 F g^{-1} for current densities of 5.6 to 1.1 A g^{-1}. This is approximately 15 percent higher than the 141 to 154 F g^{-1} for current densities of 3.8 to 0.8 A g^{-1} obtained with a-MEGO in the TEABF$_4$/AN commercial organic electrolyte.[9]
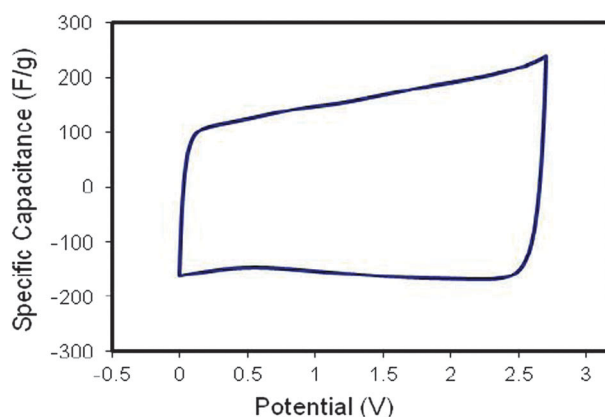

Fig. 1 CV curve (40 mV s^{-1}) for symmetrical a-MEGO cell with Li-ion electrolyte.
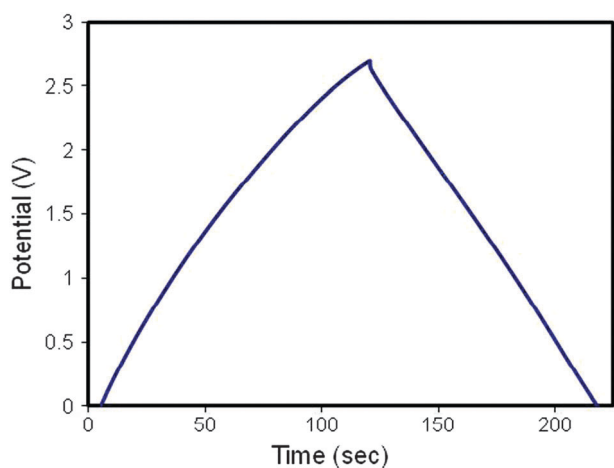
Fig. 2 CC charge discharge (1.1 A g^{-1}) for symmetrical a-MEGO cell with Li-ion electrolyte.

The two materials commonly used for battery anodes are graphite and LTO. Because the capacity of the graphite and LTO anode materials differ from that of the a-MEGO cathode, the respective masses of the two electrodes must be adjusted to equalize the capacity. The capacity of the graphite anode material used has been reported with a reversible capacity measured at low current densities approaching the theoretical values of 372 mA h g^{-1}.[10,14] This graphite was chosen for its good rate performance, however at the current densities typical to supercapacitors the capacity still drops significantly to approximately 40% of the theoretical value.[10] The 182 F g^{-1} specific capacitance of the a-MEGO translates to a capacity of approximately 125 mA h g^{-1}. A mass ratio of graphite to a-MEGO of 1 : 1 was chosen to keep the capacity of the two electrodes roughly equal for the current densities expected for the hybrid cell. LTO has a calculated theoretical capacity of about 171 mA h g^{-1}. To determine the practical LTO capacity, half-cells were assembled and the capacity measured at different scan rates. The capacity of LTO does not decrease with increasing current density as quickly as with graphite, however, since the initial capacity is less than half that of graphite, the required ratio of LTO to a-MEGO was 1.15 : 1.

Results and discussion

Fig. 3 shows a CV curve and Fig. 4 shows CC curves for a full hybrid cell assembled with 1 : 1 weight ratio of graphite anode to a-MEGO cathode. From the discharge portion of the CC curves, the specific capacitances were 266, 246, and 213 F g^{-1} for current densities of 1.0, 1.5 and 2.1 A g^{-1}, respectively. The a-MEGO hybrid cell assembled with the LTO electrode gave specific capacitances of 204 and 191 F g^{-1} for current densities of 0.31 and 0.63 A g^{-1}, respectively. Table 1 lists the specific capacitances for the four cells: two a-MEGO symmetric cells with organic and Li-ion electrolytes and two a-MEGO hybrid cells with graphite and LTO anodes. The calculated energy density for the mass of the active electrode materials is shown as well as that for packaged cells. As seen, the combination of a lower specific capacitance along with the lower operating voltage result in a much lower energy density for the LTO anode based hybrid as compared to the graphite anode hybrid.
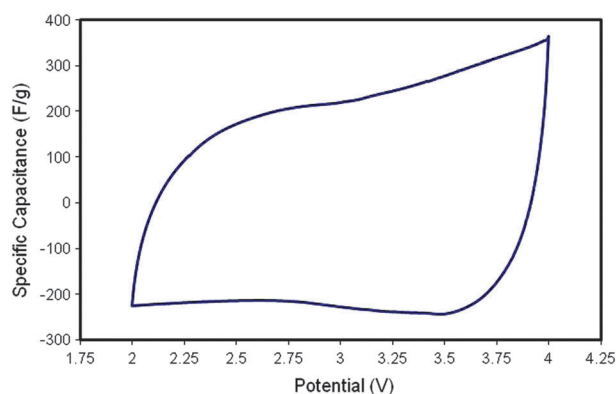

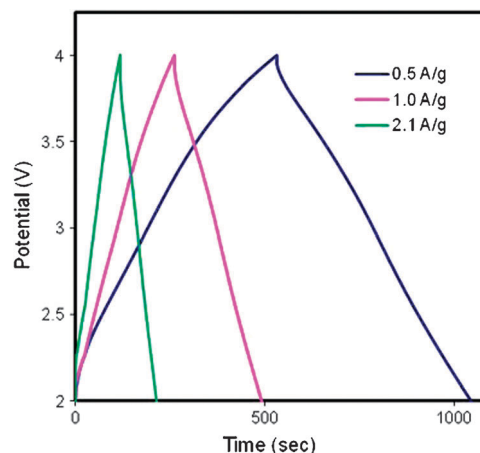**Fig. 3** CV curve (5 mV s^{-1}) for a-MEGO/graphite hybrid cell.

Fig. 4 CC charge discharge for a-MEGO/graphite hybrid cell.

Table 1 Cell specific capacitances and energy densities

Electrode electrolyte system	Specific capacitance (F g^{-1})	Operating voltage (V)	ESR (ohms)	Active material energy density (W h kg^{-1})	Packaged cell energy density (W h kg^{-1})
a-MEGO/ a-MEGO/ Org	154	2.7	3.5	39.0	11.7
a-MEGO/ a-MEGO/ Li	182	2.7	13.0	46.1	13.8
a-MEGO/ LTO/Li	204	2.4	16.0	40.8	14.7
a-MEGO/ Graphite/ Li	266	4.0	45.0	147.8	53.2

Org denotes TEABF$_4$/AN electrolyte; Li denotes Li-ion electrolyte.

For packaged cells, the active material energy density must be adjusted for the percent mass of the cell made up of the active anode and cathode materials. The percent by weight of active material in a high energy packaged Li-ion cell has been reported as 57.4 wt% (16.4 wt% for the graphite anode material and 41.0 wt% for the cathode material).[15] In the hybrid cell configuration, the Li-ion battery cathode material is replaced with a-MEGO. With a 1 : 1 ratio of a-MEGO to graphite, the mass of a-MEGO in the hybrid is 2.5 times less than that in the battery cathode. However, a-MEGO has a
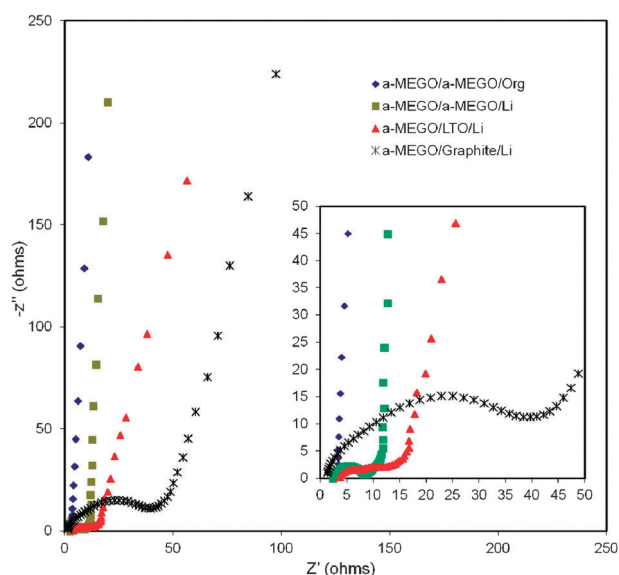
3390 | *Phys. Chem. Chem. Phys.*, 2012, **14**, 3388–3391

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Fig. 5 Nyquist plots for each electrode/electrolyte system.

density approximately 5 times lower than the battery cathode material, requiring an a-MEGO cathode in the hybrid cell to be about twice the volume of the battery cathode. This increased electrode volume leads to an increased case size and additional electrolyte. As a result, while the active material of the anode and cathode are about 57.4 wt% of a packaged Li-ion battery, for the a-MEGO hybrid, the active material will be about 36% of the total packaged mass. For symmetrical cells with a-MEGO for each electrode, the mass percentage of the electrode material is expected to be the same as for current commercial symmetrical supercapacitors and thus a value of 30% was used for the calculations. The table shows that the graphite anode combined with a-MEGO cathode has by far the highest energy density at 53 W h kg^{-1}. While the LTO based hybrid has approximately twice the energy density of current activated carbon based supercapacitors, it offers little advantage in terms of energy density over either of the two symmetrical cells with a-MEGO electrodes. This is due to the approximately 1.6 V lower operating voltage as compared to the graphite anode as well as the slightly lower capacity of the LTO material.

The hybrid cells do come with the tradeoff of higher ESRs. Fig. 5 shows Nyquist plots for the four cell configurations. The ESR as estimated from the horizontal position on the Nyquist plots tracks very closely to that calculated from the IR drop at the beginning of constant current discharge. The symmetrical cell with the Li-ion electrolyte has an ESR of 13 ohms and is significantly higher than the 3.5 ohms measured with a-MEGO cells in organic electrolytes. This increase is consistent with the higher resistance and viscosity of the Li-ion battery electrolyte. The hybrid cell configurations with their faradic battery electrodes have an even higher ESR, with the a-MEGO the highest at 45 ohms.

Conclusion

Li-ion hybrid supercapacitors combine the high voltage and capacity of a battery with the rapid charge and discharge

capability of a supercapacitor and current hybrid cells store approximately twice the energy of symmetrical supercapacitors. The graphite battery anode material has up to five times the capacity of the activated carbons used in the cathode, and so the hybrid's storage capacity, while greatly improved, is still limited by the activated carbon material, or supercapacitor side of the cell. A new carbon material from the Ruoff group, chemically activated graphene, when used to replace the activated carbon cathode material and used in combination with a graphite anode yields specific capacitances as high as 266 F g^{-1}. The energy density for a hybrid cell based on this new carbon is over five times that of current symmetrical supercapacitors and greater than current lead acid batteries and will likely accelerate the adoption of energy storage devices based on this novel carbon.

Acknowledgements

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Phys. Chem. Chem. Phys., 2012, **14**, 3388–3391 | 3391