

Conductive Carbon Coatings Enhance the Performance of Lithium Ion Batteries

The Pitch

A relatively simple method for optimizing the carbon coatings on nonconductive battery cathode material powders has been developed at Lawrence Berkeley National Laboratory (Berkeley Lab). The enhancement of the electronic conductivity of the carbon coating enables minimization of the amount of carbon in the composites, allowing improvements in battery rate capability (ability to sustain high current densities in a lithium battery configuration) without compromising energy density.

The invention is applicable to lithium iron phosphate (LiFePO_4) and other cathode materials used in lithium ion or lithium metal batteries for high-power applications such as power tools and hybrid or plug-in hybrid electric vehicles. The market for lithium ion batteries in consumer applications is currently \$5 billion/year. Additionally, lithium ion battery sales for vehicular applications are projected to capture 5% of the hybrid and electric vehicle market by 2010 and 36% by 2015 (see www.greencarcongress.com).

LiFePO_4 has the disadvantage of having a low intrinsic rate capability (inability to sustain high current densities in a lithium battery configuration), which has been attributed to its low electronic conductivity ($10^{-9} \text{ S cm}^{-1}$). One of the most promising approaches to overcome this problem is the addition of conductive carbon. Co-synthesis methods are generally the most practical route for coating particles with carbon. At the relatively low temperatures ($<800^\circ\text{C}$) required to synthesize LiFePO_4 particles, however, only poorly conductive disordered carbons are produced from organic precursors. Thus, the carbon content has to be high to produce the desired enhancement in rate capability, which decreases the cathode energy density.

The Technology

When certain readily decomposed organic compounds and graphitization catalysts are selected as precursors, conductive carbons with more graphitic structures are produced at temperatures compatible with synthesis of LiFePO_4 (patent pending). Small amounts of the organic compounds and the inorganic or organometallic catalysts are initially added to the precursor mix prior to calcination. The optimized process results in a

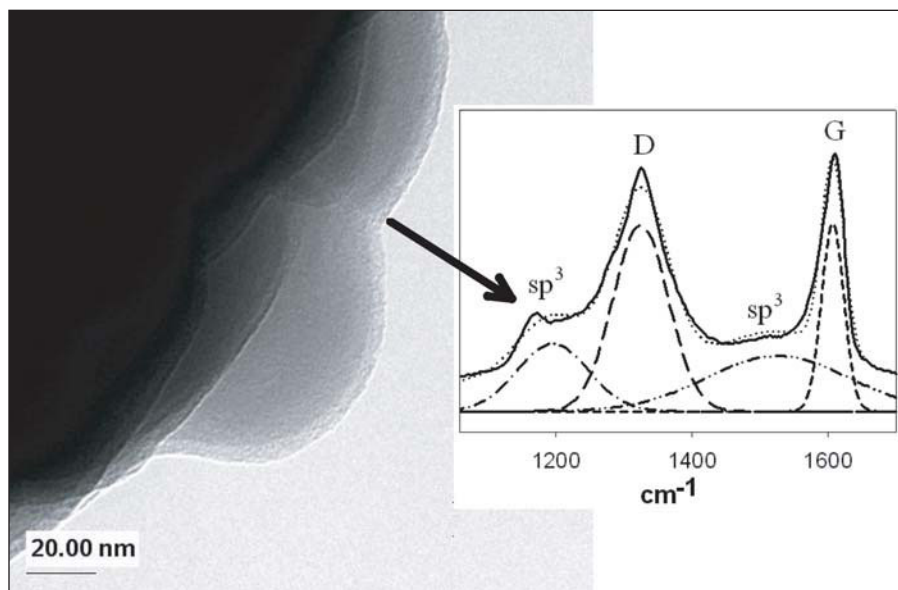


Figure 1. Scanning electron micrograph of a coated LiFePO_4 particle and a typical Raman spectrum of the carbon coating. Deconvoluted peaks correspond to disordered (D) and graphene (G) (highly graphitic conductive carbon) bands of carbon.

phase-pure LiFePO_4 product consisting of small particles homogeneously coated with a $<10\text{-nm}$ -thick layer of highly graphitic conductive carbon coating (Figure 1) that can withstand prolonged cycling and high rate discharges. The carbon coatings on LiFePO_4 produced by Berkeley Lab's technology result in an enhancement of the conductivity of the composite by as much as six orders of magnitude, thereby improving the electrochemical performance of lithium ion batteries without sacrificing their energy density. The coatings are also highly durable. No degradation has been found after 100 full charge-discharge cycles.

The key to these features is the less disordered and more graphitic structure of the carbon arising from the additives used during co-synthesis as determined by Raman spectroscopy (Figure 1 inset). This structure results in higher composite conductivity and is closely correlated with the improved rate capabilities in lithium cells

at low carbon contents ($<2 \text{ wt}\%$). For example, a one-order-of-magnitude increase in composite conductivity results from a 25% higher ratio of graphene carbon to more disordered or amorphous carbon. This produces up to 45% better electrochemical utilization in lithium batteries when compared to coated LiFePO_4 materials having the same carbon contents. The proposed additives and methodologies are low-cost and can readily be integrated into existing manufacturing processes.

Opportunities

Berkeley Lab is seeking licensees for their conductive coating technologies and academic and industrial partners for collaborative research and development.

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Deep-UV LEDs Kill Bacteria Showing Potential to Replace More Hazardous Mercury Lamps

The Pitch

Solid-state ultraviolet (UV) light sources enable many applications, from sterilization of water, air, and surfaces to biohazard detection; and applications in medicine, dentistry, and industrial processes. Their small size, low power consumption, emission wavelengths in the germicidal range, and fast on/off switching times down to a few nanoseconds make ultraviolet light-emitting diodes (LEDs) an environmentally friendly alternative to bulky, expensive, and hazardous mercury lamps—traditional UV sources.

Sensor Electronic Technology, Inc. (SET) has developed deep-UV LEDs with peak emission below 365 nm. UV light produced by mercury lamps has been used for decades for many applications including air and surface sterilization in hospitals, laboratories, and food processing plants. Rays with wavelengths falling into the so-called UVC band ($100 \text{ nm} < \lambda < 290 \text{ nm}$) are highly effective in killing bacteria, viruses, yeasts, and molds with the maximum germicidal effectiveness peaking at $\sim 265 \text{ nm}$. The current conventional UV technology uses the 254 nm line generated by low-pressure mercury lamps for germicidal effects. There are several disadvantages of using mercury lamps as UV light sources: the lamp is usually bulky and fragile and works only under high voltages; it contains mercury, an environmental hazard; and its UV power density is low, in the range of a few hundred $\mu\text{W}/\text{cm}^2$. By comparison, UV LEDs are tiny, robust, efficient, and environmentally friendly light sources that can produce orders-of-magnitude-higher surface power densities (W/cm^2).

Solid-state UV light sources can be fabricated from AlInGaN materials using advanced semiconductor epitaxial growth methods, such as metalorganic chemical vapor deposition (MOCVD). Their bandgap energies can be extended from the visible to the deep-UV spectral region using group-III nitride alloys, depending on the Al content. The bandgap of AlN at room temperature is 6.1 eV (corresponding to a wavelength of 203 nm).

In 2004, SET introduced 280 nm deep-UV LEDs with continuous-wave (cw) powers of greater than 1 mW under a driving current of less than 30 mA. Subsequently, milliwatt-level UV LEDs with emissions from 365 nm to 250 nm have been produced. These are expected to compete with conventional mercury lamps in the market for portable UV water/air/surface sterilization.

The Technology

This progress is attributed to SET's development of a patented epitaxial growth technique, migration-enhanced metalorganic chemical vapor deposition (MEMOCVD); the use of patented quaternary AlInGaN technology; and a patent-pending phonon engineering approach that enables a dramatic improvement in LED efficiency and output power. The advantage of MEMOCVD is that it allows growth of layers at lower temperatures than conventional MOCVD ($400\text{--}1200^\circ\text{C}$).

State-of-the-art deep-UV LEDs are deposited layer-by-layer on UV-transparent double-polished *c*-plane sapphire substrates through MOCVD and MEMOCVD. MEMOCVD is particularly advantageous for high-Al-content AlGaIn film growth and can separate NH_3 and metalorganics to achieve reduced gas-phase reactions

and enhanced migration of adatoms (atoms adsorbed on a surface).

By enabling the formation of abrupt high-quality heterostructures, accurate thickness and composition control, and increased wafer uniformity, the SET process, which works with 4-in. wafers, improves both the quality of the material produced and the manufacturing throughput. Thus, both the performance and the reliability of the resulting electronics are improved.

A power progress plot for these UV LEDs is shown in Figure 1. The wavelengths are roughly divided into the ranges of 325–365 nm and 265–300 nm. As can be seen, over the past five years, the UV LED power has increased by more than a factor of 30. One advantage of UV LEDs is that they can be switched on and off very rapidly (up to 200 MHz and higher) demonstrating nanosecond operation. This provides frequency-domain measurements for the identification of bioagents.

The UV LEDs also enable the flexibility of integrating different UV emissions into a single package, thereby providing users the control of UV emissions with spectrum selection. For example, SET can integrate UV LEDs with peak emissions covering the UV spectrum from 250 nm to 365 nm. Users can digitally select the desired wavelengths or even design a UV spectrum by customizing different emission intensities.

The deep-UV LEDs with peak emissions longer than 295 nm show stable performance. The accelerated lifetime measurements predict more than 2000 h of stable operation for wavelengths of 295 nm and above. The power for most 280 nm LEDs drops to 70% of its initial value after 700 h of continuous dc current stress at 20 mA.

One of the potential applications of the deep-UV LEDs is for water sterilization.

Opportunities

SET is seeking marketing partners to penetrate into traditional UV markets and explore new applications for their innovative solid-state deep-UV light sources.

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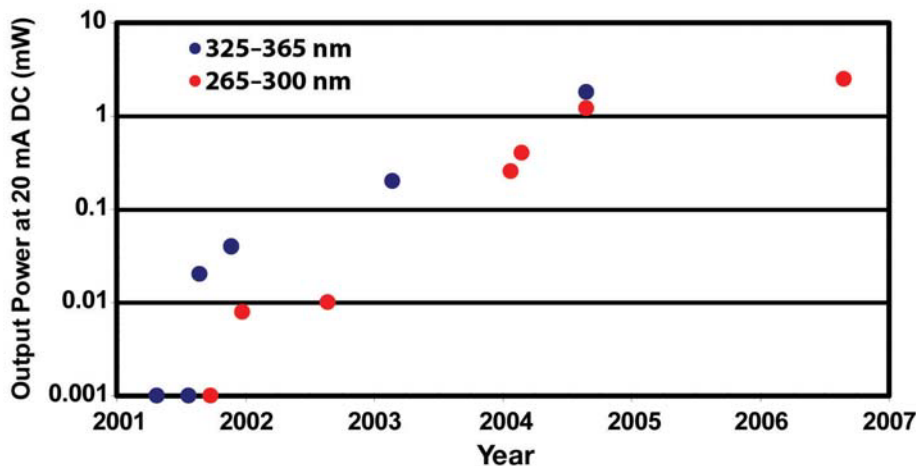


Figure 1. Increase in the power of UV LEDs over several years.

Nanomaterials Improve Charge Efficiency of Flexible OLED Devices and Organic Solar Cells

The Pitch

Two approaches have been developed for reducing the cost of organic light-emitting diode (OLED) packaging and encapsulation by inventing new stable cathode materials and structures. These have the potential to improve significantly the electrical performance (charge efficiencies) and product life of both flexible OLED devices and organic solar cells. These inventions by researchers at Lawrence Berkeley National Laboratory (Berkeley Lab) include creating smoother electron charge injection from the cathode, providing a more balanced charge distribution in the device, decreasing the environmental sensitivity of the cathode, and reducing both heat generation near the cathode and exciton quenching (decay of an exciton, an electrically neutral excited state of an insulator or semiconductor, to its lower-energy state without emitting an electron).

These Berkeley Lab inventions address the core challenge of OLED encapsulation technology by offering a fundamental shift in the design of OLED cathode materials and structures. The electron injection property of the cathode is improved by altering its surface structure on a nanometer scale, and it is less sensitive to the environment, thereby reducing the need for costly vacuum processing and packaging.

The Technology

The Berkeley Lab researchers have developed two innovative approaches for increasing the charge injection efficiency of the electrodes used for transparent and flexible OLEDs. The same technologies can be applied to enhance photoelectron conversion for organic solar cells. Both approaches are expected to enable cost-effective manufacturing and packaging.

The first approach involves solvent-processable nanotube composites for efficient OLEDs and solar cells. The new class of conductive polymers developed at Berkeley Lab uniformly suspends and disperses carbon nanotubes and enables them to function efficiently as charge injectors in the electrodes and light-emitting layers of both OLEDs and organic solar cells. Currently, OLED cathodes are thermal-vacuum-evaporated because of the use of reactive metals for electron injection. By comparison, devices made using Berkeley Lab's air-stable cathode materials can be



Figure 1. Transmission electron micrograph of a conductive polymer poly(di(oxytrioxadecane)fluorine) single-walled carbon nanotube film. The sample was prepared by microtoming the bulk composite film.

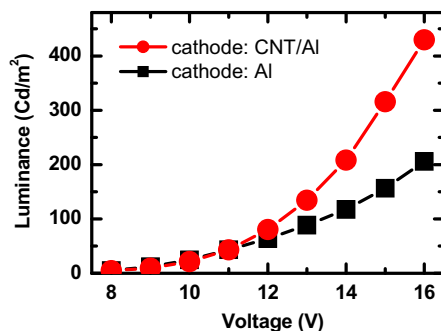


Figure 2. Brightness as a function of voltage for the organic light-emitting devices. (The size of the circles and squares represent the error bar.)

solvent-processed and applied using inkjet printing or spin coating. They also have less demanding packaging requirements. Unlike most OLEDs that incorporate metals in the cathode, the Berkeley Lab OLEDs could be transparent. In addition, the materials are flexible and are anticipated to be cost-effective to produce.

New materials and processes have also been developed that provide superior dispersion and stabilization of single-walled carbon nanotubes (SWNTs). A nanotube/

polymer [poly(di(oxytrioxadecane)fluorine) or PFO] suspension made with these nanotubes allows the unmodified SWNT to remain suspended in the PFO for at least four months. This is demonstrated by a film cast out of the solution (Figure 1) showing a network of SWNTs. Both the backbone and side chains of the conductive polymer can be adapted to accommodate various applications. Charge injection from the nanotubes to the conductive polymer occurs at much lower voltage.

The second approach involves OLEDs with air-stable structured electrodes. In this second approach, the researchers have developed electrodes with nanostructured geometry for improving the electrical-optical energy conversion efficiency of both flexible OLEDs and solar cells. The new transparent electrodes are less reactive to water and oxygen than their metal counterparts, which is expected to reduce the costs of fabrication and packaging.

An ordered array of nanotubes (or stable nanoclusters) is used at the cathode-organic layer interface as charge injectors to efficiently overcome the large energy barrier at this interface. These structured electrodes are expected to significantly reduce the drive voltage required to induce light emission inside organic materials and thereby increase the energy conversion efficiency of the resulting devices. As shown in Figure 2, implementation with carbon nanotubes improves the brightness (above 12 V) compared to devices without a nanotube cathode.

Opportunities

Both of these approaches for increasing the charge efficiencies of the electrodes used to produce flexible OLEDs and solar cells, thereby reducing their manufacturing and packaging costs, have patents pending and are available for licensing. Berkeley Lab is also seeking partners for collaborative research and development.

Source: For technical information and development partners: Gao Liu, Solvent Processable Composites Technologies, Lawrence Berkeley National Laboratory, MS 70R0108B, Berkeley, CA 94720, USA; tel. 510-486-7207 and e-mail gliu@lbl.gov and Sam Mao, Structured Electrodes Technologies, tel. 510-486-7038 and e-mail ssmao@lbl.gov. For licensing: Michael Mueller, LBNL Technology Transfer Department, 90R1070, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA; tel. 510-486-4303 and e-mail mmmueller@lbl.gov.