

### Lithium Batteries Improved by Use of a Nonflammable Electrolyte plus CNT

A major drawback to the widespread adoption of lithium rechargeable batteries, particularly for electric vehicles, is their flammability. A rechargeable lithium battery system that couples high-energy density with a safe, nonflammable and non-volatile electrolyte is under development at Phoenix Innovation Inc. It is based on phosphorus (specifically, polyphosphonate) chemistry and does not use any carbonates, the conventional solvents of choice with lithium systems. In addition to its nonflammability, the electrolyte is stable up to 5 V. The polyphosphonate electrolyte family investigated includes a number of possible chemistries that allow the electrolyte's properties to be tailored over a wide range of conductivity and power density, depending on the desired application. Figure 1 shows a typical calorimetry scan of a polyphosphonate electrolyte compared with a standard carbonate electrolyte. These scans were run in the presence of lithium metal, which melts at  $\sim 180^\circ\text{C}$ . Figure 1 also shows that the reaction between the carbonate mixture and the molten lithium is highly exothermic, while the phosphonate is much less reactive.

By modifying the substituents attached to the phosphorus and/or the chemical group between the phosphonate moieties in the backbone of the polymer chain (see Figure 2), the properties can be tailored to give improved battery performance, including stability and flame retardation. A primary goal has been to achieve both cost-effectiveness and improved performance; only one synthetic step is required, and the product yield is very high.

The second objective of the rechargeable lithium battery research, which is synergistic with the nonflammable electrolyte work, is the development of carbon nanotube (CNT)-based electrodes with very high capacities. These materials can be easily and economically processed into flexible papers that can be fashioned into virtually any size, shape, or dimension. Depending on the conditions under which electrodes are prepared, a wide range of properties can be realized.

After synthesis, the nanotubes are heat-processed at various temperatures and under an inert or oxidizing atmosphere. Depending on the processing conditions

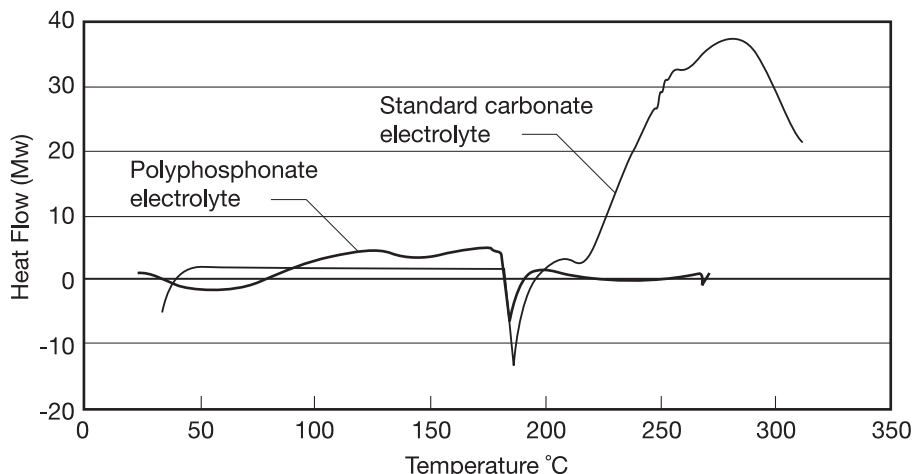


Figure 1. Differential scanning calorimetry results (with molten lithium present) of a polyphosphonate electrolyte and of a standard ethylene carbonate/ethyl methyl carbonate electrolyte mixture.

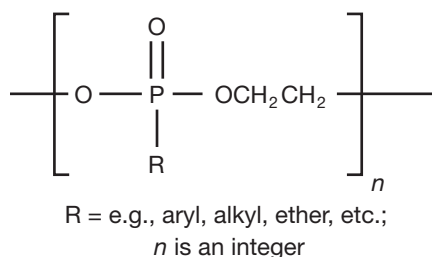


Figure 2. The structure of a typical polyphosphonate monomer. Phosphonates have two P–O linkages and one P–C linkage, as well as one P=O linkage.

(i.e., duration of heating, temperature, and gas composition of the treatment atmosphere), the electrochemical properties of the product can vary substantially; for example, in an oxidizing atmosphere of  $\text{CO}_2$  or  $\text{O}_2$ , the capacities of the nanotubes can change markedly. The company is working to optimize the conditions to obtain optimal performance. For example, reversible capacities (the capacity available for cycling after any initial irreversible losses) of up to 600 mAh/g have been obtained.

Although CNT anodes can be configured with standard lithium cathode materials ( $\text{LiCoO}_2$ ), electrolytes, and salts, the company suggests that coupling the nano-

tube electrodes with its nonflammable polyphosphonate electrolyte would result in an improved battery package. The company is now working on the development of an all-carbon battery in which both the anode and cathode are nanotube-based. This system uses the inherent lower density of carbon, compared with metal oxide cathodes based on cobalt.

#### Opportunities

Phoenix Innovation welcomes inquiries concerning commercialization of its lithium battery technologies.

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**Miniature Chemical Sensor Developed for Ultra-Sensitive Spectroscopy of Oxide Surfaces**

The surface properties of silica are of particular importance in many areas of technology including microelectronics, chemical separations, catalysis, and biosensing. As key reactive sites, the surface hydroxyl (-OH) (or silanol -SiOH) groups largely control the surface chemistry of silica. Yet, a monolayer of silanol produces an absorption signal near the detection threshold of conventional techniques, requiring the use of silica gels, porous silica, or powders to enhance the surface area in spectroscopic studies. Moreover, the surface silanol absorption is often overwhelmed by large internal -OH absorption. Researchers at the National Institute of Standards and Technology and Eindhoven University of Technology in The Netherlands have

developed a technology enabling high-sensitivity spectroscopy of an ultra-smooth silica surface.

The technology employs a miniature (~1 cm<sup>3</sup>), low-loss, high-quality optical resonator. The resonant modes are very sharp, and therefore, optical loss is very small; only ~20 ppm of the light is lost during one pass through the resonator. This is achieved by fabrication using extremely low-OH fused silica, high-reflectivity coatings, and ultrasmooth (RMS roughness, <0.05 nm) surfaces including at least one total internal reflection (TIR) surface, where the surface silanol and adsorbed species can be probed using weak overtones or combination bands.

Figure 1a shows a monolithic, folded optical resonator formed from low-OH fused silica, where "folded" refers to the beam path inside the resonator. As

depicted in the schematic in Figure 1b, the two planar surfaces at right angles to each other are coated for ultrahigh reflectivity (>99.997%) in the wavelength range of interest, while the ultrasmooth convex TIR surface provides a (broadband) reflectivity of ~99.9999%. A laser pulse is injected at normal incidence through one of the coated planar faces, exciting modes that circulate between the planar surfaces, undergoing a 90° fold at the convex TIR surface. The intensity of the circulating mode is monitored in time by detecting the residual transmitted light at the opposite planar face, producing an exponentially decaying ring-down transient (i.e., the light intensity diminishes on each pass), where the decay rate yields the absolute optical loss-per-pass of the resonator at a given wavelength.

The ring-down rate of the folded resonator is very sensitive to optical absorp-

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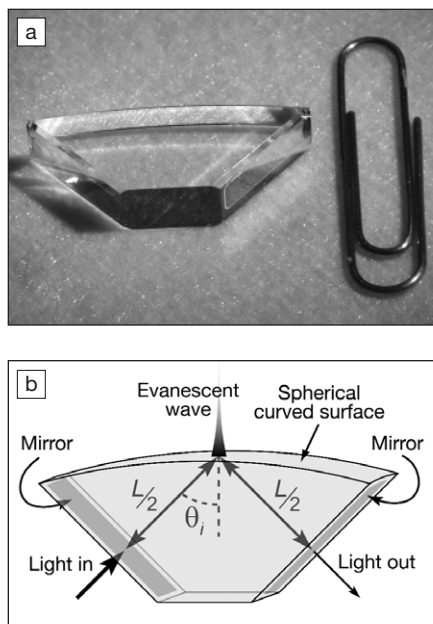


Figure 1. (a) Photograph and (b) schematic illustration of a miniature monolithic folded optical resonator formed from low-OH fused silica.

tion by molecules in the evanescent field at the apex of the convex TIR surface within the mode spot, which has a diameter of  $\sim 100 \mu\text{m}$  as fixed by the monolithic design. The resonator shown in Figure 1a has a minimum intrinsic loss per pass of  $2 \times 10^{-5}$  at 1200 nm, which produces a ring-down time of 4.8  $\mu\text{s}$  and enables detection of optical absorptions of  $\sim 10^{-8}$  (minimum detectable optical loss of one part in  $10^8$ ). High signal-to-noise ratio spectra of a weak second-order combination band of surface SiOH in the near-IR have been obtained using the design shown.

While the monolithic folded resonator, which is readily incorporated into a flow cell or other reaction vessel, is appropriate for studies of the silica-vacuum, silica-gas, or silica-thin-film interfaces, other resonator designs enable liquids to be probed by using a steep angle of incidence at a TIR surface (without introducing astigmatism) or enabling broad spectral coverage by exclusive use of TIR mirrors to eliminate the bandwidth restriction of high-reflectivity coatings. Using the fold-

ed resonator or related designs, a complete measurement is accomplished with a single laser pulse, thereby eliminating noise from light-source fluctuations, which occurs in conventional absorption spectroscopy.

The product of the resonator intrinsic loss and the relative uncertainty in the ring-down time determines the limit of detection. With an intrinsic loss of about  $10^{-5}$  and a ring-down time uncertainty of about  $10^{-3}$ , a detection limit of  $10^{-8}$  can be obtained routinely, which is at least 1000 times more sensitive than conventional absorption spectrometers. In addition, the folded resonator also enables absolute surface coverage measurements for adsorbed species, as recently demonstrated for several chloroethylenes with submonolayer sensitivity. Similar absolute coverage measurements may enable studies of, for example, the absolute coverage and average orientation of DNA adsorbed onto silica from solution, which would provide insight into gene chip operation.

In addition to providing a unique tool for fundamental and applied research, the folded resonator and related designs also form a new class of chemical sensors. In contrast to waveguide devices, where sensitivity increases with increasing device size (increasing sample path length), the technology described here increases in sensitivity in the bulk-loss-limited case with decreasing device dimensions, since the resonator intrinsic loss is decreased. Although the ultra-smooth silica surfaces are robust and easily cleaned, polymer coatings that concentrate the species being analyzed in the vicinity of the evanescent wave could be used to enhance detection limits while providing additional protection from particulates or other contamination.

**Opportunities**

Four patents have been issued and one is pending. Inquiries are welcomed regarding collaborative research, development, or licensing.

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**Oriented ZnO Nanowires Produced by Large-Scale, Low-Temperature Method**

Since the first report of ultraviolet lasing from ZnO nanowires, effort has been devoted to the development of synthetic methodologies for making one-dimensional ZnO nanostructures. Among the various techniques, evaporation and condensation processes are favored for their simplicity and high-quality products. But these gas-phase approaches generally require economically prohibitive temperatures of 800–900°C. The commercial potential of gas-phase-grown ZnO nanowires remains constrained by the expensive and/or insulating (for example, Al<sub>2</sub>O<sub>3</sub>) substrates required for orient-

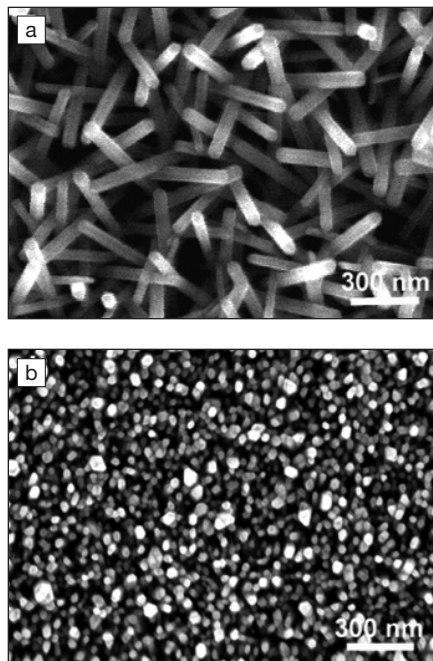


Figure 1. ZnO nanowire array grown from (a) preformed ZnO nanocrystals and (b) nanocrystals formed in situ from a zinc salt precursor. The array alignment is controlled by the initial nanocrystal deposition.

ed growth, as well as the size and cost of the vapor deposition systems. A low-temperature approach to the large-scale production of dense, aligned ZnO nanowires has been optimized by researchers at the University of California, Berkeley, and Lawrence Berkeley National Laboratory.

Homogenous arrays of ZnO nanowires were synthesized at 90°C with a tunable aspect ratio using a mild, environmentally benign aqueous solution. This synthesis yields complete and conformal nanowire coverage on a wide range of substrates of virtually any size. The substrates include planar surfaces as well as nonplanar solids made of diverse materials including silicon wafers, insulating and conducting oxides, metals, and polymers. Solution approaches to nanowire growth are desirable because of the low production costs and good potential for scale-up.

This method uses a simple two-step process of depositing nanocrystals on a substrate and/or forming nanocrystals *in situ* on a substrate and then growing nanowires from these seeds. The alignment of the final array is determined in the first step of nanocrystal deposition. Quasi-aligned arrays can be achieved using preformed ZnO nanocrystal seeds (Figure 1a), while perfectly aligned arrays are produced with a zinc salt precursor (Figure 1b). The final density of the wire arrays is controlled in the first step of nanocrystal deposition/formation with the largest number density on the order of 10<sup>10</sup> cm<sup>-2</sup>. These arrays have a ZnO surface area of, conservatively, at least 50 cm<sup>2</sup> per cm<sup>2</sup> of substrate (~10 m<sup>2</sup> g<sup>-1</sup>). The ZnO wire growth is carried out in an open vessel filled with an aqueous solution of zinc nitrate, hexamethylenetetramine, and a polyamine. The wire diameter, length, and aspect ratio can be tuned by controlling the reactant concentration and growth time. A large range of sizes can be grown: wire diameters range from 10 nm to 300 nm, with lengths of 50 nm to 25 μm and aspect ratios from 5 to 150.

Figure 2 shows a scanning electron microscope cross-sectional image of an

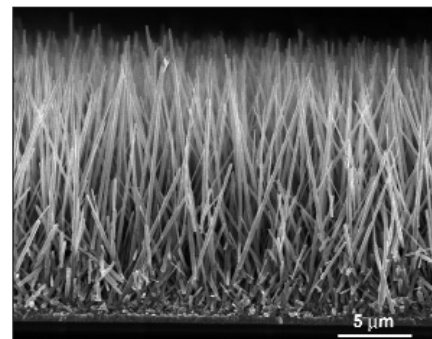


Figure 2. Scanning electron microscope cross-sectional image of a ZnO nanowire array grown on a conducting substrate using preformed ZnO nanocrystals. The wires have a length of 20 μm and an aspect ratio of 100.

array with a length of 20 μm and an aspect ratio of 100. These nanowires are single-crystalline, as confirmed with x-ray diffraction and electron microscopy studies. They also have high optical quality, with a pronounced UV bandgap emission on excitation. This low-temperature hydrothermal method is substrate-independent and produces high-quality nanowire arrays on ITO (indium tin oxide) glass, sapphire (Al<sub>2</sub>O<sub>3</sub>), titanium foil, and polymer surfaces. With this method, the dimensions of the wires can be customized for a specific application such as laser diode arrays, hydrophobic/philic surfaces, or photoanodes for solar cells.

**Opportunities**

The researchers are interested in collaborating with companies to develop these patented nanowire arrays for commercial applications.

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