TECHNOLOGY OPPORTUNITY

One-step bulk synthesis process for phosphorus (P)-doped graphitic carbon

Low oxygen content and a widely-tunable phosphorus content may allow for use of this material as stable phosphorus-based electrodes or as a catalyst of the oxygen reduction reaction (ORR) in fuel cells

Description:

Figure 1. Various photographs of the unopened quartz reaction tubes with black metallic flakes of directly-synthesized PCx deposited on the walls and as free-standing flakes.

As the energy revolution continues there is a tremendous amount of research activity in novel battery technologies to increase performance, minimize cost, and streamline manufacturing. Unique materials are being developed, characterized, and tested to lower our reliance on petroleum and minimize our impact on the environment. A key area of interest in electrode materials is for alkali-ion batteries and, more specifically, lithium-ion batteries. State of the art Li-ion batteries have a high energy density, fast charge/recharge kinetics, low self-discharge, no memory effect, and a wide operating temperature range. As such, they represent the leading technology for electric vehicles, portable electronics, and large-scale grid energy. But they are not without their faults.

Graphite was initially introduced as an anode material for Li-ion batteries to combat safety issues associated with a bare, metallic lithium electrode, and its capacity of 372 mAh/g remains the state of the art today. However, consumer demand for better performance (energy storage) remains an issue. To that end, many modifications of graphite are under investigation, such as nano-sizing as well as introduction of dopants into the carbon structure. Elements that bond with large amounts of lithium but cannot be used as electrode materials themselves are especially attractive; phosphorus, in particular, is known to bind with lithium to form the very high capacity phase Li_3P which has a theoretical capacity of 2596 mAh/g. Similar promise is apparent for phosphorus-based electrodes for sodium-ion batteries, where the phase Na_3P also has a theoretical capacity of 2596 mAh/g. Unfortunately, bulk white phosphorus is pyrophoric and toxic and therefore has been considered unsuitable for battery electrodes. Likewise, layered black phosphorus suffers from large volume expansion during lithiation/sodiation and poor conductivity.

Recently, work has been underway to synthesize a graphitic matrix that stabilizes an accessible phase of phosphorus for reversible lithiation/sodiation. The graphite in this case serves as a conducting framework while mitigating the effects of expansion upon ion insertion. Such a material shows promise in many electrochemical applications but, volume production of the material sufficient to make these applications economically feasible has been elusive. Until now.

To address the above issues, researchers at Montana State University have developed a direct (single-step) synthesis process to obtain P-doped graphitic carbon (PC_x) from inexpensive liquid precursors. This direct synthesis method has been optimized and the resulting products thoroughly characterized as a crystalline material of tunable composition and/or phosphorus environment. The one-step process involves the reaction of phosphorus trichloride and benzene at 800-1050 °C in a closed vessel at elevated pressure. Yields are quantitative for compositions up to x = 5 and the product is stable at room temperature and in ambient atmosphere.

Benefits:

- A significant content of the overall phosphorus incorporated in PC_x remains stable within the bulk material even after washing with water and storage in air for several months.
- The process is started from two miscible liquids mixed under atmospheric conditions (preferably under inert gas to achieve the lowest oxygen content). The mixture can be prepared with any initial composition, allowing tunability of the resulting product up to x = 5. The reactants are readily available chemicals that do not need specialized preparation.
- Phosphorus-doping is reported to suppress the formation of hydrogen peroxide, an undesirable byproduct of the ORR, when used in graphitic electrode materials for fuel cells.
- The reactants are readily available, cheap chemicals that are widely used in other industrial processes such as for the industrial scale synthesis of glyphosate (Roundup®).
- Synthesis can be completed from start to finish in as little as two hours, but heating rate is fully controllable to optimize the structure of the resulting product.

Opportunity:

- Bulk P-doped graphite may find application in fuel cells as a metal free replacement to the expensive and scarce platinum used on the cathode of a proton exchange membrane fuel cell to catalyze the ORR. The ORR is the technological bottleneck in conventional fuel cells.
- Electrode material in alkali metal-ion batteries, especially lithium-, sodium-, and potassium-ion batteries.
- Phosphorus-doped carbon films may be used as the active materials in solar cells.
- Electrode material in super-capacitors, pseudo-capacitors, and hybrid batteries.
- Inhibitor of graphite oxidation.
- Precursor for P-doped diamond or P-doped graphene, leading to applications in nano-devices and superfast electronics (typical methods to exfoliate graphite into graphene rely on large quantities of material being available, which cannot be provided by the other methods).
- US provisional patent filed and available for license and commercialization
- Potential for collaboration with MSU researchers to extend or tailor this technology

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