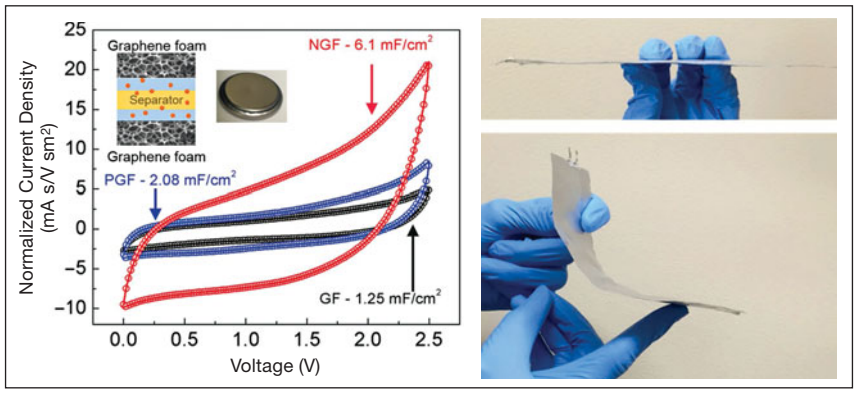
Energy Focus

Designed imperfections in graphene maximize charge-storage potential of supercapacitors



Cyclic voltammograms show that nitrogen-doped graphene foams (NGFs) and structurally defective Ar+ plasma processed graphene foams (PGFs) both outperform their pristine graphene foam (GF) counterpart. Flexible supercapacitor pouch cells can incorporate these foams into commercially viable energy-storage devices. Credit: *Advanced Materials*.

Few materials have been so extensively evaluated for electrical energy-storage applications as graphene; since 2009, over 1000 articles have highlighted the advantages that this two-dimensional (2D) carbon material possesses as a supercapacitor electrode. However, a single sheet of graphene cannot power a practical device, and few-layer graphene (FLG) or graphene-containing composites offer more practical solutions. Although graphene has unique electronic and mechanical behavior and has exceptional promise as a supercapacitor electrode material, the defect-free, ideal structures have a finite maximum charge-storage capability threshold. In an attempt to overcome this barrier, several previous research efforts have simulated the benefits of defects on the electronic and charge-storage properties of graphene. Most of that work, to date, has been solely computational, and few results have provided empirical backing of the modeling simulations.

Recently, researchers from Clemson University were able to assemble graphene (FLG) electrodes with well-tailored defects into practical-scale supercapacitors. While it may appear counterintuitive, imperfections in the sp^2-bonded graphene sheet—such as holes, vacancies, and atom dopants—offer critical benefits that are absent in the perfect graphene structure. Such disruptions of the π–π carbon bonds affect the density of states of the entire graphene sheet and enhance metallic conductivity of the (originally semiconducting) material. Density functional theory simulations point to higher quantum capacitance in materials with tailored defects; this, in turn, enhances graphene's maximum charge-storage capability. Pores in the 2D sheets also enable ion transport perpendicularly through to the sheet planes of FLG and ensure high rate capabilities and power densities.

Ramakrishna Podila, who heads the Laboratory of Nano-biophysics at Clemson University, underscores the significance of this work. "Defect configuration in graphene is critical to achieving high-energy density supercapacitors beyond quantum capacitance limitations. In the right configuration, defects allow [the] electrolyte to access the interlayer spaces in few-layer graphene. This can increase the energy density as there is plenty of room in the middle." Jingyi Zhu, Anthony S. Childress, Mehmet Karakaya, and Apparao M. Rao—all of Clemson University—joined Podila for this effort. They collaborated with Sushmita Dandeliya and Anurag Srivastava (of ABV-Indian Institute of Information Technology and Management) and Ye Lin (University of South Carolina). The publication appeared in a recent issue of *Advanced Materials* (doi:10.1002/adma.201602028).

The researchers synthesized FLG sheets and low-density, highly porous three-dimensional cohesive structures (graphene foams) on nickel foils using atmospheric-pressure chemical vapor deposition (CVD), which involved thermal decomposition of methane at 850°C and subsequent chemical etching (with hydrochloric and nitric acids) of the metal substrates. The researchers used argon ion-beam etching to perforate the graphene structures to form nanopores. In an alternative approach, the researchers flowed Ar gas through mixtures of benzylamine and acetonitrile to anneal CVD-grown graphene and dope nitrogen into the layers. Their publication describes the materials characterization of the resulting structure, its electrochemical performance in supercapacitor cells, and a computational analysis of defect-induced changes to the electronic band structure and densities of state of graphene.

The researchers found that imperfections in the graphene sheets enhance the performance of these electrode materials in electrochemical energy-storage tests. The nanopores in the graphene sheets facilitated transport of ions through the multilayer structure, which improved the volumetric capacitance of the electrodes. Reactive edge sites showed strong interactions with ammonium-based cations and facilitated efficient electrosorption. Although both vacancies and nitrogen defects drove electrons from the valence to the conduction bands and maximized quantum capacitance contributions, nitrogen-containing pyrrolic and pyridinic groups improved overall electrical conductivity and offered the highest power densities.

Perhaps the biggest challenge that graphene must overcome in its quest to become a commercially viable supercapacitor material is its high manufacturing cost and low electrode density. The researchers were able to manufacture dense graphene foams, coat current collectors with them, and package them into conventional pouch cells. This approach, which optimized the defect composition of graphene electrodes for maximum capacitance, is a promising pathway for a new generation of energy-storage devices with high energy and power densities.

Boris Dyatkin

https://doi.org/10.1557/mrs.2016.284 Published online by Cambridge University Press