Batteries: Recent Advances in Carbon Materials

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We welcome readers to this Special Issue of *C*. From the standpoint of economics of energy storage, carbon electrodes offer the practicality of large-scale applications with the promise of improved performance. Key to increases in energy storage and power delivery are the heterogeneous electron transfer (HET) rates with dissolved redox species. Perhaps the most common allotrope of carbon, graphite suffers from slow HET kinetics across its basal plane. Two papers in this issue specifically examine the HET rates for carbon electrodes with aqueous redox species. One study examines the HET rate with $V^{3+/2+}$ for application in the proposed application of the vanadium redox flow battery [1]. The carbon material of this investigation, GUITAR (Graphene from the University of Idaho Thermolyzed Asphalt Reaction) superficially resembles a crystalline graphite but with much improved HET kinetics across its basal plane. Paradoxically, it was found that parasitic hydrogen evolution reaction rates were slower on GUITAR's basal plane relative to graphite's. The second paper examines various carbon materials in the application of mediatorless sulfide sensing [2]. An edge plane material, glassy carbon (GC) and carbon screen printed electrodes (SPE) proved to be kinetically the fastest in the electro-oxidation of sulfide when compared with other carbon materials. The basal plane graphite electrode was voltammetrically non-responsive towards sulfide. Sensor fouling by irreversible sulfide adsorption afflicted both GC and SPE, however the latter offers the ability of one-shot disposable analyses with greater reproducibility over the former.

The importance of carbon materials in batteries cannot be underemphasized, especially in the area of ion intercalation anodes. It is remarkable that the lithium ion battery has seen its energy density increase by a few hundred percent since its introduction in 1991 with the market growing to over $20 billion (2016) in the US alone. Applications range from personal electronic devices, automotive to grid-level storage. The Li ion graphite anode offers a theoretical storage capacity of 372 mA·h/g. There is ongoing research into the materials that offer an increase over that quantity while maintaining cycling capacity. Bhat et al. describe the formation of B–C–N ceramics as lithium ion intercalation anodes. The BC_4N material demonstrates a stable capacity of 500 mA·h/g over 135 cycles [3]. While the Li ion storage mechanism is not fully characterized, the authors hypothesize that boron can act as an electron acceptor giving fast Li ion diffusion through the disordered network of doped carbon. Sodium ion offers a cost-effective alternative to Li^+. The review in this issue offers insights into the considerations for sodium ion anodes [4]. As Na is a larger ion, it is less favorable to insertion than Li. The d_{002} spacing (i.e., between graphene layers) of graphite is 3.34 Å. This review explores the literature aimed at increasing that spacing with empirical methods of deriving carbons from biomasses. Also discussed is the micro/nanostructures that enable better performance of Na ion intercalation. Such consideration for nanostructures still influences Li ion intercalation performance. A review by Kang et al. examines efforts at constructing 3D networks of nanocarbon materials [5]. Many of these 3D structures exceed the graphite's storage capacity of 372 mA·h/g. Such performance is based on carbon hybrid materials. Many materials exceed graphite in charge capacity. For example, silicon nanowires have the highest known theoretical charge capacity of 4200 mA·h/g [6]. However, large volumetric changes in Si cause capacity fading [7]. Kang et al. describe the considerable efforts being made to develop hybrid materials with the nanostructure and porosity that can withstand these volumetric changes [3]. This issue provides a sample of the efforts towards the application of carbon to batteries.

The efforts described in this issue of *C* indicate that the promise of carbon in this application is being met and will continue with more innovations.

References

1. Kabir, H.; Gyan, I.O.; Foutch, J.D.; Zhu, H.; Cheng, I.F. Application of GUITAR on the Negative Electrode of the Vanadium Redox Flow Battery: Improved $V^{3+/2+}$ Heterogeneous Electron Transfer with Reduced Hydrogen Gassing. *C* **2016**, *2*, 13. [CrossRef]
2. Thakur, B.; Bernalte, E.; Smith, J.P.; Linton, P.E.; Sawant, S.N.; Banks, C.E.; Foster, C.W. The Mediatorless Electroanalytical Sensing of Sulfide Utilizing Unmodified Graphitic Electrode Materials. *C* **2016**, *2*, 14. [CrossRef]
3. Bhat, S.; Sasikumar, P.V.W.; Molina-Luna, L.; Graczyk-Zajac, M.J.; Kleebe, H.-J.; Riedel, R. Electrochemical Li Storage Properties of Carbon-Rich B–C–N Ceramics. *C* **2016**, *2*, 9. [CrossRef]
4. Górka, J.; Vix-Guterl, C.; Matei Ghimbeu, C. Recent Progress in Design of Biomass-Derived Hard Carbons for Sodium Ion Batteries. *C* **2016**, *2*, 24. [CrossRef]
5. Kang, C.; Cha, E.; Patel, M.D.; Wu, H.F.; Choi, W. Three-Dimensional Carbon Nanostructures for Advanced Lithium-Ion Batteries. *C* **2016**, *2*, 23. [CrossRef]
6. Chan, C.K.; Peng, H.; Liu, G.; McIlwarth, K.; Zhang, X.F.; Huggins, R.A.; Cui, Y. High-performance lithium battery anodes using silicon nanowires. *Nature Nanotech.* **2008**, *3*, 31–35. [CrossRef] [PubMed]
7. Gao, Y.F.; Zhou, M. Strong stress-enhanced diffusion in amorphous lithium alloy nanowire electrodes. *J. Appl. Phys.* **2011**, *109*. [CrossRef]