Bromomethylation of carbon: A versatile synthetic building block for functional surfaces

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A novel bromomethylation procedure for carbon materials has been investigated. Activated carbon (AC) can be bromomethylated efficiently and reproducibly under relatively mild conditions using easy to handle, commercially available reagents, resulting in reproducible surface Br loadings of 1.2 mmol g^{-1}. The resulting material, Br-AC, displays excellent stability over the course of months when stored under ambient conditions. Further functionalization of Br-AC by substitution reactions with variety of nucleophiles proceeds efficiently. Example nucleophiles include azide, amines, ammonia, and iodide and exhibit high conversion yields (typically > 90 %). We show that other carbon materials including ordered mesoporous carbon (CMK3), XC-72R (Vulcan), and two types of Ketjenblack (KB300 and KB600) can undergo this reaction and exhibit similar characteristics to Br-AC.

To demonstrate the utility of the bromomethylation reaction, we employed this two-step functionalization scheme in the context of lithium-sulfur (Li-S) batteries. Bromomethylated Vulcan and CMK3, Br-Vulcan and Br-CMK3, were functionalized with diallylamine (All_2NH) and ethylenediamine (EN), which were used as the conductive additives for the sulfur cathode. The presence of surface-bound All_2NH allows for the polymerization of sulfur directly on the carbon surface (Figure 1) while the grafted polar EN groups allow for improved polysulfide retention [1, 2]. Cathodes derived from the amine-functionalized carbons demonstrate enhanced capacities and cyclability compared to their unfunctionalized precursors. These preliminary results provide proof of principle of the versatility of bromomethylated carbons as a useful feedstock for a variety of functional materials.

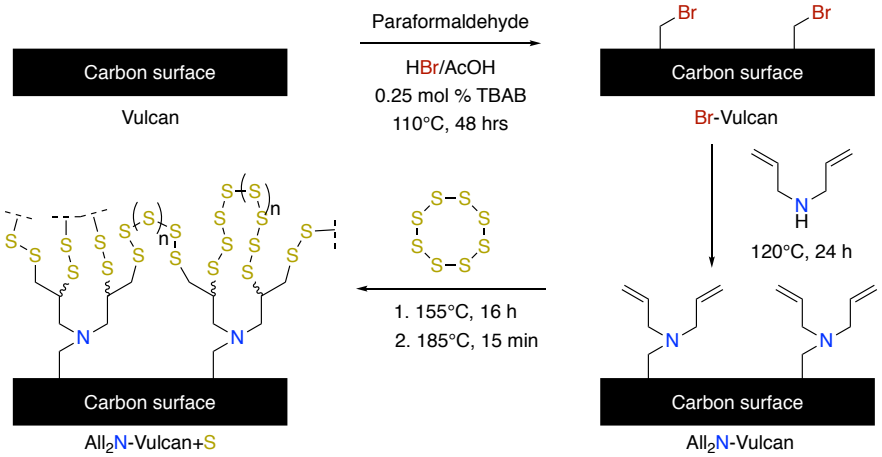

Figure 1. Preparation of surface-polymerized sulfur via Br- and All_2N-Vulcan.

References:

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[2] Chung WJ, Griebel JJ, Kim ET, Yoon H, Simmonds AG, Ji HJ, et al. The use of elemental sulfur as an alternative feedstock for polymeric materials. Nat Chem. 2013;5:518-24.