Surface oxidized mesoporous carbons derived from porous silicon as dual polysulfide confinement and anchoring cathodes in lithium sulfur batteries

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HIGHLIGHTS

- Porous silicon is a new versatile platform for templating high porosity carbons.
- Oxidized carbons are demonstrated to enhance polar binding of soluble polysulfides.
- Oxidized mesoporous carbon enables physical and chemical polysulfide confinement.
- Measured 81% capacity retention after 100 cycles at 0.2 C.

GRAPHICAL ABSTRACT
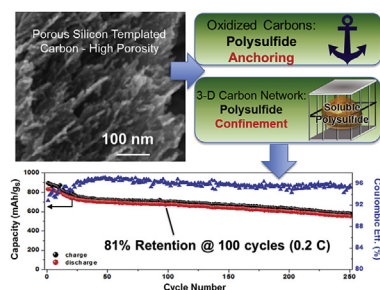
ARTICLE INFO

ABSTRACT

Despite widespread focus on porous carbons for lithium-sulfur battery cathode materials, electrode design to preserve mass-specific performance and sustained extended cycling stability remains a challenge. Here, we demonstrate electrochemically etched porous silicon as a sacrificial template to produce a new class of functional mesoporous carbons optimized for dual chemical and physical confinement of soluble polysulfides in lithium-sulfur battery cathodes. Melt infiltration loading of sulfur at 60 wt% enables initial discharge capacity of 1350 mAh/g_{sulfur} at rates of 0.1 C - approaching theoretical capacity of 1675 mAh/g_{sulfur}. Cycling performance measured at 0.2 C indicates 81% capacity retention measured over 100 cycles with 830 mAh/g_{sulfur} capacity. Unlike other carbons, this template combines structural properties necessary for sulfur containment and polysulfide confinement to achieve high specific capacity, but also boasts surface-bound oxygen-containing functional groups that are able to chemically anchor the soluble Li_2S_n species on the interior of the mesoporous carbon to sustain cycling performance. In turn, this elucidates a scalable and competitive material framework that is capable, without the addition of additional membranes or inactive anchoring materials, of providing the simultaneous anchoring and confinement effects necessary to overcome performance limitations in lithium sulfur batteries.

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1. Introduction

Lithium sulfur batteries are poised as a technology to provide a midpoint between the energy storage capability of lithium-ion batteries, and emerging batteries that have promise to compete with the energy density of fossil fuels. This advance is critical due to the increasing reliance of modern technology on portable power storage [1]. The most primitive design of a lithium-sulfur battery incorporates an elemental sulfur cathode and lithium metal anode which exhibits a high theoretical energy density (2600 Wh/kg [2]) with the inherent benefit of the low cost and earth abundance of sulfur. However, practical routes to achieve lithium-sulfur batteries based on complete conversion of elemental sulfur to lithium sulfide have proven to be quite challenging due to three major issues 1) large volumetric expansion 2) poor electrical conductivity and 3) polysulfide stability in electrolyte [3]. This has led to an immense interest in using carbon as a backbone material for cathodic sulfur loading since lightweight carbons can be produced with high porosity, carbons are natively conductive, and high sulfur loading of carbons can enable total electrode capacities that significantly surpass traditional lithium-ion cathodes.

Among the most studied materials are mesoporous carbons. Early studies by Ji et al. demonstrated a mesoporous carbon composite cathode by melt diffusing CMK-3 with 70 wt% S. The cathode was capable of delivering high capacity of 1320 mAh/g, but with durability only analyzed over 20 cycles [4]. Subsequent efforts with mesoporous carbons exhibit high capacity with rapid linear decay of storage capacity that has provided a bottleneck for these materials [5–8]. This capacity fade is attributed to polysulfide shuttling, where elemental sulfur (stored as S_8 crystals) is reduced to the soluble S_6^{2-} (bound to $2Li^+$) state during the multistep transition to lithium sulfide. If out-diffusion of the soluble compound (Li_2S_6) is permitted from the cathode side, fouling of the lithium metal anode can occur leading to rapid loss of storage capability [2]. Whereas some attempts have been made to address this through electrolyte additives [9], recent efforts have mostly been aimed toward materials-level approaches to mitigate these challenges.

The first of these approaches employs an interlayer between the cathode and separator to trap dissolved polysulfides near the cathode and instigate precipitation on the cathode before formation of the final discharge product Li_2S [10,11]. This strategy shows enhanced cycling performance but requires addition of mass and volume with the interlayer as added element in device configuration. Recent work has shown the ability to achieve high areal loadings of sulfur (>16 mg/cm^2) with the use of this interlayer approach [12] although whether the use of interlayers can be competitive on the benchmark of mass-specific performance, which is the current standard benchmark of the battery industry, remains a challenge. Another strategy for preventing polysulfide dissolution is sulfur encapsulation using synthesized constructs such as yolk-shell structures [13,14], graphene wrapping [15,16], and microporous carbons [5–7,17–26]. Encapsulation in microporous carbon is most commonly carried out in carbide derived carbon materials due to the uniform micropore sizes (<2 nm) that arise based on removal of metal clusters from the carbide which are interconnected through mesoporous networks [19]. Building on this approach, recent efforts have proposed that confinement in *ultra-small* pores (<0.5 nm) can prevent the formation of soluble Li_2S_6 [27–30] which can improve performance. Most recently, anchoring materials with polar surface characteristics such as metal oxides [31–34] and functionalized carbon materials [35,36] have been demonstrated to pin soluble polysulfide species to the cathode and reduce capacity fade [26]. However this requires use of heavy metal oxides resulting in low sulfur loading or expensive material processing. Overall, current efforts build upon either

structural or chemical roles of confinement in sulfur cathode materials, leading to an emerging research area that can simultaneously combine these confinement strategies into the framework of a single electrode material.

In this spirit, our work demonstrates a new family of mesoporous carbon materials that are derived from porous silicon and unlike other reports on mesoporous carbons, *simultaneously* exhibit both structural confinement and chemical anchoring of soluble polysulfides for lithium sulfur batteries. Defective carbons are directly grown in a self-limiting manner onto porous silicon templates, and the porous silicon is dissolved in aqueous basic (saltwater) conditions to yield mesoporous carbons with structural features correlated to the porous silicon template, and surface chemical features dictated by the material synthesis. Unlike other routes to produce mesoporous carbons such as carbide-derived carbons, our work enables a route to decouple the carbon chemical properties and the structural properties in the framework of scalable low-cost processing based on conventional semiconductor manufacturing techniques. In this manner, low-cost and scalable silicon processing can be extended to form templates that can be thermally treated with hydrocarbons (in parallel to combustion processes used to make cheap carbons such as carbon black) and rapidly dissolved in water. Unlike carbide-derived carbons, this provides a true templating approach due to the self-limited growth of carbon on the template, and highly tunable nano- and microscale features building upon over five decades of demonstrated structural control of porous silicon fabrication, which is more versatile than the processing of micron sized spherical particles possessing mesopores used for other mesoporous carbons [4,6,19,20]. We demonstrate high initial capacity and excellent capacity retention of these cathode materials approaching key cathodic performance targets that arises from a two-fold strategy to inhibit polysulfide shuttling.

2. Experimental

2.1. Sample preparation

2.1.1. Porous carbon preparation

Porous silicon was formed through electrochemical etch of highly boron doped (p++) silicon wafers using an AMMT porous silicon etching system. The etch applied was 60 mA/cm^2 current density for 100 s in 8:3 (v:v) ethanol, hydrofluoric acid (50% water by volume Sigma Aldrich) electrolyte. The wafer was then fully rinsed in ethanol and then loaded into a Lindberg Blue 1″ tube furnace for carbon growth by chemical vapor deposition (CVD). The furnace was ramped to 650 °C under 1 SLM of Ar and 200 SCCM of H_2. Then 10 SCCM of C_2H_4 is allowed to flow as the furnace ramps to 750 °C. Upon reaching 750 °C the temperature is maintained for 10 min and then ramped to 850 °C and held for 10 min. The acetylene was then turned off and the system is allowed to cool to room temperature under hydrogen and argon. After removing the sample from the tube furnace it is heated to 60 °C in a 2 M solution of NaOH for 48 h. The freestanding carbon flakes are washed in nanopure water while monitoring pH until the solution is neutral. The material are allowed to rest in a water bath for 1 h and exchanged once. The water is then removed and material suspended in ethanol. The carbon and ethanol solution is probe sonicated for 2 min to form uniformly sized particulates. The solution is centrifuged for 15 min at 9000 rpm and the ethanol is removed leaving micron scale mesoporous carbon flakes in powder form.

2.1.2. Porous carbon/sulfur composite preparation

This powder is then mixed with elemental sulfur in a 1:3 ratio and heated just above the melting point of sulfur 120 °C for 6 h. The