



Graphene derived carbon confined sulfur cathodes for lithium-sulfur batteries: Electrochemical impedance studies



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ABSTRACT

Sulfur nanocomposites are prepared by using graphene derived carbon (GDC), with controlled porosity characteristics, as confining matrix and are studied as efficient cathodes for lithium-sulfur (Li-S) batteries. To understand the effect of micro-/mesoporosity in porous carbon for the effective encapsulation of sulfur and polysulfides towards improved Li-S battery performance, two different GDC samples with controlled porosity characteristics, one with predominantly micropores (GDC-1) and a surface area of $1970 \text{ m}^2 \text{ g}^{-1}$ and the other with a surface area of $3239 \text{ m}^2 \text{ g}^{-1}$, having more or less equal contribution of micro- and mesopores (GDC-2), are used to synthesize nanocomposite sulfur electrodes following melt diffusion process. Electrochemical studies are carried out by using cyclic voltammetry, galvanostatic charge/discharge cycling and electrochemical impedance spectroscopy (EIS). EIS spectra collected at different depth of discharge (DOD) in the first cycle as well as upon cycling give valuable insights into the Li-S redox reactions and capacity fading phenomena in these electrodes. The impedance response of GDC-S electrodes suggests a detrimental effect of the mesopores, where insoluble reaction products can easily accumulate, resulting in the loss of active material leading to capacity fading of Li-S cells.

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1. Introduction

Lithium-sulfur (Li-S) batteries are under intense scrutiny for the last few decades due to the high theoretical specific capacity (1.675 Ahg^{-1}) and energy density (2600 Whkg^{-1}) of sulfur, which are three to five times higher than those of the state-of-the-art Li-ion batteries [1–4]. In addition, sulfur is non-toxic, inexpensive, naturally abundant and environmentally benign. Despite all these factors, wide scale commercial implementation of Li-S batteries is still hampered by reduced cycle life associated with the detrimental effects of electrolyte soluble higher order polysulfides (Li_2S_x , $x = 4-8$), leading to active material loss, capacity fading, and self-discharge. Apart from this, other factors such as the insulating nature of sulfur and Li_2S discharge products and large volumetric expansion (80%) of sulfur upon lithiation affect the performance of these electrodes [2–6]. Significant efforts have been made to

address some of these problems, for instance, (i) forming composites of sulfur with conductive matrices such as graphene, [7–12] carbon nanotubes (CNT), [11–13] conductive polymers [14,15] and various porous and activated carbon materials, [16,17] to improve the electronic conductivity and to serve as a polysulfide reservoir, [11,12,18,19] and (ii) modifying the electrolyte composition and cell configurations [19–24]. However, a systematic investigation of the electrochemical processes is very essential to further explore the various other possibilities to improve the cycling performance and rate capability of the Li-S cell.

Here, we present detailed studies on the electrochemical properties of graphene derived carbon-sulfur (GDC-S) nanocomposite cathodes for Li-S battery. Highly porous graphene derived carbon, obtained through chemical activation of few layer thermally exfoliated reduced graphene oxide (rGO) sheets [25,26] with a good BET surface area ($561 \text{ m}^2 \text{ g}^{-1}$), [27] provides large active microporous sites to accommodate sulfur resulting in enhanced electrochemical performance of the nanocomposite cathode. To understand the effect of micro/meso-porosity in porous carbon for the effective encapsulation of sulfur and polysulfides towards improved Li-S battery performance, two different GDC samples with controlled porosity characteristics, one

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with predominantly micropores (GDC-1) and a surface area of $1970\text{ m}^2\text{ g}^{-1}$ and the other with a surface area of $3239\text{ m}^2\text{ g}^{-1}$, but having more or less equal contribution of micro- and mesopores (GDC-2), are used to synthesize nanocomposite sulfur electrodes following melt diffusion process [3,16]. Detailed electrochemical studies have been performed on these nanocomposite electrodes by using cyclic voltammetry and galvanostatic cycling. Further, an attempt has been made to understand the redox reaction mechanism in these systems employing electrochemical impedance spectroscopy (EIS). EIS is a very powerful electro-analytical tool for studying kinetics in different electrochemical systems and has been used to study the electrochemical behaviour of Li-S cells by several groups [28–32]. However, data reported in literature are often collected in two-electrode cell configurations. As it is known that Li metal can severely affect the impedance response of a cell, EIS measurements have been carried out in the three-electrode configuration. EIS spectra were collected at different depth of discharge (DOD) in the first cycle, as well as upon further cycling.

2. Experimental section

2.1. Materials synthesis and characterization

Two different graphene derived porous carbon samples (GDC-1 and GDC-2) were prepared from graphite oxide (GO), through thermal exfoliation followed by a finely controlled KOH chemical activation, as described in details elsewhere [27,33]. Briefly, graphite oxide (GO) was synthesized by oxidising graphite powder (Bay carbon) in a strong acidic medium using an improved Hummer's method [33]. Thermally exfoliated graphene oxide (TEGO) was then prepared from the as-synthesized GO following thermal treatment at $300\text{ }^\circ\text{C}$ for 10 min under ambient air. Activation procedure involves the mixing of TEGO (800 mg) with 7 M KOH aqueous solution (40 ml) and stirring for 6 h at room temperature at 800 rpm, followed by another 20 h of static soaking in ambient conditions. The extra KOH solution was removed by filtering the mixture through a polycarbonate membrane (Whatman, $0.2\text{ }\mu\text{m}$); then the mixture was dried at $65\text{ }^\circ\text{C}$ for 24 h. The dried TEGO-KOH mixture was then transferred to an alumina boat and heated at $800\text{ }^\circ\text{C}$ for 1 h under argon flow (170 sccm) in a quartz reactor (50 mm diameter). The temperature was increased from room temperature to $800\text{ }^\circ\text{C}$ at a ramp rate of 5° per min. Two samples were prepared under different conditions. For GDC-1, the activation was carried out under flowing argon gas (170 sccm) for 1 h without applying vacuum. For GDC-2, the reactor was initially evacuated to 10^{-3} bar for 30 min, followed by the argon flow. The annealing temperature and argon flow rate was kept unchanged under both conditions. The samples were allowed to cool down gradually and were later washed repeatedly with de-ionized water, until pH of final washing solution reached ~ 7 . The samples were then dried at $65\text{ }^\circ\text{C}$ in ambient air for 4 h followed by vacuum drying at $120\text{ }^\circ\text{C}$ for 24 h [27]. The GDC-S nanocomposite was synthesized from the as-prepared GDC samples following a melt-diffusion strategy [16]. For this, both GDC and sulfur were ground together in an agate mortar in the weight ratio 1:3 and the mixture was heated at $155\text{ }^\circ\text{C}$ for 6 h under argon flowing at 100 sccm . The heating ramp rate was maintained at 5° per min.

GDC and GDC-S nanocomposites were characterized by using various analytic and spectroscopic techniques including powder X-ray diffraction (XRD) (Empyrean, PANalytical XRD instrument with Cu-K α radiation, $\lambda = 1.54\text{ \AA}$), X-ray photoelectron spectroscopy (Kratos Analytical Axis Ultra), Raman spectroscopy (LabRAM HR Raman spectrometer – HORIBA Jobin-Yvon with 632 nm laser beam), FT-IR spectroscopy (IR Prestige-21, FT-IR SHIMADZU), Scanning electron microscopy (Nova NanoSEM 450, FEI) and Transmission electron microscopy (Tecnai G2 TF20 – ST electron

microscope, 200 kV). Thermogravimetric analysis (TGA) was performed at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ using the SDT Q600 Thermogravimetric analyser (TA Instruments) under N_2 atmosphere. Electrical conductivity measurements were performed on GDC samples using four-probe method.

2.2. Surface area and porosity measurements

Porosity characteristics of the sample, including Brunauer-Emmet-Teller (BET) surface area, total pore volume, pore size distribution were analysed using N_2 adsorption/desorption isotherms measured at 77 K up to a maximum relative pressure of 1 bar with the 3-Flex surface characterization analyser (Micromeritics). Prior to the N_2 adsorption measurements, the GDC samples were degassed at $350\text{ }^\circ\text{C}$ under vacuum for $\sim 12\text{ h}$ in a separate vacuum degassing unit followed by in-situ degassing at $300\text{ }^\circ\text{C}$ for 3 h under turbomolecular pump vacuum ($\sim 10^{-12}$ bar) at the sample ports to remove the adsorbed impurities and water content from the sample and to make the surface active for N_2 adsorption. For GDC-S nanocomposites, the degassing procedure was carried out at $60\text{ }^\circ\text{C}$ for $\sim 12\text{ h}$ in the vacuum degassing unit. In addition to this, degassing under high vacuum conditions was also performed at the sample ports ($60\text{ }^\circ\text{C}$ for 3 h). Owing to the volatility of sulfur, high temperature activation was not performed for GDC-S nanocomposite material [6]. From the N_2 isotherms, specific surface area was measured in the relative pressure range of 0.05 to 0.3, according to the BET method. The pore volume and the pore area distributions in the micro and meso ranges were obtained by non-local density functional theory (NLDFT) calculations in which carbon slit like pore geometry was assumed. Meso pore size distribution was also deduced from the BJH (Berrett, Joyner and Halenda) and Dollimore Heal (DH) methods with Harkins and Jura correction. In addition to NLDFT, micropore distribution was determined from Horvath – Kawazoe (HK), Dubinin-Astakhov (DA), t-plot and α_s plot methods as well. The total pore volumes of all the samples were calculated from the amount of N_2 gas adsorbed by the material at a relative pressure of 0.990.

2.3. Electrochemical measurements

Positive electrodes were fabricated by mixing the GDC-S nanocomposite, conductive carbon (Super P), and polyvinylpyrrolidone (PVP) binder in the weight ratio 8:1:1. A slurry containing the above mixture, prepared by using N-methyl-2-pyrrolidinone (NMP) as solvent, was spread on to an aluminium foil ($15\text{ }\mu\text{m}$ thickness) using the Hohsen minicoater (Model MC20). The electrodes were dried at $65\text{ }^\circ\text{C}$ for 1 h followed by vacuum drying at $60\text{ }^\circ\text{C}$ for 24 h. Punched electrodes of 14 mm diameter were then roll pressed using a rolling press (MSK-HRP-MR100A, MTI Corporation) to get electrodes with uniform thickness and mass loading. Typical sulfur loadings of $1.0\text{--}1.2\text{ mg cm}^{-2}$ were maintained during electrode preparation. A lithium foil was used as the negative electrode and Whatman glass fibre filter as the separator. A solution of 1 M lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) in a mixture of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) ($v/v = 1:1$) with 2 wt.% LiNO_3 additive was used as the electrolyte. Standard CR2032 coin cells were assembled in an argon filled glove box (MBRAUN, UNILab, Germany) and the electrochemical characterization was performed using cyclic voltammetry (CV), galvanostatic cycling and rate capability tests.

Electrochemical impedance spectroscopy (EIS) studies were conducted by fabricating Li-S test cells in the 3-electrode configuration (Swagelok T-cell) with lithium foil as the reference and counter electrodes. All the measurements were performed at $20\text{ }^\circ\text{C}$ in the voltage range between 1.7 V to 3 V vs Li^+/Li using a

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