

S/C Composites with Different Carbon Matrices as Cathode Materials for Metal–Sulfur Batteries [†]

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Abstract: This work is devoted to a comparative study of the electrochemical properties of S/C composites with different carbon matrices, namely, carbon nanotubes, mesoporous carbon and N-doped carbon nanoflakes, as cathode materials for lithium–sulfur and sodium–sulfur batteries. The best among the investigated samples was the composite based on sulfur and mesoporous carbon (S/MC) due to the partial encapsulation of the sulfur into the pore of the mesoporous carbon. The first-cycle discharge capacities of S/MC in the Li-S and Na-S battery cells were 1247 and 323 mAh·g^{−1}, respectively. The discharge capacities of S/MC in the Li-S and Na-S battery cells after 10 cycles were 270 and 235 mAh·g^{−1}, respectively.

Keywords: lithium–sulfur batteries; sodium–sulfur batteries; cathode material; sulfur; carbon



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1. Introduction

Metal–sulfur battery technology promises an energy storage capacity that is much higher than that of common Li-ion commercial batteries (the theoretical capacities of lithium, sodium and sulfur amount to 3860, 1165 and 1672 mAh/g, respectively). Sulfur undergoes a conversion reaction and forms lithium or sodium polysulfides [1–3], allowing for a larger accommodation of two ions and electrons per sulfur atom [2,4]. At the same time, sulfur is a non-toxic, abundant and low-cost element. This explains the interest in lithium–sulfur batteries and sodium–sulfur batteries, which are capable of operating at room temperature (RT-Na/S batteries). Unfortunately, few issues are still hindering their commercialization. Among them, the low electrical conductivity of sulfur, significant change in the volume of the cathode during the discharge/charge process and migration of soluble polysulfides of alkali metal between electrodes should be mentioned [3,5]. In this regard, in recent years, much attention has been paid to the development of materials for metal–sulfur batteries. Among the above-mentioned problems, the mitigation of the shuttle effect is the most important. To overcome this problem, such approaches as composite cathode formation, covalent sulfur bonding, the use of electrocatalyst-containing cathodes and the insertion of an interlayer or selective separators are used [5,6].

This work is devoted to a comparative study of the electrochemical properties of S/C composites with different carbon matrices, namely, carbon nanotubes (CNTs), mesoporous carbon (MC) and N-doped carbon nanoflakes (N-CNFs), as cathode materials for lithium–sulfur and sodium–sulfur batteries.

2. Methods

Carbon nanotubes (Taunit-MD) and mesoporous carbon were industrially obtained (NanoTechCenter LTD, Russia). The synthesis of N-doped carbon nanoflakes is described elsewhere [7]. Carbon materials were purified from the remains of the catalyst used in the synthesis according to the manufacturer's procedures: materials were suspended in 30% (by weight) HNO_3 in a 1:8 weight ratio, and the suspension was kept for 1 h at 90 °C with continuous stirring. After that, they were washed with a large amount of water to neutral pH and dried in air for 24 h at 90 °C.

Sulfur-loaded composite materials with carbon were prepared using the conventional melt diffusion method. The prepared MC, CNTs and N-CNFs were ground with elemental sulfur in a mass ratio of 1:1. They were mixed well and placed in a glove box filled with argon for 10 min. The reaction was carried out in a Teflon-lined reactor at 155 °C for 20 h. Finally, the samples S/MC, S/CNT and S/N-CNF were obtained.

An X-ray diffraction (XRD) analysis was performed with the use of a Rigaku D/MAX 2200 diffractometer ($\text{CuK}\alpha$). The XRD patterns were analyzed using Rigaku Application Data Processing software. A microstructure analysis of the samples was performed using a scanning electron microscope (SEM) TESCAN AMBER GMH. The specific surface area was studied using the BET method with a Sorbtometr-M analyzer (LLC Katakoni). The samples were degassed at 200 °C for 1 h prior to the measurement. Raman spectra were collected using a DXRxi Raman Imaging Microscope (Thermo Fisher Scientific). A 532 nm laser with a power of 0.2–0.6 mW was used.

The electrochemical testing of the S/C composites was carried out in sealed three-electrode cells with lithium (or sodium) as counter and reference electrodes. The working electrodes were manufactured using standard casting technology. The active paste was prepared by mixing the S/C composite with carbon black (Ketjen Black) and polyvinylidene fluoride (Kynar) dissolved in N-methyl-2-pyrrolidone (NMP) with a mass ratio of 85/10/5. The slurry was coated on a stainless steel substrate and then dried in a vacuum oven at 50 °C until NMP evaporation. The electrodes were pressed under a 1000 kg/cm² pressure and then vacuum-dried at 50 °C for 16 h. The electrochemical cells were assembled in a high-purity argon-filled glove box with the content of water and oxygen ≤ 1 ppm (Spectroscopic Systems) using a non-woven polypropylene separator. Then, 1 M Li_2NH in a dioxolane/dimethoxyethane (1:1 by volume) or 1M NaClO_4 in a triglim was used as the electrolyte. The water content in the electrolyte measured using Fischer titration (917 Coulometer, Metrohm) did not exceed 30 ppm. The cyclic voltammetry (CV) results were obtained with a P-20X potentiostat (Elins) at a scan rate of 0.1mV/s. The values of capacity were calculated on the content of sulfur.

3. Results and Discussion

The specific surface areas of the carbon materials used in this work for S/C composite formation are equal to 3200, 270 and 1028 m²*g⁻¹ for MC, CNT and N-CNF, respectively. In the Raman spectra of MC and N-CNF, an intensive band with a maximum intensity at $\sim 1590\text{ cm}^{-1}$ can be assigned to the G-band of crystalline graphite (sp^2 -hybridized carbon) and the band at $\sim 1350\text{ cm}^{-1}$ can be assigned to the D-band of disordered graphite. In addition to these, two wide bands can be distinguished around 1200 and 1500 cm^{-1} , corresponding to carbon fragments with different structures. For example, the band at 1500 cm^{-1} can be assigned to the vibrations of sp^3 -hybridized carbon [8]. The contributions of these additional bands amount to 40% for MC and 47% for N-CNF. This indicates that the carbon coating is represented mainly by sp^2 -hybridized carbon. The ratio of the integral intensities of the D- and G-bands can be used to estimate the degree of defectiveness of carbon materials (ID/IG). The ID/IG is lower for MC (2,7 for MC and 3,7 for N-CNF).

The XRD patterns of MC, CNT and N-CNF are presented by a poorly resolved diffraction peak at 2Θ of $\sim 24\text{--}26^\circ$, which can be assigned to the (002) crystallographic plane of graphene. This reflection also can correspond to CNTs [7]. The peak position shifts to the smaller angles in the series CNT, MC and N-CNF, and the interplanar spacing correspond-

ingly increases. The XRD patterns of the S/CNT and S/N-CNF samples are combinations of the XRD patterns of sulfur and the corresponding carbon material of a noticeably lower intensity. The XRD pattern of S/MC contains no peaks of S (Figure 1). The decrease in the intensity or the disappearance of peaks of sulfur can be attributed to the reduced size of the sulfur after the sulfur-loading process and the successful encapsulation of sulfur in the pores of MC for S/MC.

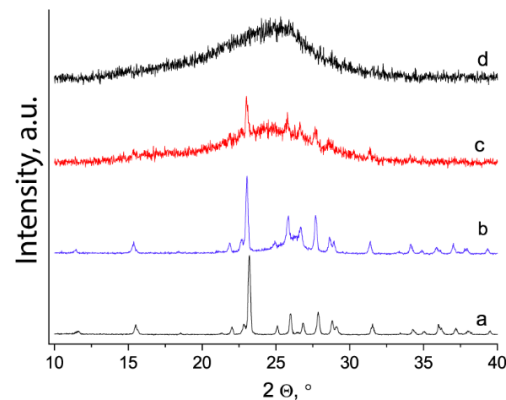


Figure 1. Fragments of XRD patterns of sulfur (a), S/CNT (b), S/N-CNF (c) and S/MC (d) in the region of $2\theta = 10\text{--}40^\circ$.

The obtained SEM images of the samples are presented in Figure 2. In the S/CNT composite (Figure 2a,b), sulfur is distributed rather uniformly over the carbon material, which forms a conductive support. In the S/N-CNF and S/MC samples, one can see both homogeneous regions and agglomerates of sulfur (Figure 2c,d).

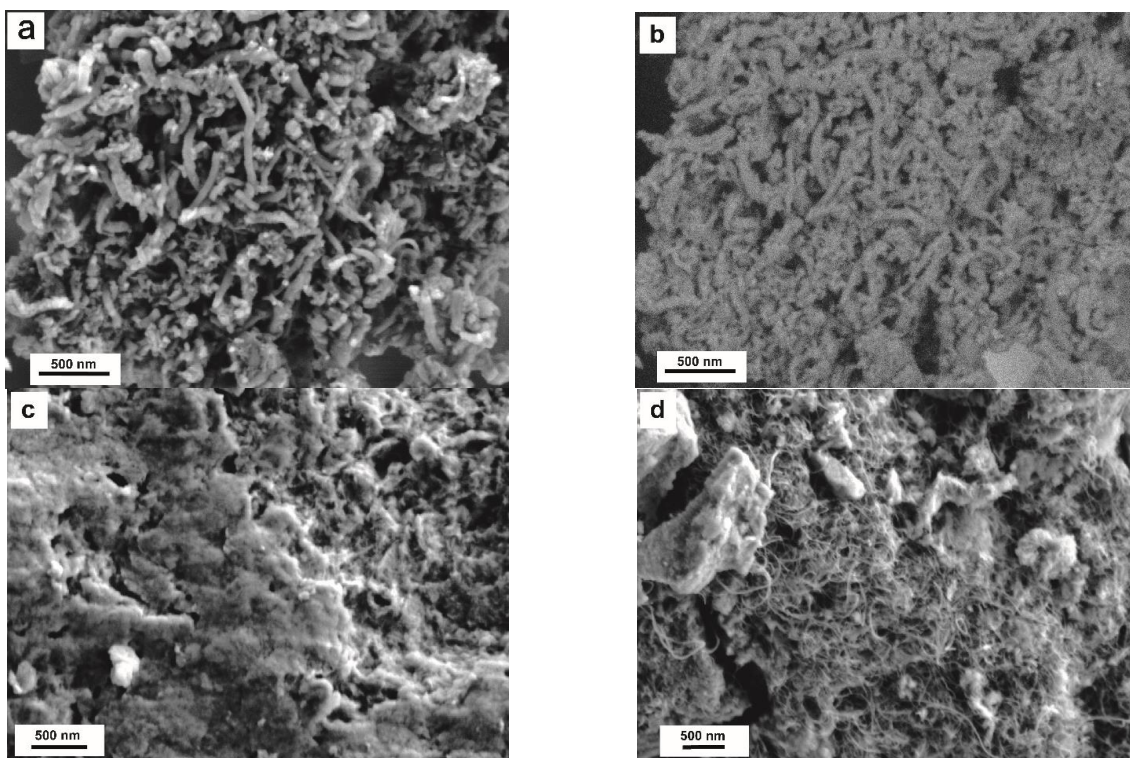


Figure 2. SEM images in the secondary (a,c,d) and backscattered (b) electron modes of the S/CNT (a,b), S/N-CNF (c) and S/MC (d) composites.

The CV measurements for Li-S cells were performed within a potential range of 1.4–3 V. One main anodic peak and two cathodic peaks are caused by the electrochemical conversion of element sulfur and Li-polysulfides, respectively. The typical characteristic peaks of S/MC are displayed in Figure 3a. The CV curves of S/CNT show similar shapes, indicating that the same reaction process and reversible transformations occur. The CV curves of S/N-CNF differ to those of S/MC (Figure 3a). The reduction and oxidation peaks of S/N-CNF occur at lower and higher peak voltages, respectively, than those of S/MC. The peak currents are lower, indicating that the Li-S battery has worse electrochemical reaction kinetics. The discharge capacities of S/MC and S/CNT amount to 1247 and 585 mAh·g^{−1}, respectively. However, the discharge capacity values rapidly decrease during cycling. The discharge capacities are 270 and 237 in the 10th cycle for S/MC and S/CNT, respectively. The decrease in the capacities most likely results from the dissolution of polysulfides and the detachment of active materials. S/MC is the best among the investigated samples due to the partial encapsulation of the sulfur into the pore of the mesoporous carbon. The cyclic performance of S/MC is presented in Figure 3b.

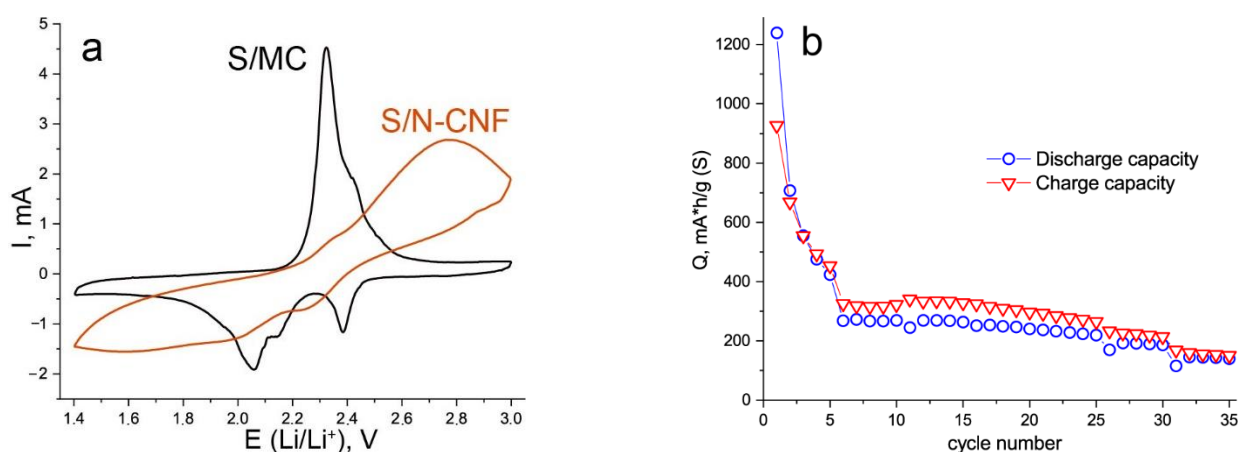


Figure 3. CV curves of S/MC and S/N-CNF (a) and cyclic performance of S/MC (b).

The sample S/MC was tested in a sodium–sulfur cell. The CV measurements for Na-S cells were performed within a potential range of 1–3 V. The CV curves are typical for RT-Na-S batteries and show cathodic waves at ~2.2 and ~1.6 V [3]. There are differences in the anodic waves between the Li-S and Na-S cells. The Na-S cells show two clean-cut oxidation waves at ~1.9 and ~2.4 V. The discharge capacities of S/MC are 323 and 235 mAh·g^{−1} in the 1st and 10th cycles, respectively.

4. Conclusions

S/C composites with different carbon matrices, namely, carbon nanotubes, mesoporous carbon and N-doped carbon nanoflakes, were prepared using the conventional melt diffusion method and tested as cathodes for lithium–sulfur and sodium–sulfur batteries. The best among the investigated samples was the composite based on sulfur and mesoporous carbon (S/MC) due to the partial encapsulation of the sulfur into the pore of the mesoporous carbon. The first-cycle discharge capacities of S/MC in the Li-S and Na-S battery cells were 1247 and 323 mAh·g^{−1}, respectively. The discharge capacities of S/MC in the Li-S and Na-S battery cells after 10 cycles were 270 and 235 mAh·g^{−1}, respectively.

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Conflicts of Interest: The authors declare no competing financial interests.

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