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A Lithium-Ion Sulfur Battery Based on a Carbon-Coated Lithium-Sulfide Cathode and an Electrodeposited Silicon-Based Anode

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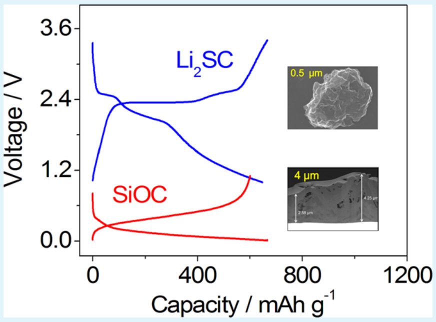
ABSTRACT: In this paper, we report a lithium-ion battery employing a lithium sulfide cathode and a silicon-based anode. The high capacity of the silicon anode and the high efficiency and cycling rate of the lithium sulfide cathode allowed optimal full cell balance. We show in fact that the battery operates with a very stable capacity of about 280 mAh g^{-1} at an average voltage of 1.4 V. To the best of our knowledge, this battery is one of the rare examples of lithium-metal-free sulfur battery. Considering the high theoretical capacity of the employed electrodes, we believe that the battery here reported may be of potential interest as high-energy, safe, and low-cost power source for electric vehicles.



KEYWORDS: *lithium sulfide, silicon composite, lithium metal free, sulfur battery*

1. INTRODUCTION

In recent years, there has been an increasing interest in the widespread of electric vehicles (EVs) and hybrid vehicles (HEVs) with the final goal of reducing the reduction of greenhouse gas emission and atmosphere pollution in large metropolitan areas. Clearly, the success of this operation depends on the availability of an efficient power source for the electric engine. Because of its high energy density, the lithium-ion battery is as an ideal candidate.[1] However, although appropriate for the consumer electronic market, the present lithium-ion battery technology is still inadequate for the electric road transportation one. Improvements in energy density and safety, as well as reduction in cost, are mandatory steps to meet the EV and HEV severe targets.[2,3] To achieve these operative improvements, battery chemistry alternatives to intercalation are required.[4,5] A very promising example is provided by the lithium−sulfur battery, characterized by a conversion chemistry leading to high specific energy, i.e., of about 2600 Wh kg^{-1}, combined with the low cost of the earth abundant sulfur. However, several issues still prevent the practical development of this battery.[6−8] Among others, such as the solubility of polysulfides in the course of the discharge process and the high resistance, almost insulating nature of both reactants and products, a major issue still not satisfactorily solved is in the safety hazard associated with the use of lithium metal as anode. As is well-known, upon cycling in liquid electrolytes the lithium-metal electrode can easily experience dendrite growth with eventual cell shorting accompanying by fire evolution if not explosion.[9] Accordingly, battery manufacturers are quite reluctant to use lithium metal, unless for battery systems using electrolyte media compatible with the metal.[10]

Therefore, the replacement of the lithium metal with an alternative, metal-free anode is mandatory to ensure the practical development of the Li/S battery. Surprisingly, there are not many examples of efficient Li-ion sulfur batteries. A pioneering example is provided by the work of Cui and coworkers who demonstrate the feasibility of replacing lithium with silicon, used in combination with a lithium sulfide cathode.[11] The concept was confirmed by Hassoun and Scrosati who reported a Sn-anode-based, lithium-ion sulfur battery.[12] To the best of our knowledge, not many other papers have been appeared reporting efficient lithium-metal-free/sulfur systems.

In this work, we report a rechargeable lithium-ion battery based on the combination of a high capacity Si−O−C anode with a high-rate Li_2S-MCMB (mesophase carbon micro beads) composite in a tetraglyme electrolyte. We show that this Si/Li_2S battery operates around 1.4 V, delivering a very stable capacity of about 280 mAh g_{Li2S}^{-1} with a resulting theoretical

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energy density of the order 400 Wh kg_{Li2S}^{-1}. We believe that by optimizing the cathode morphology, the energy value of the battery can be further increased.

2. RESULTS AND DISCUSSIONS

2.1. The Li_2S-MCMB Cathode. The operation of "lithium-free" sulfur batteries requires a lithium source. Similarly to the common structure of lithium-ion batteries, the source can be provided by the cathode, there $LiCoO_2$, here Li_2S. The latter has a theoretical capacity of about 1170 mAh g^{-1}; however, Li_2S suffers by the same drawback affecting the sulfur electrode, namely a poorly conducting, almost insulating nature. A proper way to address this issue is the addition of conductive additives, such as carbon, to form Li_2S−C composites.[13,14] Following this trend, we have prepared by ball-milling a Li_2S-MCMB composite to be used as the preferred cathode for our Li-ion/S battery.

Figure 1 shows the FE-SEM images of the pristine Li_2S (Figure 1a), of the MCMB powders (Figure 1b) and of the Li_2S-MCMB composite after 1 h (Figure 1c) and after 16 h (Figure 1d) of high-energy mechanical milling (HEMM). These figures confirm that the micrometric Li_2S and MCMB particles are well mixed after 1 h milling and progressively refined upon the 16 h treatment (see Experimental Section for details). Figure 1e and Figure 1g, h illustrate the STEM and the HR-TEM, respectively, of the final composite. In particular, the image of Figure 1h reveals an amorphous carbon morphology and residual ordered plans due to crystals of lithium sulfide (underlined by yellow circles). In summary, the combination of the images shows that the particles are evenly dispersed in each other, as finally demonstrated by the STEM-EDX of Figure 1f.

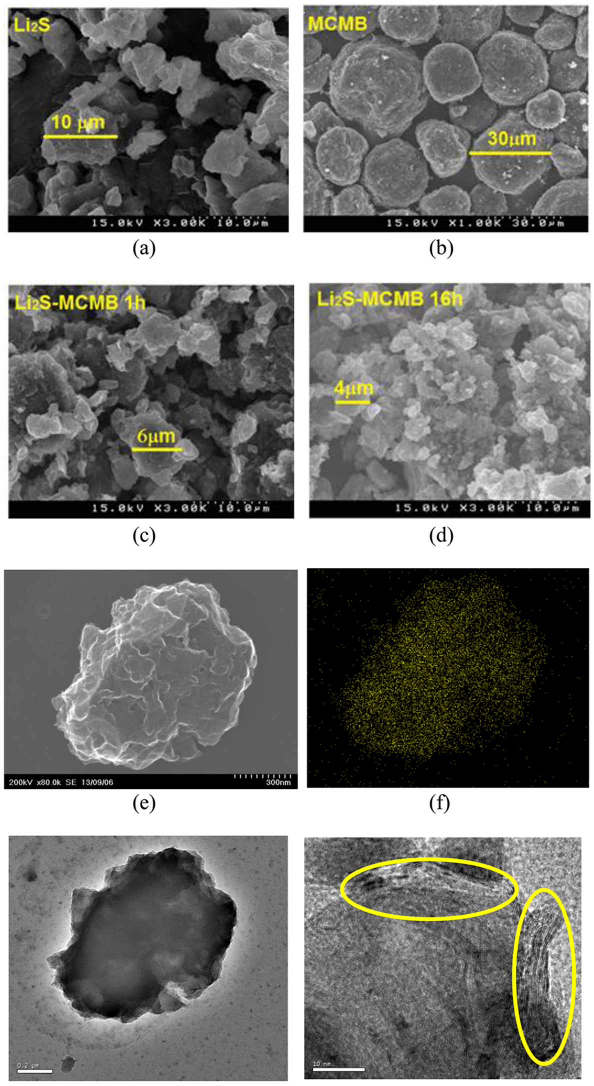


Figure 1. Field-emission scanning electron microscopy (FE-SEM) of (a) Li_2S powder, (b) MCMB powder, Li_2S-MCMB compound upon (c) 1 and (d) 16 h of HEMM; scanning electron microscopy image observed in the (e) STEM mode and (f) energy-dispersive X-ray mapping of the final Li_2S-MCMB composite; (g, h) high-resolution transmission electron microscopy images (HR-TEM) of the Li_2S-MCMB composite.

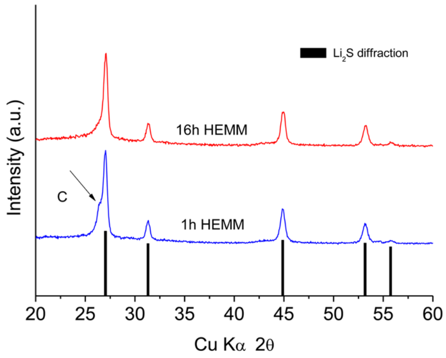
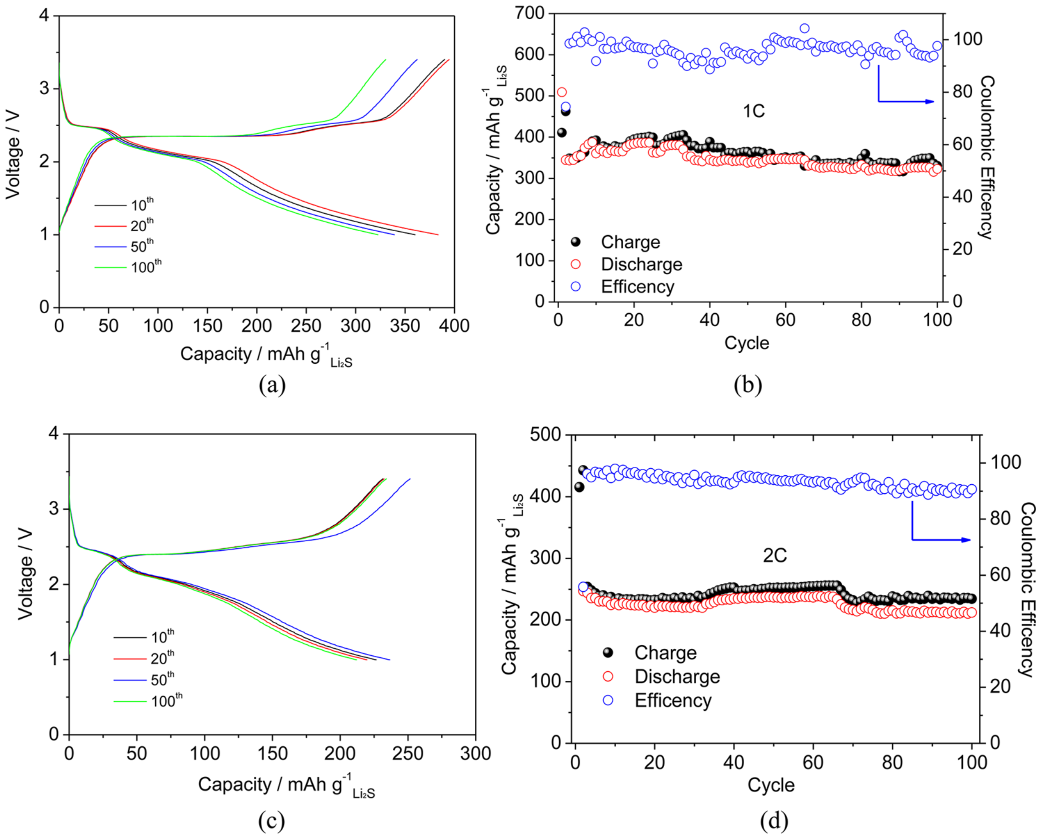


Figure 2. X-ray diffraction of the Li_2S-MCMB after 1 h (red pattern) and 16 h (blue pattern) of HEMM.

Figure 2 reports the X-ray diffraction of the Li_2S-MCMB sample after 1 h (red pattern) and 16 h (blue pattern) of HEMM. The patterns confirm that the crystalline structure of the Li_2S (JCPDS #772145) is preserved upon HEMM and that the peak associated with the crystalline graphite at about 27° (JCPDS #75−2078) indicated with C in the figure, vanishes upon milling, in agreement with the assumptions made on the basis of the HR-TEM result, see Figure 1h.

Figure 3a shows the voltage profiles of the charge (conversion into S and Li)-discharge (reconversion into Li_2S) of the Li_2S-MCMB electrode in a lithium semicell at 1C (1166 mAh g_{Li2S}^{-1}) rate for one hundred cycles. The cycling polarization is lower than that previously obtained with other Li_2S electrodes (typically extending up to 4.0 V),[14] confirming that the morphology here adopted assures an optimized behavior for the Li_2S-MCMB electrode that in fact cycles with an average working voltage of 2.1 V, a good energy efficiency and a stable reversible specific capacity of the order of 350 mAh g_{Li2S}^{-1}, see Figure 3b. The electrode has also a good rate capability, as shown by figures 3c, d, reporting the cycling response at 2C (2332 mAh g_{Li2S}^{-1}). As expected, at the high rate the polarization slightly increases and the capacity decreases to 250 mAh g_{Li2S}^{-1}; however, still with a stable and reproducible trend for over 100 cycles.

2.2. Silicon-Based Electrodeposited Anode. Lithium−silicon alloys are basically very high capacity anode materials and, accordingly, they have been widely studied under a series of configurations and structures.[15−18] In this work, we have directed our attention on an electrode structure formed by silicon electrodeposition on a copper substrate (see Experimental Section).



(a) (b)

(c) (d)

Figure 3. Galvanostatic voltage profiles at the 10th, 20th, 50th, and 100th cycle and cycling behavior of the Li/LiCF$_3$SO$_3$(TEGDME)$_4$/Li$_2$S-MCMB cell at the current rate of (a, b) 1C and (c, d) 2C. Voltage limits: 1.0−3.5 V vs Li. Temperature: 25 °C.

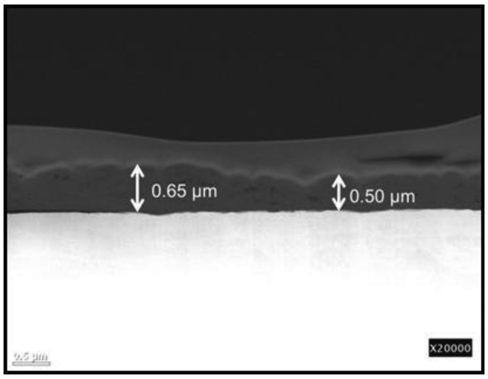


Figure 4. Cross-sectional STEM image of the electrodeposited Si−O−C electrode. Current, 1.0 mA cm^{-2}; charge level, 2.0 Coulomb.

The cross-sectional STEM image of the Si-based electrode upon synthesis, reported in Figure 4, shows that the electrodeposition process leads to a thin-film with a thickness ranging between 500 and 650 nm and containing silicon, oxygen and carbon, with an amorphous Si content of about 60% w:w, as revealed by ICP analysis[19] (data here not reported). We can then refer to this electrode as Si−O−C. The electrochemical properties of Si−O−C have been extensively reported in a previous paper,[19] to which the reader is referred for details. Here we can only recall that Si−O−C cycles in lithium semicells with a discharge (lithium-alloying) capacity of the order of 1000 mAh g^{-1} with a voltage of about 0.1 V. These conditions make our Si−O−C material a valid candidate to be used in combination with the Li$_2$S-MCMB cathode for the development of an efficient, lithium-ion sulfur cell. However, as typical of low-voltage operating electrodes, also the Si−O−C one is defected by a very high initial irreversible capacity resulting from side reactions including solid electrolyte interface film formation.[20−24] An irreversible capacity is an unwanted phenomenon, hence, prior to use in the full cell, the Si−O−C electrode has been treated by direct lithiation, following a procedure proposed by us[25] and by Cui and co-workers.[17]

2.3. Silicon−Lithium Sulfide Battery. The two electrodes above-described are ideal for being combined in a full lithium-ion sulfur battery. The Si−O−C has a low voltage, this assuring a reasonably high overall voltage, and its capacity is about double that of the cathode, this assuring an easy cell balancing, also considering that the irreversible capacity is eliminated by the quoted lithiation process. The Si/Li$_2$S battery is its discharge state, hence its operation requires an initial, "activation" charge process:

$$Li_2S + Si \leftrightarrows Li_{2-x}S + Li_xSi \qquad (1)$$

that is then reversed in discharge and repeated upon cycling as

$$Li_2S + Si \underset{\text{charge}}{\overset{\text{discharge}}{\leftrightarrows}} Li_{2-x}S + Li_xSi \qquad (2)$$

The battery is anode-limited due to the low loading of the silicon-based electrode, i.e., typical characteristic of the electrodeposited samples, and its charge−discharge voltage profiles at a C/5 rate are shown in Figure 5a. The profiles match the signature expected by process 2, evolving with an average voltage of 1.4 V and a stable capacity of 280 mAh

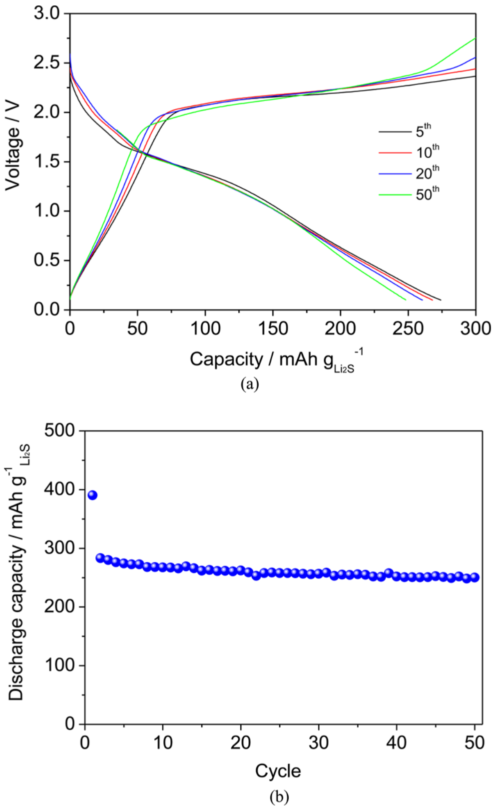


Figure 5. Galvanostatic voltage profiles at the (a) 5th, 10th, 20th, and 50th cycle and (b) cycling response of the Li_2S-MCMB/ $LiCF_3SO_3(TEGDME)_4$/ Si−O−C full cell. Current 232 mA g_{Li2S}^{-1}.

g_{Li2S}^{-1} for over 50 cycles, see Figure 5b. The battery energy density is on the order of 390 Wh kg^{-1} and we anticipate that this value can be increased by further optimizing the electrodes' structure (e.g., increasing the anode loading) and the battery configuration (e.g., developing cathode-limited cells). In fact, the cell capacity may reach suitable values by using silicon-based anode with a higher active material loading in order to exploit the maximum cathode capacity, of about 1200 mAh g^{-1}, thus leading to a full cell with improved characteristics in terms of energy density. To the best of our knowledge, a lithium-metal-free sulfur battery matching the performance of the one here disclosed in terms of efficiency and cycling stability has rarely been seen before.

3. EXPERIMENTAL SECTION

The Li_2S-MCMB Cathode. The Li_2S-MCMB cathode was synthesized by high energy ball milling process with a Retsch (Mill MM400) system, using Li_2S (Aldrich,99.9%) and MCMB (Mesophase Carbon Micro Beads, Osaka Gas) at 1:1 weight ratio, as starting materials. Two grams of powder were inserted in a stainless steel jar (25 mL volume) equipped with three stainless steel balls (10 mm of diameter) and sealed under argon atmosphere. The milling process was carried out alternating one-hour milling steps, with a frequency of 25 Hz and 30 min of rest between steps in order to cool down the jar. The total mechanical treatment time was of 16 h.

Silicon−Oxygen−Carbon Anode. An electrolytic solution containing 0.5 mol dm^{-3} of $SiCl_4$ (Sigma Aldrich) and 0.5 mol dm^{-3} of TBAP (tetrabutylammonium perchlorate, Kanto Chemical) in ethylene carbonate-propylene carbonate (EC/PC (1:1), Kishida) mixture, was prepared in glovebox (dew point lower than −90 °C) and used for the electrodeposition of the Si−O−C composite. The electrochemical cell, using a Li reference electrode (soaked in a 0.5 M TBAP EC/PC 1:1 solution), a copper foil acting both as substrate and working electrode, and a Pt counter electrode, was assembled in an Ar filled glove- box (dew point lower than −90 °C). Before use, the Cu substrate (12 mm of diameter) was pretreated with a 10% of H_2SO_4 solution for 10 s, rinsed with distilled water and dried. The electrodeposition was performed by using a constant current of 1.0 mA cm^{-2} to reach a total charge of 2.0 Coulomb, using a BioLogic VSP potentiostat system.[19] The final electrode loading on the Cu surface was of 1 mg. The electrode was composed by Si, O, and C with a Si weight ratio of 60%.

Electrolyte Preparation. The liquid electrolyte was prepared in an argon-filled gloves box (dew point lower than −90 °C) by dissolving a lithium trifluoromethan sulfonate ($LiCF_3SO_3$, Aldrich 99.995%) salt in tetraethylene glicole dymethylether (TEGDME, Aldric 99%) in the molar ratio of 1:4.[14]

Morphological and Structural Characterization. The characterization of the electrode morphology was performed by using an EDX-equipped scanning transmission electron microscopy (STEM-EDX, Hitachi, HD-2700), whereas the structure of the samples was measured by X-ray by a Rigaku D-max using CuK$_\alpha$ radiation.

Electrode Preparation and Electrochemical Measurements. The Li_2S-MCMB thin-film electrode was prepared by mixing the active material powder with AB (acethylene black, conducting agent) and PEO (polyethylene oxide 600 kDa, binder, Aldrich) in a weight ratio of 6:2:2, using acetonytrile as solvent. The slurry was deposited on Al foil by Doctor Blade obtaining a final thickness of approximately 50 μm. The electrodes were cut in 12 mm diameter disks and then dried at 80 °C under vacuum. The Si−O−C composite anode was rinsed with TEGDME solvent and subjected to direct lithiation process for 15 h prior use in the full cell.[25] All the electrochemical measurements were conducted using R2032 coin-type cells with a Celgard 2500 separator soaked by the electrolyte. The galvanostatic tests of the Li_2S-MCMB half cell were performed at various c-rates and under a 1.0 V-3.5 V voltage limit. The Si−O−C/MCMB-Li_2S battery was anode limited and the related cycling tests were performed by using a TOYO SYSTEM Co., LTD TOSCAT-3100.

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Notes

The authors declare no competing financial interest.

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