



Proof of concept for a novel, binder-free and conducting carbon-free sulfur battery cathode: Composite electroformation of copper foil with incorporated polythiophene wrapped sulfur particles



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HIGHLIGHTS

- Proof of concept for binder- and conducting carbon-free sulfur electrodes.
- Novel one step composite electroformation production process.
- Novel electrode architecture.

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ABSTRACT

This work, for the first time, presents sulfur electrodes for lithium/sulfur (Li/S) batteries produced by a newly developed single-step electroforming process, which allows simultaneous sulfur incorporation during electroformation of an electrically conducting electrode. This metal is used as binding matrix for the sulfur particles and thereby makes any binder and conducting carbon additives redundant. Furthermore, it serves by itself as the current collector, so that all functionalities (current collector, binder and electrical conductor towards sulfur) are fulfilled by the electroformed metal, while modified sulfur particles are directly incorporated (composite electroformation). In this way, the sulfur cathode can be produced in a single continuous step in form of a metal foil with adjustable thickness and sulfur loading. The process requires functionalization of sulfur to improve its wettability, incorporation homogeneity and volume which is provided by wrapping sulfur particles with polythiophene. Electroformed copper-sulfur composite foils are chosen as a first proof of the new concept. The achieved battery capacity, cycling stability and coulombic efficiency are presented. It is shown that the electroformed copper-sulfur composite foil operates very well as a battery cathode and a discharge capacity of over 400 mAh g⁻¹ at a rate of 0.5 C over 100 cycles is preserved.

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1. Introduction

The demand for high energy density batteries is increasing as they are required especially in the area of mobile applications. The technology of Li/S batteries seems promising concerning the batteries' high theoretical specific energy density (2500 Wh kg⁻¹) and theoretical capacity (1672 mAh g⁻¹). Additionally, sulfur as an active material is cheap, abundant, and environmentally friendly. However, the realized capacity and cycle life of these batteries are

lower than the theoretical values which is mainly due the i) low electrical conductivity of sulfur (5×10^{-30} S cm⁻¹ at 25 °C) which leads to a poor electrochemical accessibility and accordingly low sulfur utilization, ii) irreversible loss of sulfur active material from the cathode and parasitic reaction of dissolved polysulfides on the Li anode (shuttle-mechanism) and iii) morphology/volume change of the cathode upon battery cycling [1–6]. Improvements of the capacity and cycle life of the batteries have already been achieved recently by addressing some of the above mentioned problems [7–12]. Most of the research concentrates on reducing polysulfide shuttle mechanism and/or improving conductivity of the electrode by optimizing the generally used sulfur/conducting carbon composites [13–32]. Various modifications of sulfur with intrinsically

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conducting organic polymers are also intensively investigated and improvements of battery capacity and cyclability are reported [33–40].

The state-of-art sulfur electrodes consist of a multicomponent mixture which is transferred onto a current collector (typically aluminum foil) by casting. The current collector serves as a mechanical support of the casted material and additionally conducts the electrons to the external circuit. The multicomponent mixture contains, in addition to the sulfur active material, electrically conducting carbon particles to improve conductivity and electrically non-conducting binder material to stabilize the mechanical integrity of the cathode. The inclusion of binder and electrically conducting particles increases the costs of production and also limits the energy density of the cell, given that the volume/or weight of binder and conductive particles reduces the volume/or weight available for the active material. The non-conducting binder has also the disadvantage of reducing the overall conductivity within the casted layer and increasing the resistance at the interface between the current collector and the casted layer. Additionally, mechanical integrity within the casted layer and its adhesion to the current collector diminish upon battery cycling [41].

This work brings a new perspective to the development of sulfur cathodes for Li/S batteries. For the first time, the sulfur electrode for the use in Li/S batteries is produced by a newly developed single-step composite electroforming process [42], which allows simultaneous sulfur incorporation (known as composite plating [43]) during the electroformation of an electrically conducting metal foil. Therefore we call this process composite electroformation. The metal is used as binding matrix for the sulfur particles and thereby makes any binder and conducting carbon additives redundant. Furthermore, it serves by itself as the current collector, so that all functionalities such as current collector (whole composite material), binder (metal matrix), electrical conductor towards sulfur (metal matrix) and electroactive material (incorporated modified sulfur particles) are fulfilled by one single composite material.

For a first proof of concept, in this work, copper as a metal matrix is selected. The results with other matrix metals will be reported later. In order to improve wettability, incorporation homogeneity and incorporation volume of the sulfur particles during the electroforming process, the particles are wrapped with the intrinsically conducting polymer polythiophene [44] before their use in the composite electroformation process [42]. Besides the colloidal chemistry of the sulfur particles, the electroforming parameters themselves greatly influence not only the incorporation behavior of the particles, but also the topography of the deposited metal matrix. In this way, by attaining a specific surface structure in combination with a suitable metal or alloy, the overpotential effects occurring during battery cycling can be diminished. Together with the decreased internal resistance due to the use of a binder free metal matrix, this can further improve the efficiency of the battery.

The developed new method composite electroformation for the electrode production, as a combination of composite plating and electroformation, is promising with respect to the following potential advantages: i) reduction of material and costs (separate current collector foil, binder, solvent for dissolving binder are not required), ii) reduction of production steps and time, iii) improvement of energy density (higher fraction of active material), iv) reduction of morphology/volume changes (binder-free electrode morphology is mechanically more stable upon cycling), v) improvement of sulfur utilization as it is tightly attached to the metal matrix and due to the electrode structure, sulfur particles are in good contact with the electrolyte.

2. Experimental

2.1. Preparation of polythiophene functionalized sulfur particles (S-PTh)

The general synthesis and the structure of the sulfur-polythiophene particles have been described in detail by Wu et al. [44]. The preparation of the used S-PTh particles was done as follows. The synthesis was carried out under an inert gas atmosphere. A dispersion of 15 g of sulfur (Sigma–Aldrich, $\geq 99.5\%$) in 150 mL of chloroform (Sigma–Aldrich, water free) and 16.08 g of iron(III) chloride (Merck, $\geq 98\%$, waterfree) was stirred for 30 min at room temperature and then cooled down to a temperature of 0 °C. 2.01 g of thiophene (Sigma Aldrich, $\geq 99\%$) was dissolved in 25 mL of chloroform. The thiophene solution was added slowly into the above mentioned sulfur dispersion, stirred for another 5 h at a temperature of 0 °C and afterwards for 48 h at room temperature. In order to stop the polymerization reaction and to dissolve the remaining iron(III) chloride, 100 mL of methanol (Häffner GmbH & Co. Holding KG, technical purity) were added into the dispersion. The latter was then filtered and the residue was washed twice with methanol. After this, the solid was transferred into a flask in which 300 mL of 1 M hydrochloric acid (Häffner GmbH & Co. Holding KG, puriss) was added in order to dissolve the remaining iron chloride and avoid hydroxide precipitation. After stirring for 2 h, the dispersion was filtered and the remaining insoluble solid was washed by using deionized water until a neutral pH was obtained. Finally, it was dried at 40 °C and 110 mbar for 24 h to obtain brownish S-PTh particles.

2.2. Battery cathode preparation by composite electroformation (Cu-S-PTh)

Sulfuric acid based copper electrolyte was prepared by mixing 1400 mL of deionized water, 200 mL of concentrated sulfuric acid (96%, Häffner GmbH & Co. Holding KG), and 0.05 mL of concentrated hydrochloric acid (37%, Häffner GmbH & Co. Holding KG) into which 100 g of copper salt FG (Slotocoup Cu 40, Dr. Ing. Max Schlötter GmbH & Co. KG) was added and dissolved thoroughly. The prepared electrolyte was filled up with deionized water to a volume of 2 L. Commercially used additives were not added.

7.5 g of the prepared S-PTh particles were added into 500 mL of the above described electrolyte and the dispersion was stirred with a magnetic stirrer for 30 min. The composite electroformation was performed in a crystallizing dish (diameter 115 mm) with a current density of 4 A dm⁻² for 20 min. A polished stainless steel (1.4301) cylinder with a diameter of 25 mm and a length of 40 mm was used as rotating cathode. The copper sheet anodes (50 mm × 30 mm) were placed opposite of each other with the vertically aligned cathode centered at a distance of 30 mm.

Before composite plating, the cathode sheet was pretreated by cathodic degreasing (SLOTOCLEAN EL DCG, Dr.-Ing. Max Schlötter GmbH & Co. KG) with a voltage of 5 V for 30 s and subsequent pickling with 10% sulfuric acid (Häffner GmbH & Co. Holding KG) to obtain a defined and homogeneous surface. In this way, the typical oxide layer present on stainless steel is not fully removed, so that after being plated, the metal foil can be easily peeled off without any remaining damage.

In this way, a free standing Cu-S-PTh composite foil was obtained. This foil is subsequently dried in a vacuum oven at 80 °C and 110 mbar and then immediately transferred into an argon filled glove box.

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