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Short communication

Cell energy density and electrolyte/sulfur ratio in Li–S cells

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HIGHLIGHTS

- Li–S cells usually have an excess of electrolyte and Li to improve the performance.
- The cell energy density drastically depends on the added electrolyte amount.
- Only small electrolyte/sulfur (E/S) ratios ≤3:1 enable high energy density cells.
- Pouch cells were created to examine electrode specific electrolyte/sulfur ratios.
- Low electrolyte/sulfur ratios decrease the sulfur utilization.

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ABSTRACT

Li–S cells have high potential gravimetric cell energy densities between 200 and 600 Wh kg^{-1}. To obtain a high cell energy density, the sulfur fraction in the electrode and the sulfur load per cm^2 electrode should be as high as possible next to a good electrochemical sulfur utilization. The quantity of electrolyte added to a cell is crucial for the latter, and an excess of electrolyte is generally beneficial for the electrochemical results. Existing publications on Li–S cells therefore use an excess of electrolyte leading to high electrolyte/sulfur (E/S in ml g^{-1}) ratios as these enable high cycle numbers and good sulfur utilization. However, these studies do not take account of the high passive weight of the electrolyte. The high E/S ratios involved mean that the obtained cell energy density is below commercial lithium-ion cell level.

To emphasize the impact of the electrolyte on the cell energy density we calculated possible cell energy densities from material test cell experiments for various E/S ratios, sulfur and carbon loads. Furthermore small pouch cells with only a very small dead cell volume absorbing electrolyte are created to examine ideal E/S ratios for a specific electrode.

1. Introduction

Li–S cells have significant potential as a next generation energy storage system with possible energy densities between 200 and 600 Wh kg^{-1} on cell level. These energy densities are up to three times higher than those of commercialized Li-ion cells (150–250 Wh kg^{-1}). For high energy densities on cell level the active material fraction and load should be as high as possible combined with ideally 1672 mAh g^{-1} theoretical sulfur utilization. Over the last few years it has been observed that in particular the sulfur fraction in the electrodes could be improved from relatively low values between 20–50% and 60–80%, while tailored carbon materials even improved the electrochemical performance [1]. Nevertheless, the sulfur load per cm^2 electrode can still be seen as too low, with values between 0.5 and 2.0 mg cm^{-2}. To exploit the cost advantage of the cheap, abundant sulfur in comparison to commercialized Co and Ni containing electrodes, we believe that the sulfur load should be at least 3 mg cm^2 or preferably higher. Otherwise these Li–S cells may be even more expansive ($ kWh^{-1}) than commercialized systems because of their relatively low cell voltage [2]. Additionally the sulfur load has a significant effect on the achievable cycle number and possible Li-induced short-circuits. The higher the sulfur load, the more Li will be stripped and replated at the negative electrode, resulting in a much higher chance that Li dendrites will pierce through the separator. With high sulfur loads Li-induced shorts may even occur in the first 10 cycles [3]. For the same reasons high sulfur loads lead to the creation of a larger fresh Li surface during charge, when Li is redeposited at the negative electrode. For this fresh surface Li and electrolyte are consumed to create a new SEI layer, the composition of which is described in Ref. [4] for ether based electrolytes. Consequently ether-based Li–S electrolytes cannot be seen as stable. In particular the

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dimethoxyethane (DME) fraction in DME:dioxolane (DIOX) electrolytes is depleted and the fraction of electrochemically active Li decreases [5]. As a result the system loses electrochemically active Li and electrolyte solvent, which therefore have to be added in excess when assembling the cell. This significantly decreases the possible cell energy density and explains why in the literature high cycle numbers above 1000 generally correspond to small sulfur loads, usually below 1.0 mg cm^{-2}.

- Sulfur load: 0.8 mg cm^{-2}, capacity per g sulfur at 1000th cycle: 500 mAh g^{-1}, capacity decay rate: 0.039% per cycle, electrode area: 1.27 cm^2, electrolyte amount: 60 μl, E/S: ~59/1 [1].
- Sulfur load: 0.4–0.6 mg cm^{-2}, capacity per g sulfur at 1000th cycle: 700 mAh g^{-1} [6].
- Sulfur load: 1.28 mol l^{-1} electrolyte, capacity per g sulfur at 1000th cycle: 600 mAh g^{-1} [7].

Furthermore important information which significantly affect the cyclability of a Li–S cell, such as the quantity of electrolyte and the mass of Li electrode added, or the Li excess, are missing in almost every Li–S publication. We would like to shift the focus away from approaches that try to maximize the sulfur utilization or the long-term cycle stability without taking the passive weight of the electrolyte into account, as these have a low practical relevance.

We therefore used experimental material test cell results to calculate possible E/S ratios, still allowing high gravimetric cell energy densities and assembled pouch cells with defined sulfur load and electrolyte volume to experimentally determine ideal E/S ratios for the here used Kynol electrode.

2. Experimental

2.1. Calculation of energy densities on cell level with a binder-free vertical aligned CNT electrode

To evaluate the jelly roll energy densities for various E/S ratios, we used experimental results with binder-free CNT-coated GDL10AA from the company SGL Carbon as sulfur cathodes [2]. The electrode thickness depends on the CNT coating load and is between 300 and 700 μm before assembly. In the test cells the electrodes are compressed to a thickness of 250–400 μm by a stainless steel spring with a force of approximately 10 kg cm^{-2}. The binder-free CNT electrodes can work with sulfur loads between 0.5 and 20.0 mg cm^{-2} electrode and show capacities between 800 and 1000 mAh g^{-1} sulfur (mAh g_S^{-1}) for these sulfur loads at 0.6 mA cm^{-2} [2]. The electrolyte volume added to the test cells was constant at 100 μl, leading to effective experimental E/S ratios between 5 and 20. The estimated dead volume of the test cells that had to be filled with electrolyte was around 20 μl.

For the energy density calculations we used the following data:

- Sulfur cathode mass: S_8 load + CNT load + carbon current collector (GDL10AA) + 6 μm Al current collector (for single side coated electrode).
- Lithium metal anode: Li load without excess of Li (Li capacity matching S_8 cathode capacity) + 5 μm Cu current collector (for single side coated electrode).
- Separator with 1.0 mg cm^{-2} and electrolyte with 1.0 mg μl^{-1} (1 g ml^{-1}).
- We did not include the weight of the housing and the tabs because this passive weight fraction greatly depends on cell type and size. To obtain the cell energy density the calculated jelly roll energy density values could be multiplied with 0.75–0.95. We suggest that an electric vehicle pouch cell with ~60 Ah might be close to 0.95. Cells with a higher relative housing weight should be close to 0.75.
- To obtain the energy densities on jelly roll level we divided the obtained capacity by the masses stated above, used various notional E/S ratios, and multiplied the result by an average cell voltage of 2.1 V.

2.2. Pouch cell assembly using a Kynol 5092-20 electrode

The Li–S pouch cells were created by infiltrating S_8 in Kynol 5092-20 electrode (weight: ~13.5 mg cm^{-2}, thickness: ~550 μm, electrode surface: ~1800 m^2 g^{-1}). The sulfur load was 6.6 mg cm^{-2} and the sulfur electrode fraction was 33%. The Kynol-S_8 and the Li electrode (Sigma Aldrich, 99.9%) were cut in a rectangular shape (5 × 3 cm). Beforehand the Li was scraped with a ceramic knife to remove undesired surface layers and pressed through a calendar to obtain a homogenous and reproducible surface. The Li thickness was around 180 μm (Li excess of 234%, referred to the theoretical S_8 capacity). The Kynol-S_8 electrode was conductively glued to a 12 μm thick Al current collector with an electrodag and the Li electrode was pressed onto a 10 μm Cu current collector using a small calendar. A Ni/Cu tab was welded to the copper current collector and an Al tab was welded to the Al current collector using a Branson ultrasonic welding device. As a separator a Celgard ECT2015 (size 6 × 4 cm) was used and directly laminated onto the electrodes to obtain a stack. The stack was placed in the middle between two pouch foils (size 8 × 5 cm) and the pouch foil was sealed with a vacuum sealing device. Before sealing the last edge of the cell we introduced a defined amount of 0.7 M LiTFSI in DME:DIOX (2:1, v:v) (BASF) + 0.25 M $LiNO_3$ (ABCR 99.98%) with a water content below 20 ppm electrolyte. Unfortunately we discovered that 5–30% of the injected electrolyte evaporated out of the cell when the final sealing took place under vacuum. Since the aim of this work was to examine defined E/S ratios we developed a new method to guarantee that the injected electrolyte volume was equal to the final test cell electrolyte volume. We therefore inserted a polytetrafluorethylene (PTFE) filled polyethylene (PE) tube into a silicone tube mounted to the pouch cells edge which worked as a kind of septum (Fig. 1a, b). This allowed us to inject the electrolyte when the pouch cell was completely sealed and evacuated. The projecting end with the silicone/PTFE/PE tube was cut away after a final sealing step (Fig. 1c).

The assembly of all test cells and pouch cells took place in an argon-filled glove box (MBraun) with an O_2 and H_2O content below 1 ppm.

2.3. Electrochemical characterization

The binder-free CNT electrodes were cycled with 0.5 mA (0.64 mA cm^{-2}) between 1.8 and 2.8 V. The cycle station used was a Basytec CTS-LAB system.

The Li–S pouch cells with Kynol electrode were cycled with 10 mA (0.67 mA cm^{-2} or 0.1 A g^{-1} sulfur or C/16) between 1.8 and 2.8 V.

3. Results and discussion

3.1. Calculated gravimetric jelly roll energy densities based on binder-free vertical aligned CNT electrode – E/S ratio vs. specific energy density

Fig. 2 shows the calculated jelly roll energy densities with binder-free, vertically aligned CNT-S_8 cathodes for various S_8 loads, CNT loads and different E/S ratios. The CNTs provide a high