A new lithium sulfur battery using a polymer coated separator and carbon encapsulated lithium sulfide

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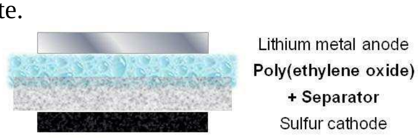
Lithium metal batteries provide very high theoretical energy densities and are therefore promising for use in automotive applications [1]. A suitable high capacity cathode material is sulfur or respectively lithium sulfide (Li_2S) [2]. Nevertheless, a commercial breakthrough has failed so far because of some serious issues.

One of these issues is the poorly controlled lithium-electrolyte interface generated by the spontaneous reaction of electrolytes in contact with lithium metal. The SEI (Solid Electrolyte Interphase) formed at the surface of lithium is not effective in preventing further reactions or dendrite growth during charge [3]. Hence, the use of conventional electrolytes based on flammable organic solvents has led to serious accidents in the past.

A second issue is caused by the insulating nature of sulfur and Li_2S while the third is certainly associated to the dissolution of polysulfides during charge and discharge. The diffusion of polysulfides to the lithium anode, known as "shuttle effect", leads to the loss of active materials, isolation of the Li/electrolyte interface (Li_2S is also a poor ionic conductor) and low coulombic efficiency [4]. Due to the low melting point of sulfur, a coating of the material to prevent the polysulfide migration is not easy to develop. Thus, in state of the art sulfur cathodes, the sulfur is impregnated in porous carbons to immobilize the intermediate products [5].

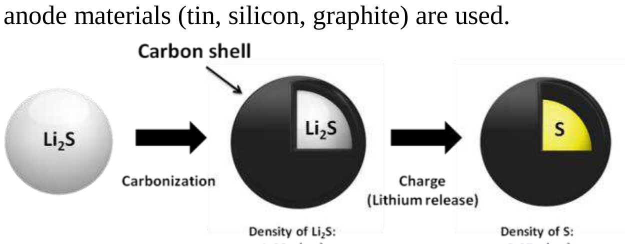
The new lithium sulfur battery presented in here combines two approaches:

1) Ternary polymer electrolytes based on PEO show a good stability with lithium metal [6]. To make use of this peculiar property, which might help preventing dendrite growth, commercial separators were coated on one side with a thin film (10 µm) of PEO. This multilayer separator was in-situ gelled with carbonate-based electrolytes as well as annealed with ionic liquid electrolytes to form an amorphous ternary polymer electrolyte.



Scheme of a polymer coated separator in a Li-S cell

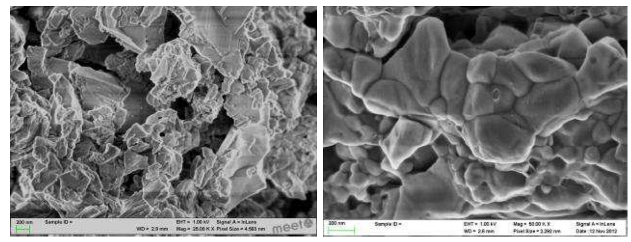
2) Lithium sulfide is used as active material which leads to a discharged battery after cell assembling. The higher thermal stability of Li_2S allows its encapsulation in a carbon shell using appropriate carbon precursors (e.g. polyacrylonitrile or sucrose) [7]. Another advantage of lithium sulfide is that no lithiation has to be done if other anode materials (tin, silicon, graphite) are used.



Scheme of encapsulation process of Li_2S particles

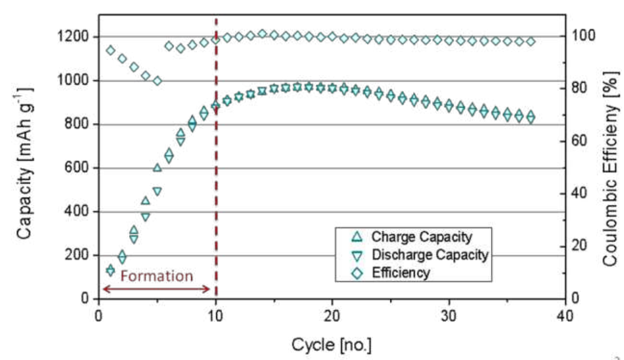
Tests with the multilayer separator have been done in symmetrical lithium cells to show long-term stability of the SEI forming on the lithium metal electrodes. Conductivity tests showed a high ionic conductivity. The best results were achieved in combination with a commercial ceramic/PET separator.

Several carbon precursors were tested and the coatings investigated in cycling tests with conventional separators. SEM with EDX mapping was used to investigate the carbon coating.



Pristine Li_2S Carbon coated Li_2S

Finally, lithium cells were assembled in Pouchbag and T-cells. The separator was in-situ swelled either with organic electrolyte (0.5M LiCF3SO3 in dioxolane and dimethyltetraethylether [7:3]) or with ionic liquid-based electrolytes. The cycling capability was found to depend on the carbon precursor as well as the chosen separator and electrolyte.



40°C, C/50, Electrolyte: Pyr_{14}TFSI/LiTFSI, Pouchbag

30 cycles with over 98 % coulombic efficiency could be achieved with specific capacities over 550 mA g-1 for Li_2S which corresponds to 800 mA g^{-1} for sulfur. For ionic liquid-based electrolytes, the slow wetting process of the encapsulated Li_2S particles can lead to several formation cycles with low specific capacities.

References:

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