Development of innovative lithium metal-free lithium-ion sulfur battery for renewable energy, electric transport and electronics.

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Abstract.

Lithium/sulfur (Li/S) battery is a promising candidate for the next generation rechargeable battery since the negative electrode, lithium, and the cathode, sulfur, have the highest theoretical capacities of 3862 and of 1672 mAh/g, respectively, among any other active materials, e.g., graphite (372 mAh/g) or $LiCoO_2$ (274 mAh/g, only about 50% is practically available). However, there are several challenging issues in order to realize the use of this type of next generation battery. **First,** the lithium metal anode has an intrinsic safety issue, dendrite growth that can result in internal short circuit failure. **Second,** the sulfur cathode is a very insulating material; therefore, sulfur-based cathodes need a large amount of conducting additives, resulting in the decrease in the practically available gravimetric capacity per the unit mass of cathode composite. **Third,** lithium polysulfides, reduced (discharged) forms of sulfur, dissolve into an electrolyte solution, resulting in capacity fading. For realistic battery applications, these issues from both the anode and the cathode need to be solved or mitigated. To this end, we integrate three practically possible solutions: **(1)** manufacture-friendly pre-lithiation of anode or cathode materials, **(2)** practically optimal choice of conducting agent and of the method for S/conductive-agent integration, and **(3)** stabilization of discharged forms of the cathode.

1. Introduction.

Lithium-ion batteries have been leading power sources for small consumer electronics such as mobile phones and laptop computers; however, their wider application such as an application for electric vehicles is restricted due to the limited capacity per the unit mass of materials. Currently, graphite and $LiCoO_2$ are mainly used for small consumer electronics as an anode and a cathode material, respectively. The theoretical (practically available) capacities and the costs are 372 mAh/g (372 mAh/g) and around USD10/kg for graphite, and 274 mAh/g (about 140 mAh/g) and around

USD40/kg for $LiCoO_2$, respectively. The cost performance has been improved mainly by “China shift” on manufacturing sites: the cost performance of graphite is USD5.4/200 Ah (about 200 Ah is considered the minimum requirement for electric vehicles); that of $LiCoO_2$ is USD57/200 Ah. The required mass of graphite is about 540 g/200 Ah, and that of $LiCoO_2$ reaches about 1400 g/200 Ah.

Lithium/sulfur (Li/S) battery is a promising candidate for the next generation rechargeable battery that can be used as power sources for electric vehicles since the negative electrode, Li, and the cathode, S, have the highest theoretical capacities of 3862 and of 1672 mAh/g, respectively. However, there are several challenging issues in order to realize the use of this type of next generation battery.

First, the lithium metal anode has an intrinsic safety issue, dendrite growth that can result in internal short circuit failure. Therefore, it is likely that the conventional anode materials will be used for electric vehicle applications. The problem is the combination of conventional anode materials (such as graphite, hard carbon, and silicon) and S-based cathode materials does not contain Li; thus, the pre-lithiation of anode or cathode materials is required. Pre-lithiated graphite (LiC_6) has been used for pseudo electric double layer capacitors. In this paper, we report the combination of LiC_6 and S. The capacity of LiC_6 is 339 mAh/g; thus, about 590 g is required for a 200 Ah battery. Only the mass increase of 50 g does not cause any problems for one electric vehicle (Section 2).

Second, sulfur is a very insulating material; therefore, S-based cathodes need a large amount of conducting additives that can result in the decrease in the practically available gravimetric capacity per the unit mass of cathode composite. Therefore, the optimal choice of conducting agents and of the method for S/conducting-agent integration is required. So far, the capacity per the unit mass of cathode composites (including S and various types of conducting agents) ranges 340-570 mAh/g [1-6]; thus, only about 590-350 g is required for a 200 Ah battery (about 810-1050 g decrease is expected compared to $LiCoO_2$). The price of elemental sulfur is USD2/tonne. Although a transportation cost increases the price up to USD0.1/kg, it is still incredibly cheaper than $LiCoO_2$. In this paper, we report the progress on S-based cathode composite (Section 3).

Third, lithium polysulfides, reduced (discharged) forms of sulfur, dissolve into an electrolyte solution, resulting in capacity fading. Therefore, the stabilization of polysulfide is required. In this paper, we report a candidate methods on the stabilization of polysulfides (Section 4).

2. Pre-lithiation of anode materials.

Since the combination of conventional anode materials (such as graphite, hard carbon, and silicon) and S-based cathode materials does not contain lithium-ion source, the pre-lithiation of anode or cathode materials is required. At manufacturing sites (of pseudo electric double layer capacitors), pre-lithiated graphite is prepared by directly contacting graphite-based anodes with Li foils; however, in this paper, we show the results of pre-lithiated graphite in coin cells to readers since the completion of lithiation is easily confirmed by monitoring the cell voltage. Figure 1 left shows the voltage profile at 0.2 C of a Li|1.0 M $LiPF_6$/EC+DEC+EMC (EC denotes ethylene carbonate; DEC, diethyl carbonate; EMC, ethyl methyl carbonate) (1/1/1, v/v/v)|graphite coin cell in which a commercially available graphite electrode pasted onto a Cu foil with a mass-loading of 9.3 mg/cm^2 was used. As shown in Fig. 1 left, the pre-lithiation of graphite was successfully conducted. The capacity difference between the 1st cycle and 2nd-3rd cycles is due to the solid electrolyte interface (SEI) formation. Even after the SEI formation, the capacity at the 2nd-3rd cycles is higher than the theoretical one (372 mAh/g): it may be due to the carbonaceous additional conducting agent since pulverized-graphite-based conducting agents has become widely used recently.

With this pre-lithiated graphite anode and a typical S-based cathode composite, a full cell was assembled and tested. As a typical S-based cathode composite, S/PAN/KB (PAN denotes polyacrylonitrile; KB, ketjen black.) was chosen. The cathode composite material was prepared by the procedure described in the ref. [7], which is a simplified and an optimized procedure compared to procedures described in the refs. [4-6]. This composite was pasted onto an Al foil current collector with a binder (PVdF, polyvinylidene fluoride) and an additional conducting agent (AB, acetylene black) with a mass-loading of 2 mg/cm^2: the mass ratio of the cathode was S(35 wt.%)/PAN(43 wt.%)/KB(2 wt.%)+PVdF(10 wt.%)+AB(10 wt.%). As an electrolyte solution, 1.0 M $LiPF_6$/EC+DEC+EMC (1/1/1, v/v/v) was used. Figure 1 right shows the voltage profile at 0.2 C of a pre-lithiated graphite|1.0 M $LiPF_6$/EC+DEC+EMC (1/1/1, v/v/v)|S/PAN/KB coin cell. As shown in Fig. 1 right, the double-plateau profiles disappeared after the 1st lithiation: this is due to the nano-scopic re-distribution of sulfur/polysulfides that is a well-known phenomenon among S/PAN-based composites [8-12]. This result shows the possibility of lithium metal-free lithium-ion sulfur battery.

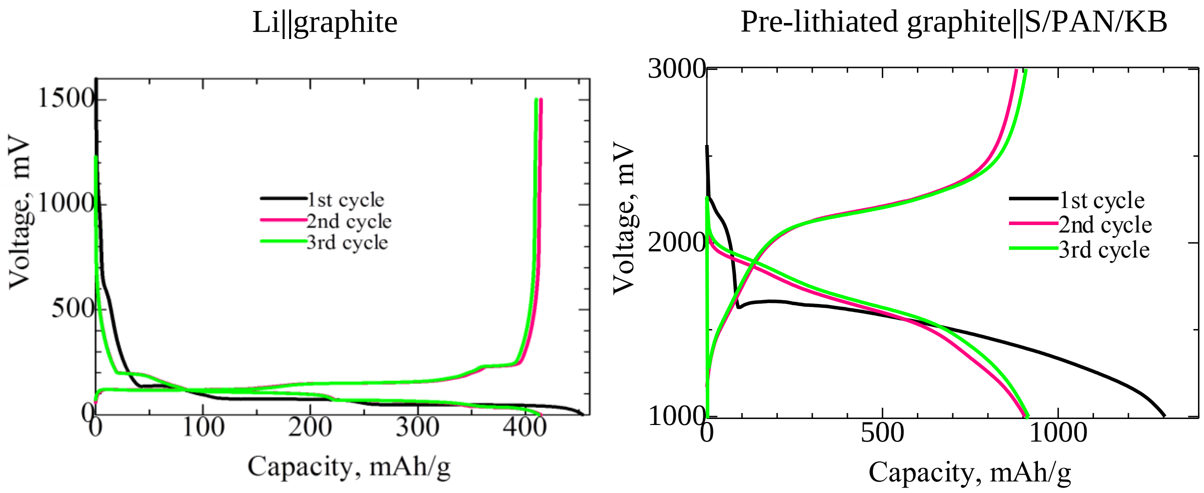

Fig. 1. (Left) Voltage profile at 0.2 C of Li|1.0 M $LiPF_6$/EC+DEC+EMC (1/1/1, v/v/v)|graphite. (Right) Voltage profile at 0.2 C of pre-lithiated graphite|1.0 M $LiPF_6$/EC+DEC+EMC (1/1/1, v/v/v)|S/PAN/KB.

3. Choice of conducting agent and of the method for S/conductive-agent integration.

Since sulfur is a very insulating material, S-based cathodes need a large amount of conducting additives that can result in the decrease in the practically available gravimetric capacity per the unit mass of cathode composite. Therefore, the optimal choice of conducting agents and of the method for S/conducting-agent integration is required.

As S-based composites containing conducting agents, S/carbon binary composites [13], S/conducting polymer binary composites [14], S/conducting polymer/carbon ternary composites [15], S/PAN binary composites [16], S/PAN/carbon ternary composites [9] etc., have been suggested. However, the problem was their lower mass-loadings (typically, 2 mg/cm^2) than conventional $LiCoO_2$ (typically, 20 mg/cm^2). Recently, nano-sized S/polypyrrole (PPY) binary composites [1], nano-sized S/polypyrrole (PPY)/nano-sized carbon ternary composites [2, 3], S/PAN/nano-sized inorganic filler ternary composites [4], and S/PAN/nano-sized carbon ternary composites [5, 6] were intensively studied in order to increase sulfur utilization, and some of them succeeded in the increase in the mass-loading. So far, the capacity per the unit mass of cathode composites (including S and various types of conducting agents) ranges 340-570 mAh/g [1-6], which are higher than conventional ones such as $LiCoO_2$ (typically 140 mAh/g), and some of them show higher capacities than the S-based composite without using any nano-sized materials, as shown in Table 1. Although these results imply the possibility of S-based high-capacity cathodes, the low mass-loading is still problematic compared to conventional ones (Table 2).

Table 1. Gravimetric capacity (at 0.1-0.2 C, around 50-100 cycles) on various types of S-based cathode composites. Here, S denotes sulfur; PPY, polypyrrole; CNT, multiwall carbon nanotube; G, graphene; PAN, polyacrylonitrile; MNO, $Mg_{0.6}Ni_{0.4}O$; RGO, reduced graphene oxide. Note that all the components have the capacities of >1000 mAh/g initially; however, after a few dozens of cycles the capacities degrade.

Cathode components	Ref.	Capacity [mAh/g] *(/unit mass of sulfur)*	Capacity [mAh/g] *(/unit mass of composite)*	Mass-Loading (ML), Capacity (C) [mg/cm^2], [mAh/cm^2] *(including 10 wt.% of binders and 10 wt.% of additional conducting agents)*
Nano-S/PPY *44/56 wt.%*	[1]	900	396	ML 2.0, C 0.63
Nano-S/PPY/CNT *52.6/47.4-x/x wt.%*	[2]	1000	526	ML 4.0, C 1.70
Nano-S/PPY/G *52.6/47.4-x/x wt.%*	[3]	640	338	ML 2.0, C 0.54
S/PAN/MNO *38.5/48.7/12.8 wt.%*	[4]	1100	424	ML 4.0, C 1.40
S/PAN/G *47/26/7 wt.%*	[5]	1060	500	ML 3.5, C 1.40
S/PAN/RGO *44/53/3 wt.%*	[6]	1300	572	ML 7.0, C 3.20
S/PAN/KB *44/54/2 wt.%*	used in Sec. 2	900	396	ML 2.0, C 0.63

Table 2. Typical mass-loading and available capacity on conventional $LiCoO_2$ cathode and graphite anode.

Main component of Electrode	Mass-Loading [mg/cm^2]	Available capacity [mAh/cm^2] *(including 5 wt.% of binders and 5 wt.% of additional conducting agents)*
Cathode: $LiCoO_2$	20	2.5
Anode: Graphite	10	3.3

Compared to Nano-S/PPY composites, S/PAN composites show higher capacities even at higher mass-loadings and even without using nano-sized sulfur (e.g., Nano-S/PPY/graphene (G) vs. S/PAN/G): this is probably due to the two-dimensional structure of cyclized PAN after the heat treatment with sulfur that can make the electron transfer between PAN and sulfur easier than the electron transfer between one-dimensional PPY and sulfur. Among S/PAN composites, S/PAN/reduced graphene oxide (RGO) shows the best results, and is comparable with conventional $LiCoO_2$: this is probably due to the strong affinity between polar functional groups such as -OH and polysulfides. However, the expensive RGO should be replaced into other inexpensive materials such as polyaniline that has polar -NH- and aromatic rings. Currently, we are conducting the trial use of less-expensive conducting agents, instead of nano-sized carbon materials: the results will be disclosed at the conference.

With regard to the mass of electrodes, the current collector, such as Al and Cu foils, is the dominant contributor (Table 3). In order to decrease the mass of electrodes, electrodes without current collectors, i.e., free-standing electrodes have been attracting attentions. So far, a S/CNT-based free-standing cathode [17], S/micro-mesoporous carbon (MC)/Teflon (PTFE)/CNT (53/27/10/10 wt.%) [18] etc. have been reported. The S/MC/PTFE/CNT composite shows the best results among ever reported ones: 400 mAh/g (/unit mass of the composite); 2.3 mAh/cm^2 [18]. Note that around 3 mAh/cm^2 is compatible with typical graphite anodes (Table 2). When anodes with higher capacity, such as 8 mAh/cm^2 (hard carbon is a good candidate) or higher (Si-based composites are the good candidate) are used, higher mass-loadings are required for the S-based cathodes.

Table 3. Mass of conventional current collector.

Current collector	Density [g/cm^3]	Thickness [μm]	Mass [mg/cm^2]
Al foil	3.74	15	5.61
Cu foil	8.94	9	8.05

4. Stabilization of discharged forms of the cathode.

Lithium polysulfides, reduced (discharged) forms of sulfur, dissolve into an electrolyte solution, resulting in capacity fading. Therefore, the stabilization of polysulfide is required. Recently, the use of nitrogen-doped carbon conducting agents was suggested in order to stabilize polar polysulfides since nitrogen-doped carbon materials have more polar electronic configuration than non-doped ones [19]. However, S/PAN composites already have nitrogen-rich cyclized carbon structures [4-12]. Thus, S/PAN composites are likely to be one of the best choices regarding polysulfides stabilization. Note that only S/PAN composites are chemically compatible with conventional $LiPF_6$-carbonate based electrolyte solutions [4-12]; any other S-based composites suffer from the reaction between polysulfides and carbonate-based solution, resulting in the deposition of reaction products.

5. Conclusion.

For the next generation lithium-ion batteries, lithium-ion sulfur batteries, followings have been suggested in this paper:

(1) pre-lithiation of anode in order to realize lithium metal free lithium-ion sulfur batteries;

(2) use of sulfur/polyacrylonitrile-based composites in order to increase the utilization of insulating sulfur;

(3) polysulfides stabilization is also improved by sulfur/polyacrylonitrile-based composites.

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