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Effect of sulfur loading on the electrochemical performance of a sulfur/polymer composite cathode coated on aluminium foil

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A scaling up investigation of a sulfur/polymer cathode for rechargeable lithium sulfur batteries is reported. The proposed procedure uses low cost aluminium current collector and is suitable for mass production of composite cathode, with sulfur loading levels of up to 5.9 mg cm^{-2}, and good electrochemical performance.

1. Introduction

The demands to increase the specific capacity of cathode for use in lithium-sulfur (Li-S) rechargeable batteries have recently been considered.[1-9] The theoretical specific capacity of sulfur (1672 mA h g^{-1}) is superior comparing to observed values in LiCoO$_2$ (140 mA h g^{-1}) and LiFePO$_4$ (160 mA h g^{-1}), the two most commonly used cathode materials for lithium-ion batteries. Despite the relatively low working potential of about 2 V vs. Li$^+$/Li°, the high specific capacity of Li-S batteries leads to a specific energy of ~2600 W h kg^{-1} on the basis of complete conversion to Li$_2$S. This value is five times higher than that of the existing LiCoO$_2$/graphite system.[10] In addition, sulfur is abundant, inexpensive, and of low toxicity. Therefore, many research groups and companies have been trying to develop and commercialise Li-S rechargeable batteries.

Notwithstanding its promising characteristics, the development of Li-S batteries faces great challenges. The high solubility of intermediate polysulfides in the liquid electrolyte, the insulating nature of sulfur and lithium sulfide (final product of the discharge process), and the large volume changes during insertion/extraction of lithium ions are major hindrances which must be overcome before a real Li-S rechargeable battery system could get to the market. As a consequence, low sulfur loadings (about 1-2 mg cm^{-2}) and small current densities are normally used in Li-S batteries to ensure high specific capacity and good cyclability.[2,3,8,10,11]

To resolve such problems, two major approaches have been used, namely, the incorporation of sulfur into carbon,[2-4,6-8,10] and into conductive polymer matrices.[11-15] In comparison with sulfur/carbon composites, the sulfur/pyrolyzed polyacrylonitrile (S/pPAN) composite showed much higher coulombic efficiency (close to 100 %) and excellent cyclability.[11,12] In the latter, the shuttle effect which plagues the sulfur/carbon cathodes is not any more a significant problem.[2,3,6] Moreover, preparation of the S/pPAN composites is much simpler and lower in cost in comparison with that of the "state of the art" carbon composites. In our group, S/pPAN system has been extensively studied as the cathode for Li-S batteries, from the binding mechanism of sulfur to PAN[16] to the capacity fading mechanism of constructed battery systems.[17] Additionally, we found that S/pPAN doped with Mg$_{0.6}$Ni$_{0.4}$O nanoparticles exhibits improved specific capacity and excellent cyclability comparing to the non-doped systems.[18] Thus, this composite was used as the cathode material for the scaling up process of Li-S batteries presented herein. This study encompasses optimization of the cathode composite preparation in large quantity, and evaluates the obtained cathode against the requirements of battery performance and material loadings.

2. Experimental

2.1. Material preparation procedure

2.1.1. Preparation of Mg$_{0.6}$Ni$_{0.4}$O

Mg$_{0.6}$Ni$_{0.4}$O was prepared by the typical sol-gel method. Stoichiometric amounts of Mg(NO$_3$)$_2$.6H$_2$O and

$Ni(NO_3)_2.6H_2O$ (Sigma-Aldrich®) were dissolved in deionized water and citric acid was used as a chelating agent. The obtained solution was stirred continuously and heated at moderate temperature until the gel appeared. The gel was dried at 70 °C for 12 h, and then heated at 700 °C for 5 h in air.

2.1.2 Preparation of the cathode composite

16 g sulfur (Sigma-Aldrich®, 100-mesh particle size), 1 g $Mg_{0.6}Ni_{0.4}O$ and 1 g carbon (Akzonobel) were hand-mixed and the resultant mixture was ball milled (Fritsch, Pulverisette 5/4 classic line) for 4 h at 200 rpm. After addition of 4 g of polyacrylonitrile (PAN, Sigma-Aldrich®, $\overline{MW}$ = 150,000) the mixture was ball milled again at 200 rpm for 30 min. The resulting powder was vacuum dried at 50 °C for 3 h and then heat treated at 300 °C for 3 h in argon atmosphere to afford the final sulfur cathode composite.

2.2. Material characterization

Tap density of the composite was measured by tapping an exact mass of cathode composite in a volumetric cylinder for 5 min. Sulfur content of the sample was determined using an elemental analyzer (CHNS, Vario Micro Cube, Elementar). The composite surface morphology was examined by field emission scanning electron microscopy (FE-SEM, Leo-1550, Zeiss).

The cathode comprised of a mixture with 70 wt% active composite, 15 wt% acetylene black and 15 wt% polyvinylidene fluoride (PVdF, Kynar, HSV900) binder, which were all well dispersed in 1-methyl-2-pyrrolidinone (NMP, Sigma-Aldrich, 99.5% purity). The resultant slurry was spread uniformly onto an aluminium foil using the doctor blade technique and then dried in vacuum at 50 °C for 12 h. The dry film was punched into circular discs and scraped in order to standardize the area of cathode (1 cm^2). Variation in sulfur loading was controlled by the thickness of the cast slurry film. Average sulfur loading varied from ~ 0.55 to ~ 5.9 mg cm^{-2}. The electrochemical performance of the $S/pPAN/Mg_{0.6}Ni_{0.4}O/C$ composite cathode was investigated using coin-type cell (CR2025), comprised of a lithium metal negative electrode and a $S/pPAN/Mg_{0.6}Ni_{0.4}O/C$ composite positive electrode, separated by a microporous polypropylene film (Celgard 2340). 1 M solution of $LiPF_6$ in ethylene carbonate (EC), dimethyl carbonate (DMC), and diethylene carbonate (DEC) mixture with a 1:1:1 weight ratio (LP71 SelectiLyte, Merck Chemicals) was used as the liquid electrolyte. The cell was assembled in an argon (99.9995%) filled MBraun glove box, and tested galvanostatically on a multi-channel battery tester (BTS-5V5mA, Neware) between 1 V and 3 V at 0.2 C and 1 C charge-discharge rate (1 C = 1672 mA g^{-1}). Applied currents and specific capacities were calculated based on the weight of sulfur in the cathode.

3. Results and Discussion

Aluminium foil is the cathode current collector used in commercial lithium-ion batteries. Most reports on Li-S batteries use nickel foam as the cathode current collector,[11,12,16-18] although aluminium foil has also been employed in some papers.[2-6,8,13] However, the sulfur based material loading on aluminium foil is either low (1-2 mg cm^{-2})[2,3,8] or unknown.[4-6,13] The special 3-D structure of nickel foam (Fig 1a) can hold the cathode composite, provide shorter electron pathways, and absorb the expansion/shrinkage observed upon cycling of the sulfur based cathode. Using nickel foam as cathode current collector, large cathode material loading up to ~15 mg cm^{-2} with sufficient electrochemical performance has been reported by our group.[16,17] Aluminium foil is much lighter and has smaller volume than nickel foam, as depicted in Fig. 1b and 1c, and Table 1. Therefore, use of aluminium foil can increase both the specific energy and energy density of the cell.

Table 1 Comparison of physical properties of Al foil and Ni foam

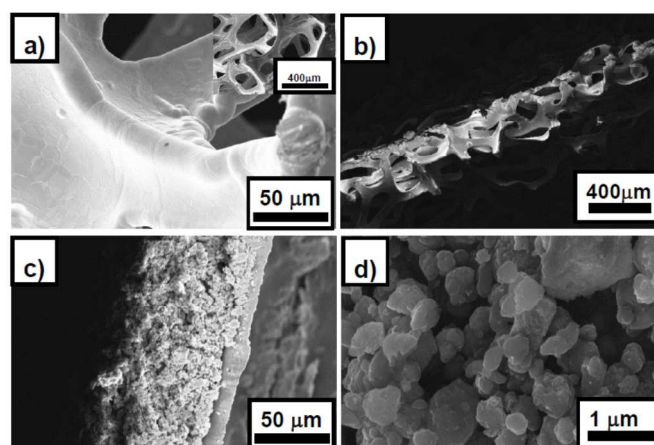| Current collector	Ni foam	Al foil
Density (mg cm^{-2})	65-75	~3.6
Thickness (μm)	~800	~20

Fig. 1 (a) Structure and (b) cross-sectioning image of nickel foam; (c) cross-sectioning image of cathode coated on aluminium foil; (d) morphology of $S/pPAN/Mg_{0.6}Ni_{0.4}O/C$.

Considering the disadvantages presented by nickel foam (for example: high cost, large volume, nickel is more expensive than aluminium), a foil current collector may be considered as an alternative for the development of commercial Li-S batteries. Moreover, the flexibility of aluminium foil is necessary if Li-S batteries are to reach industrial production stages since low-cost aluminium foil is produced at large scales for industrial and household usages. In spite of the aforementioned advantages, the low tap densities of the sulfur based cathode composites complicate the casting of these materials onto any cathode current collector. In addition, the low electronic conductivity of the cathode composites and the large volume changes experienced by sulfur during charge/discharge (~80 % of sulfur mass)[3] hinder the use of aluminium foil as cathode current collector, especially when large loadings of cathode material are required. Hence, use of aluminium foil as current collector for sulfur based cathodes depends upon the improvement of cathode composite electronic conductivity and the reduction of the effect of large volume change on the stability of cathode structure. Conductive carbon is typically added to electrode composites slurries to improve their electronic conductivity. In

the case of the sulfur composite, higher composite electronic conductivity may be achieved by introducing the carbon additive during the material preparation instead of during slurry making step. This approach, employed in this work, should produce a composite embedded with carbon, facilitating electron conduction between and within the active material particles. Optimization of the active material/conductor/binder ratio, on the other hand, may hinder or minimize the effect of the large volume change on the cathode composite structure.

For practical applications, a good preparation process must produce large yields of active material in shortest possible time. In addition, for scale up purposes, the synthesis done in laboratory should be as close as possible to the aimed industrial conditions (i.e., large ball mill containers and balls, large amount of sample, and low milling speed, etc). Similarly, the heat treatment process must also be optimized to treat a large amount of sample in a short time. The cathode loading should also be as high as possible, so as to provide more energy, without compromising the battery electrochemical performance. Figure 2 presents the details of the $S/pPAN/Mg_{0.6}Ni_{0.4}O/C$ preparation. In the outlined procedure, higher amounts of precursors were loaded in large ball mill containers; bigger zirconia balls (1 cm in diameter) and lower ball milling speeds were used in comparison to our previously reported experimental conditions.[18] The electrochemical performance of the batteries is comparable to our previous results, indicating the scaling up feasibility of the $S/pPAN/Mg_{0.6}Ni_{0.4}O/C$ preparation. The sulfur content of the heat treated $S/pPAN/Mg_{0.6}Ni_{0.4}O$ is 41 wt%, which could be increased to up to 50 wt% by reducing the $Mg_{0.6}Ni_{0.4}O$ and carbon content. Figure 1d shows that the composite has non-uniform particle size, similar to the small scale samples;[16,18] this can ultimately affect the cathode slurry quality.

Among different mass ratios of active material, acetylene black and PVdF binder, the ratio 70:5:15 produces slurries that afford good adhesiveness between the cathode composites and the aluminium foil. For other ratios (e.g. 80:5:15 and 90:5:5), separations between the solid and liquid phases were observed during the casting process. Figure 3 shows the rate capability and cyclability data of thin-film cathodes (~0.55 mg sulfur cm^{-2}) deposited on aluminium foil current collector. Coulombic efficiencies near 100 % indicate practically total suppression of the shuttle effect. Remarkably, the thin-film cathode deposited on aluminium foil exhibits fairly good cyclability and performance comparable to that obtained from the same composite on nickel foam current collector.[18] Additionally, the rate capability is significantly improved, probably due to the smaller sulfur loading and the embedding of carbon in the composite. These results suggest that aluminium foil can be used as current collector for the sulfur based cathodes.
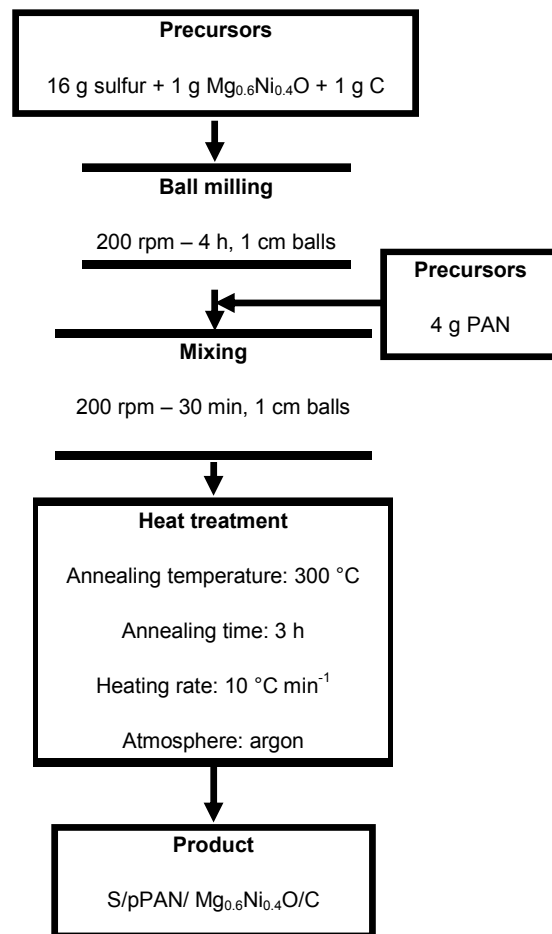

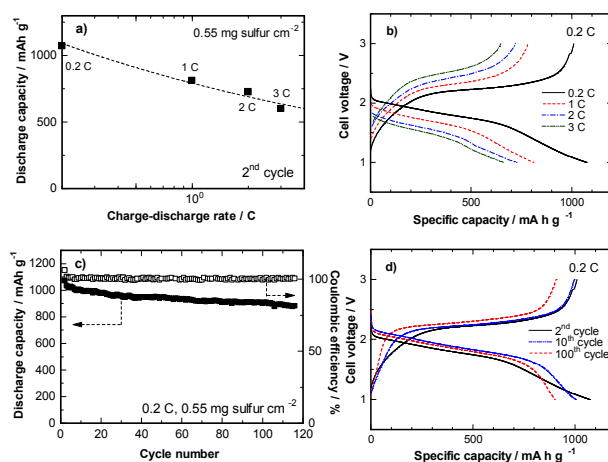**Fig. 2** Flow chart of the preparation of $S/pPAN/Mg_{0.6}Ni_{0.4}O/C$ composite.

Fig. 3 (a) Rate capability; (b) charge/discharge profiles at different C-rates; (c) cyclability and (d) charge/discharge profiles at different cycles of the cells containing $S/pPAN/Mg_{0.6}Ni_{0.4}O/C$ composite cathodes with low sulfur loading (0.55 mg sulfur cm^{-2}). Specific capacities of the cathodes were calculated based on sulfur weight.
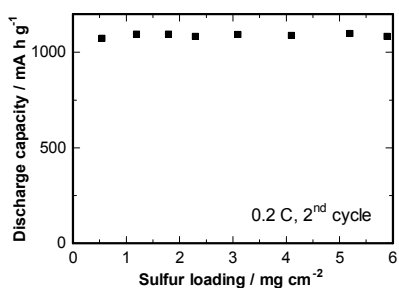
Fig. 4 Effect of sulfur loading on specific discharge capacity of S/pPAN/Mg$_{0.6}$Ni$_{0.4}$O/C composite cathodes at 0.2 C. Specific capacities of the cathodes were calculated based on sulfur weight.

In view of the promising results obtained with the thin-film cathodes, attempts were made to increase the cathode loadings. Figure 4 shows the effect of sulfur loadings on specific discharge capacity of S/pPAN/Mg$_{0.6}$Ni$_{0.4}$O/C composite cathode. At 0.2 C, sulfur loading has no effect on the initial specific discharge capacity of the Li-S batteries. Additionally, at this low current density, the battery performance is steady during the initial cycles, in agreement with the low rate of the electrochemical reactions in effect.[19]
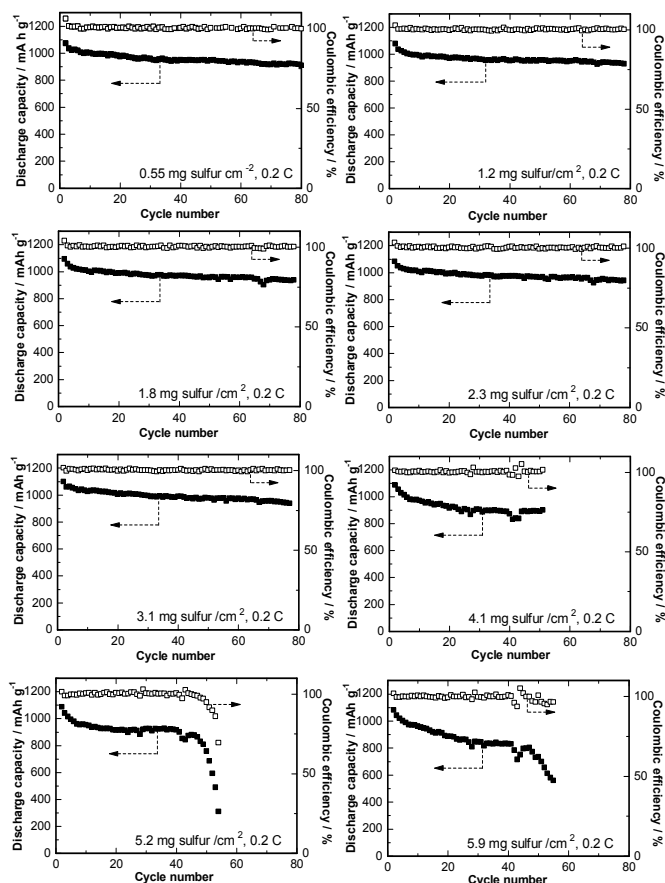

Fig. 5 Effect of sulfur loading on cyclability of S/pPAN/Mg$_{0.6}$Ni$_{0.4}$O/C composite cathodes at 0.2 C. Specific capacities of the cathodes were calculated based on sulfur.

The cathode loadings, however, has significant effects on the cyclability of the batteries, as seen in the results presented in Figure 5. Cathodes with low sulfur loadings ($\leq$3.1 mg cm^{-2}) exhibit good cyclability even after 70 charge/discharge cycles. However, higher sulfur loadings lead to significant capacity fading after 50 cycles. It was observed that thick cathodes can easily be removed from the current collector during cycling. Moreover, larger amounts of sulfur generate more polysulfides which dissolve into the liquid electrolyte.[17,20,21] Due to the limited volume of electrolyte in the coin cells, the polysulfide concentration quickly reaches a limit beyond which the shuttle effect takes place. Confirmed by the decreasing coulombic efficiency, this effect also leads to capacity fading.
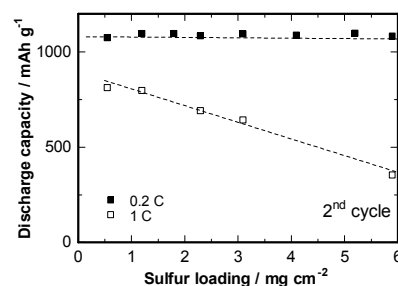

Fig. 6 Effect of sulfur loading on specific discharge capacity of S/pPAN/Mg$_{0.6}$Ni$_{0.4}$O/C composite cathodes at 0.2 C and 1 C. Specific capacities of the cathodes were calculated based on sulfur weight.
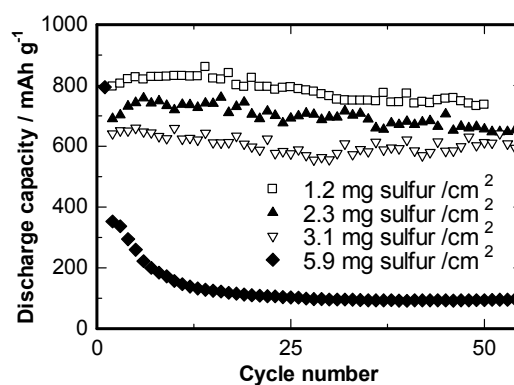

Fig. 7 Effect of sulfur loading on cyclability of S/pPAN/Mg$_{0.6}$Ni$_{0.4}$O/C composite cathodes at 1 C. Specific capacities of the cathodes were calculated based on sulfur.

Specific discharge capacities of the cathodes are hardly affected by the variation of sulfur loadings at low C-rates such as 0.2 C. However, at 1 C the specific discharge capacity decreased linearly versus the increasing of sulfur loadings, as shown in Fig. 6. Moreover, the cathodes with high sulfur loadings display poor cyclability at high C-rates (Fig. 7). Cycling at high C-rate is accompanied with fast volume change and, since thick cathodes are less flexible than their thinner analogues, they are less apt to accommodate the volume changes. Hence, the cathode structure is easily disrupted under such conditions and the contact between particles and current collector is destroyed. Consequently, rapid capacity fading occurs. In conjunction with

the cycling performance at 0.2 C, these results infer that 3.1 mg cm^{-2} is the optimum sulfur loading of the S/pPAN/Mg$_{0.6}$Ni$_{0.4}$O/C composite, for satisfactory levels of capacity and cyclability at 0.2 C and 1 C cycling rates.

After optimization of the cathode preparation, the possibility of using this composite in a commercial cell was evaluated. In batteries with lithium metal anode, the S/pPAN/Mg$_{0.6}$Ni$_{0.4}$O/C composite cathode with up to 3.1 mg sulfur cm^{-2} exhibits the high reversible specific capacity of ≈1000 mA h g^{-1} at 0.2 C, with good capacity retention. Additionally, a coulombic efficiency of almost 100 % implies that the shuttle effect is successfully suppressed by the embedding the sulfur into the polymer matrix,[16] and the absorbent properties of Mg$_{0.6}$Ni$_{0.4}$O.[18] Our results on thin film and moderate thickness cathodes prove these advantages, which are critically important for the improvement of new Li-S batteries. The use of S/pPAN/Mg$_{0.6}$Ni$_{0.4}$O/C composite affords a sustainable loading of S up to 3.1 mg sulfur cm^{-2}.

According to our theoretical calculations and experimental results, the maximum attainable sulfur content is ~50 wt%,[16] which are higher than the sulfur loading on poly(pyrrole) (30%),[14] but comparable with the sulfur loading on multi-wall carbon nanotubes (57%)[4] and approaches the highest sulfur loading levels in the sulfur/carbon system (about 70 wt%).[2,22] More importantly, our method excludes the use of expensive carbons, such as carbon nanotubes[4] and graphene.[22] Furthermore, the S/pPAN/Mg$_{0.6}$Ni$_{0.4}$O/C composite cathode derives a practical capacity of 350 mA h g^{-1} (sulfur content of the cathode, including binder and conductor, is 50 × 0.7 = 35 wt%) and the average discharge voltage is around 1.8 V vs. Li$^+$/Li. Using these values, the specific energy of the cathode is 630 W h kg^{-1}. However, packaging and current collector will reduce the practical specific energy by a factor of 3.[1] Thus, the specific energy of a Li-S cell containing the S/pPAN/Mg$_{0.6}$Ni$_{0.4}$O/C composite cathode is about 210 W h kg^{-1}, which is 1.5 times higher than that of the commercial lithium-ion cells (140 W h kg^{-1}).[1] The specific energy of the cell could be further increased by increasing the specific capacity of the cathode, because the present practical specific capacity is only about 60 % of the theoretical specific capacity (1672 mA h (g sulfur)$^{-1}$). The cell with Mg$_{0.6}$Ni$_{0.4}$O composite cathode also exhibits good cyclability thanks to the enhancement in charge transfer properties facilitated by the existence of Mg$_{0.6}$Ni$_{0.4}$O. This phenomenon is observed recently in our previous work[18] and earlier by Ahn and Lee.[23] The underlying chemistry includes the adsorbing effect of Mg$_{0.6}$Ni$_{0.4}$O toward polysulfide and the catalytic effect of promoting Li/S redox reaction. Nano-sized Mg$_{0.6}$Ni$_{0.4}$O also increases the porosity of the sulfur cathode, which mitigates the volume expansion/contraction during operation. Further optimizations toward higher energy densities are possible. First is to develop new combination methods which afford materials with higher tap densities since the tap density of S/pPAN/Mg$_{0.6}$Ni$_{0.4}$O/C is currently as low as 0.8 g cm^{-3}, which is much lower than that of LiCoO$_2$ (can exceed 2.7 g cm^{-3})[24,25] and LiMn$_2$O$_4$ (about 2 g cm^{-3}).[26,27]

Second is to improve the electrode preparation protocols for even higher loading of sulfur without losing cyclability.

Conclusions

In this study, scaling up process of the S/pPAN/Mg$_{0.6}$Ni$_{0.4}$O/C composite cathode has been carried out. The synthesis procedure is suitable for mass production of the cathodes for Li-S batteries. Aluminium foil, chosen because of its superior physical properties in comparison with nickel foam, was successfully employed as cathode current collector. Optimization of the slurry compositions affords the coating of the sulfur/polymer composite on the surface of aluminium foil with sulfur loadings of up to 5.9 mg cm^{-2}. The thin film cathodes (0.55 mg sulfur cm^{-2}) exhibit high reversible discharge capacity of about 1000 mA h (g sulfur)$^{-1}$, good cyclability and high rate capability. At the low 0.2 C, the discharge capacity is independent of the sulfur load, but decreases with increasing loadings at 1 C rate. Methods for higher loading of sulfur must be discovered since sudden capacity fading after about 50 cycles at 0.2 C is observed for sulfur loadings equal or higher than 3.1 mg cm^{-2}. However, the results presented herein lead us to conclude that S/pPAN/Mg$_{0.6}$Ni$_{0.4}$O/C composite is a good candidate for cathode fabrication for Li-S batteries.
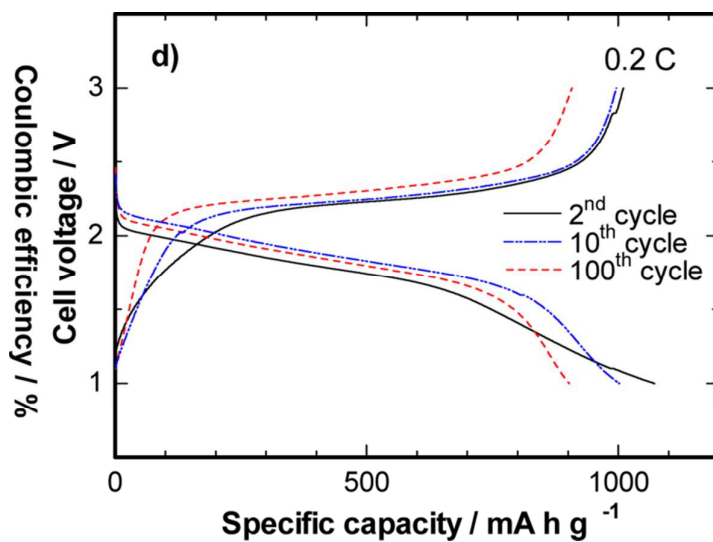
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