

RESEARCH PAPER

Improving the Performance of Lithium-Sulfur Batteries using Sulfur-(TiO₂/SiO₂) yolk-shell Nanostructure

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ABSTRACT

Lithium-Sulfur (Li-S) batteries are considered as one of the promising candidates for next-generation Li batteries in near future. Although, these batteries are suffering from certain drawbacks such as rapid capacity fading during the charge and discharge process due to the dissolution of polysulfides. In this paper, Sulfur/metal oxide (TiO₂ and SiO₂) yolk-shell structures have been successfully synthesized and utilized to overcome this problem and improve the electrochemical performance of sulfur cathode material. Prepared materials have been characterized using Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and X-ray diffraction (XRD) techniques. The results show significant improvement in the battery performance as a result of using Sulfur-SiO₂ and Sulfur-TiO₂ yolk-shell structures. The obtained Sulfur-TiO₂ electrode delivers a high initial discharge capacity (>2000 mA h g⁻¹) and discharge capacity of 250 mA h g⁻¹ over 8 charging/discharging cycles with Coulombic efficiency of 60%, while initial discharge capacity for Sulfur-SiO₂ electrode was lower (>1000 mA h g⁻¹) compared to Sulfur-TiO₂. Sulfur-SiO₂ electrode shows the discharge capacity of 200 mA h g⁻¹ over 8 charging/discharging cycles with Coulombic efficiency around 70%. The obtained galvanostatic results demonstrated that Sulfur-TiO₂ electrode possess stronger capability to prevent sulfur and its intermediate reaction products from dissolving into the electrolyte.

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INTRODUCTION

Rechargeable batteries, such as lead-acid, nickel-cadmium and nickel metal hydride have serviced humanity for over a century with their use in a variety of applications such as portable electronic devices and automobiles. Cost, energy and power density, cycle life, safety, and environmental compatibility considered the most important parameters raised the global interest towards the development of advanced generation of battery technology such as lithium

batteries [1]. Nowadays, lithium batteries as high performance energy storage devices are viewed as promising candidates to satisfy the urgent demand for advanced portable electronics [2-4]. Thus, fabrication electrode materials with high volumetric energy density and specific capacity is essential for next-generation lithium batteries. In comparison with the different types of batteries, the present lithium-ion (Li-ion) batteries revolutionized the battery industry by

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demonstrating exceptionally high energy density, low self-discharge rate, and long cycle life [5]. However, despite of the many advantages of the Li-ion batteries, they suffer from some noticeable disadvantages as well. The main drawback, apart from cost are safety concerns, scarcity of battery constituents such as cobalt (Co), and insufficient capacity for demanding uses such as transportation [6,7].

Sulfur, one of the most abundant elements in the earth's crust, offers high theoretical capacity of 1675 mAhg⁻¹ which is about an order of magnitude higher than the transition-metal oxide cathodes [8, 9]. Lithium-Sulfur (Li-S) batteries are one of the most promising next-generation energy storage systems. They have an energy density of 2600 Whkg⁻¹ much higher than that of Li-ion batteries (800 Whkg⁻¹ for conventional insertion Li-ion cathodes). Furthermore, Sulfur has other considerable advantages, such as its natural abundance, low cost, and low environmental pollution. However, the Li-S batteries need improvement in regards of their cycle life, stability and utilization efficiency of their active materials. High resistivity of Sulfur and Li₂S₂/Li₂S that reduces voltage efficiency of cathodes, high solubility and shuttle effect of polysulfides that reduce material utilization efficiency and anode corrosion due to sulfide deposits are the common performance-limiting factors in Li-S batteries [10]. To overcome these disadvantages, many efforts have been devoted to reduce the shuttle effect and improve the retention of active material within the Sulfur electrode. Some approaches are focused on the developing of Sulfur composites with favorable nanostructures and properties to improve the discharge capacity, cyclability and coulombic efficiency [11-13]. Other methods being pursued include novel cell configurations with trapping interlayers, Li/dissolved polysulfide cells and use of efficient electrolytes. Not only conductive carbons/polymers but also other proper materials could be applied in the composite synthesis with Sulfur. The alternative additives may serve as an absorbing agent for trapping the soluble polysulfides or may function as a supporting active material for generating extra capacity [14].

One attractive idea is Sulfur-metal oxide yolk-shell composites. In this paper, yolk-shell structure of Sulfur-TiO₂ and Sulfur-SiO₂ composites have been utilized. The idea of the yolk-shell structure is to avoid fracture of the TiO₂ and SiO₂ spheres

during the volume expansion of the active material, which could lead to serious leakage of polysulfides. Extra void or pore space remaining in the cathode structure is desirable to retain the dissolved polysulfides and cushion the volume change during the subsequent charge/discharge processes.

MATERIALS AND METHODS

Chemicals

All chemicals including sodium thiosulfate (Na₂S₂O₃·5H₂O, 98%), hydrochloride acid (HCl, 35%), polyvinylpyrrolidone (PVP, Mw~55,000, 0.02 wt%), isopropanol, ammonia (28%), Tetraethyl orthosilicate (TEOS), Titanium diisopropoxide bis(acetyla-cetonate), N-Methyl Pyrrolidone (NMP) and Polyvinylidene fluoride (PVDF) were purchased from Merck and used without further purification. Super P powder was purchased from Sigma-Ildrich. Deionized water (DI, 18.2 MΩ cm⁻¹) was used in all aqueous solutions and washing procedures throughout the study.

Synthesis of sulfur nanoparticles

Sulfur nanoparticles were synthesized by adding concentrated HCl (0.8 ml, 10 M) to an aqueous solution of Na₂S₂O₃·5H₂O (100 ml, 0.04 M) containing a low concentration of polyvinylpyrrolidone (PVP, Mw~55,000, 0.02 wt%). After stirring for 2 h at room temperature, the obtained sulfur nanoparticles the sulfur nanoparticles were collected and washed by centrifugation .

Synthesis of sulfur-TiO₂ and sulfur-SiO₂ yolk-shell nanostructures

The as-prepared sulfur nanoparticles were re-dispersed into the aqueous solutions of PVP (20 ml, 0.05 wt%), isopropanol (80 ml) and concentrated ammonia (2 ml, 28 wt%).After stirring for 1h, Titanium diisopropoxide bis(acetyla-cetonate) (50 ml, 0.01 M in isopropanol) was added in five portions (5 × 10 ml) with half hour intervals. After stirring for 4 h, the obtained sulfur-TiO₂ core-shell nanoparticles was washed by centrifugation to remove freely hydrolysed TiO₂ , followed by redispersion into deionized water (20 ml). To get the sulfur-TiO₂ yolk-shell nanostructures, the solution containing core-shell particles (20 ml), isopropanol (20 ml) and toluene (0.4 ml) was stirred for 4 h to achieve partial dissolution of sulfur. The as-synthesized sulfur-TiO₂ yolk-

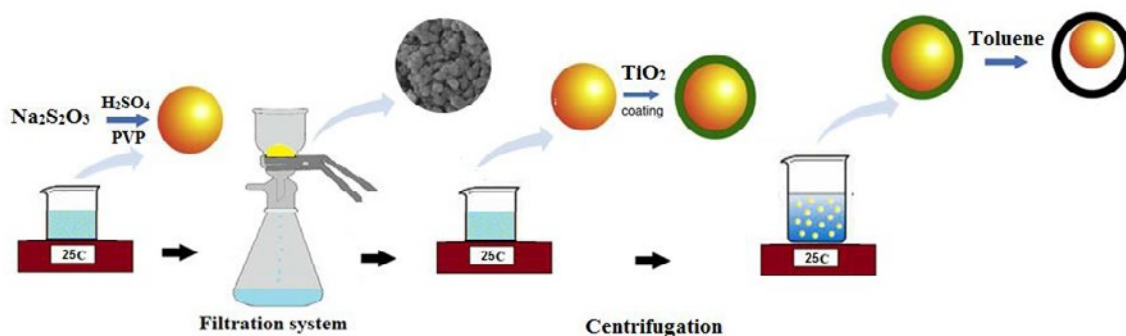


Fig. 1. The Schematic of two-step synthetic route for sulfur-TiO₂ yolk-shell

shell nanostructures were then collected using centrifugation and dried under vacuum overnight.

Same procedure as used for sulfur-TiO₂ yolk-shell was proceed to obtain sulfur-SiO₂ yolk-shell except instead of Titanium diisopropoxide precursor, Tetraethyl orthosilicate (TEOS) has been used. The Schematic of the synthetic process has been demonstrated in Fig. 1.

Characterization

Structural investigations were carried out on a Philips X'pert instrument powder X-ray diffractometer operating at 40 kV and 40 mA and using Cu-K α radiation ($\lambda=0.15405$ nm) over the 2θ range of 15–80°. Morphological studies were carried out on a Hitachi S4160 scanning electron microscopy (SEM) instrument. Transmission electron microscopy (TEM) was performed on a Philips CM30 operating at 200 KeV.

Electrochemical measurements

In order to prepare the working electrodes, sulfur-based materials were mixed with super P and poly-vinylidene fluoride (PVDF) binder in a weight ratio of 75:15:10 in N-methyl-2-pyrrolidinone (NMP) to prepare a slurry. The prepared slurry was then coated on to aluminium foil using doctor blade approach and dried under vacuum to form the working electrode. Lithium foil was employed as the anode with a Celgard separator(no. 2032) in a 2325 coin cell. The coin cells were assembled in an argon-filled glove box using freshly prepared solution of lithium bis(tri-fluoromethanesulfonyl)imide (1 M) in 1:1 v/v 1,2-dimethoxyethane and 1,3-DOL as electrolyte. The cells were charged and discharged at ambient temperature between 0.05 and 3 V using a battery testing system (Kimiastat 126).

RESULTS AND DISCUSSION

Material characterization

The schematic illustration of the synthesised sulfur-MO₂ (M=Ti, Si) yolk-shell nanostructures has been seen in Fig. 2(a). Fig. 2(b) demonstrates the XRD pattern for sulfur which has several varying diffraction peaks and typical diffraction peak around 23°, indicated that the pure sulfur exists in the crystalline state and the structure of the pure sulfur is S8 (JCPDS 4: 8-0247) [17]. The peaks of crystalline sulfur and TiO₂ (JCPDS No. 21-1272) clearly indicated that the composition of sulfur-TiO₂ composite (Fig. 2(c)). XRD pattern of sulfur-TiO₂ yolk-shell depicted additional peaks (surrounded with red circles) at $2\theta= 25.02$ and 45 related to (011) and (013) planes of TiO₂ [15]. Similarly in the case of sulfur-SiO₂ yolk-shell nanostructures, Fig 2(d) shows the distinguished peaks related to SiO₂ in the XRD pattern of sulfur-SiO₂ [16].

The SEM image of the synthesized sulfur-TiO₂ yolk-shell structures has been shown in Fig. 3(a). It can be clearly identified that the TiO₂-sulfur yolk-shell composite is globular, and the typical diameter of it is in range of 100 nm. Fig. 3(b) demonstrates the TEM image of TiO₂-sulfur yolk-shell. The TEM image somehow reveals the partial dissolution of sulphur in toluene to create an empty space between the sulphur core and the TiO₂ shell, resulting in the yolk-shell morphology. It should be mentioned that either an empty area or an area of lower intensity depending on the orientation of the particles.

SEM and TEM images of sulfur-SiO₂ yolk-shell nanostructures have been shown in Fig. 4(a) and (b), respectively. The yolk-shell structure is clearly evident in the TEM image as well.

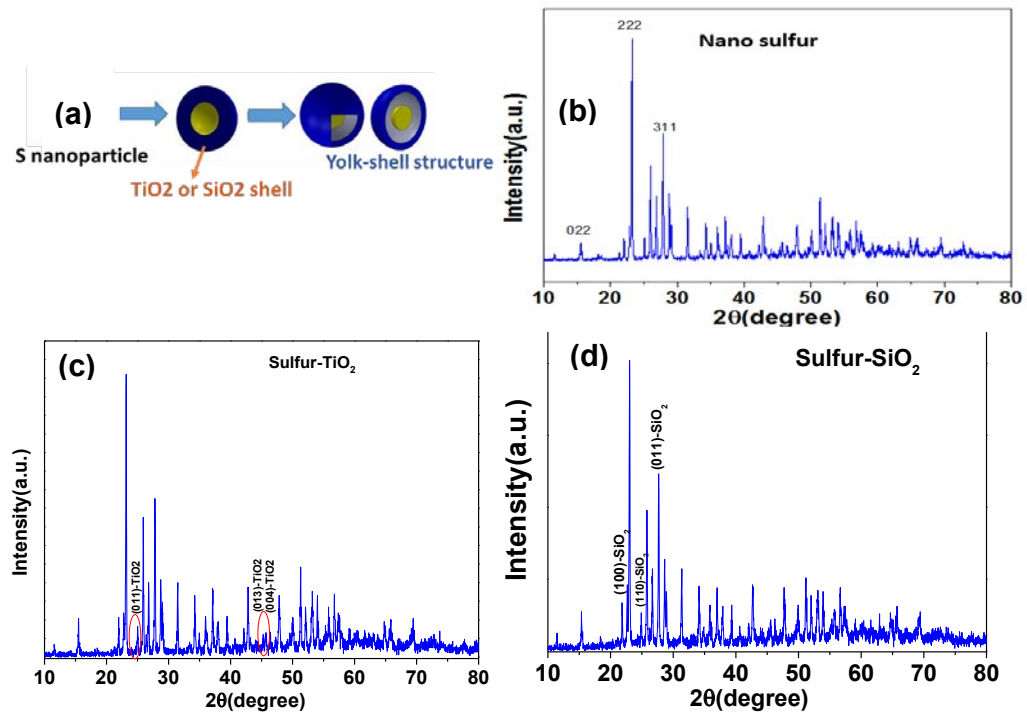


Fig. 2. (a) Schematic diagram showing the structure of core-shell. Sulfur is at the core part of this configuration. XRD result for (b) Sulfur nanoparticles, (c) Sulfur-TiO₂ core-shell, (d) Sulfur-SiO₂ core shell nanoparticles.

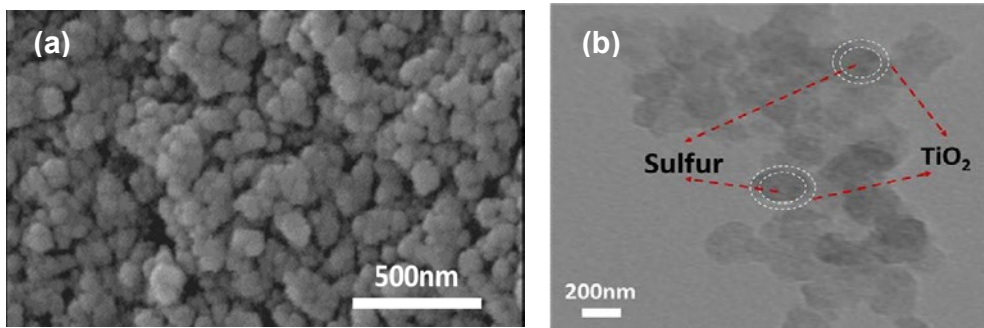


Fig. 3. (a) SEM and (b) TEM images of sulfur-TiO₂ yolk-shell nanostructure

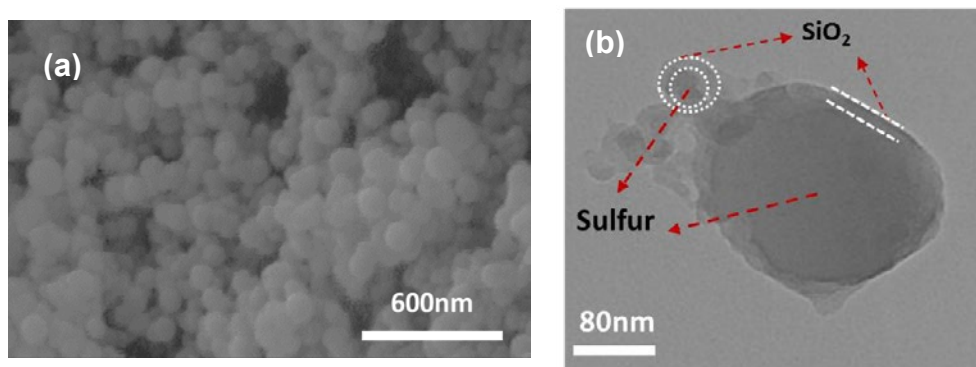


Fig. 4. (a) SEM and (b) TEM images of sulfur-SiO₂ yolk-shell nanostructures

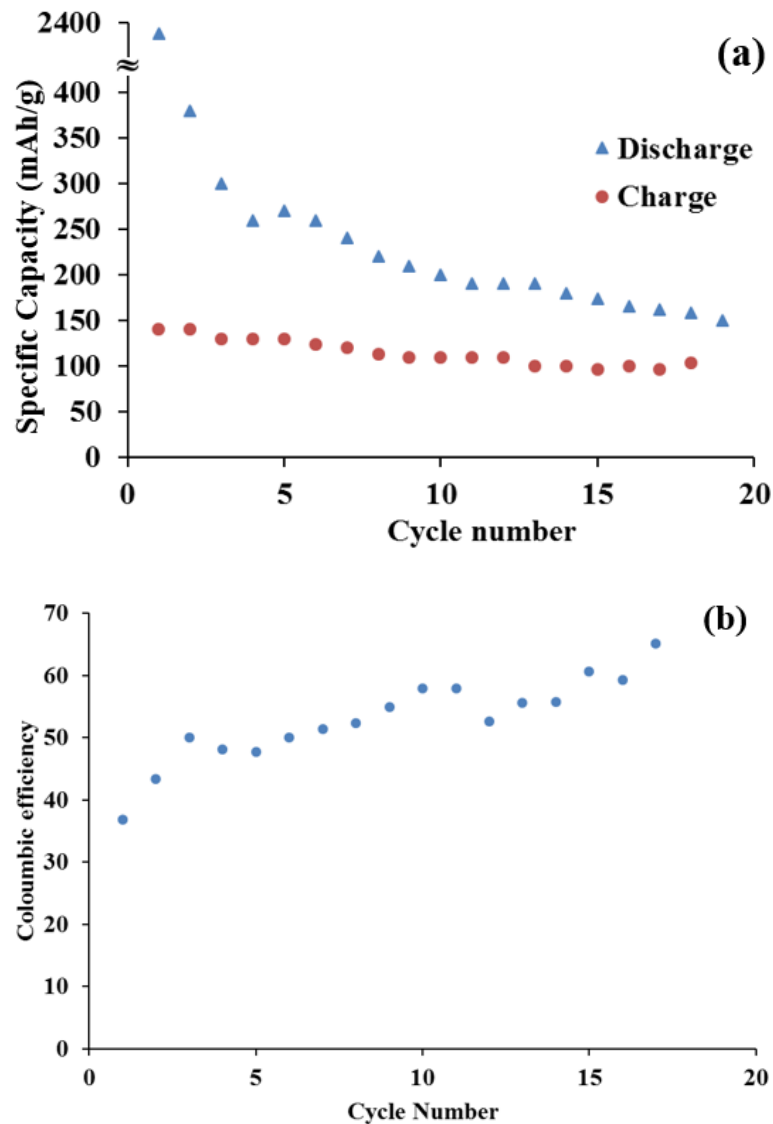


Fig. 5. Electrochemical performance of sulfur-TiO₂ anostructures. (a) Charge/discharge capacity (b) Coulombic efficiency

Electrochemical performance

Fig. 5 (a) illustrated the cycling performance of the Sulfur-TiO₂ yolk-shell cathode at the current of 10 uA for first 20 cycles. An initial discharge capacity of >2000 mAhg⁻¹ was observed. After 20 cycles, 200 mAhg⁻¹ discharge capacity was achieved. Meanwhile, the average coulombic efficiency in the 20 cycles reaches about 60% (Fig. 5 (b)).

Cycle performances and Coulombic efficiency of the sulfur-SiO₂ yolk-shell nanostructures cathode material at current of 10 uA are shown in Fig.6a and 6b respectively. After an initial discharge capacity of 1600 mAhg⁻¹, the sulfur-SiO₂ yolk-shell nanostructures achieved capacity and

Coulombic efficiency 180 mAhg⁻¹ and 80% for 20 cycles, respectively. Comparing electrochemical performance of different electrodes materials, sulfur-TiO₂ yolk-shell electrode obtained discharge specific capacity and coulombic efficiency of 220 mAhg⁻¹ and 51% after the 8th cycles, respectively shown sulfur-TiO₂ yolk-shell electrode presented a better performance over all. However, as it can be seen form cycling performance curves that sulfur-SiO₂ yolk-shell electrode possesses better capacity retention over cycling We have also used the bare sulfur for battery fabrication. The electrochemical performance of bare sulfur deminstrated the discharge specific capacity and colombic efficiency

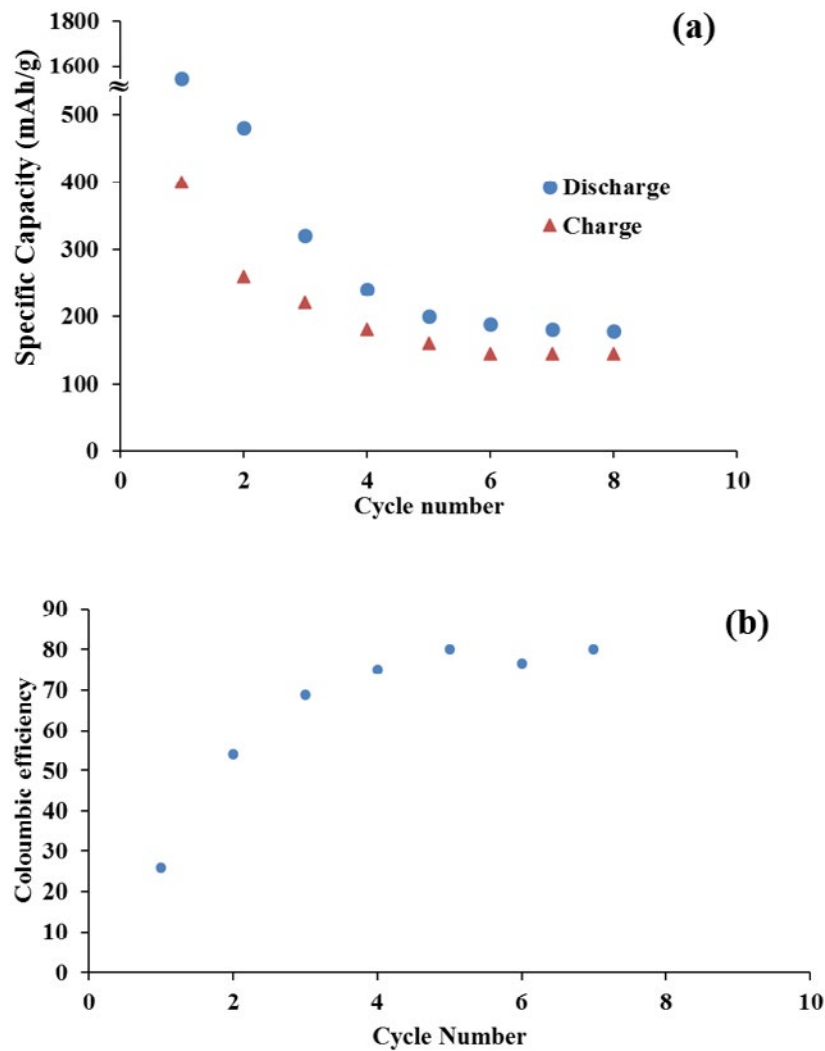


Fig. 6. Results of electrochemical tests for Sulfur-SiO₂ core-shell structure.

of 9.6 mAhg⁻¹ and 46 % respectively, which is extremely lower than the results of both yolk-shell electrode batteries. From the obtained results it can be concluded that yolk-shell structures utilized metal oxides possess surface hydroxyl which can tightly interact with sulfur, effectively prevent the diffusion of polysulfide anions, minimize the shuttle effect and improve the performance of Lithium-Sulfur batteries.

CONCLUSION

In this manuscript, successful synthesis of sulfur-TiO₂ and sulfur-SiO₂ yolk-shell nanostructures are reported. As prepared materials have been used as a cathode of Li-Sulfur batteries. The

results indicated significant improvement in the electrochemical performances such as specific capacity and coulombic efficiency of these batteries in comparison with using the bare Sulfur electrode. Therefore, results demonstrated that the metal oxides yolk-shell morphology plays an important role in preventing the dissolution of the polysulfide anions to the electrolyte and minimizing the "shuttle effect" and it can be applied to other anode and cathode systems, which undergo large volumetric expansion.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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