

# Carbonyl- $\beta$ -Cyclodextrin as a Novel Binder for Sulfur Composite Cathodes in Rechargeable Lithium Batteries

Jiulin Wang,\* Zhendong Yao, Charles W. Monroe, Jun Yang, and Yanna Nuli

As one of the essential components in electrodes, the binder affects the performance of a rechargeable battery. By modifying  $\beta$ -cyclodextrin ( $\beta$ -CD), an appropriate binder for sulfur composite cathodes is identified. Through a partial oxidation reaction in  $\text{H}_2\text{O}_2$  solution,  $\beta$ -CD is successfully modified to carbonyl- $\beta$ -cyclodextrin (C- $\beta$ -CD), which exhibits a water solubility ca. 100 times that of  $\beta$ -CD at room temperature. C- $\beta$ -CD possesses the typical properties of an aqueous binder: strong bonding strength, high solubility in water, moderate viscosity, and wide electrochemical windows. Sulfur composite cathodes with C- $\beta$ -CD as the binder demonstrate a high reversible capacity of  $694.2 \text{ mA h g}_{(\text{composite})}^{-1}$  and  $1542.7 \text{ mA h g}_{(\text{sulfur})}^{-1}$ , with a sulfur utilization approaching 92.2%. The discharge capacity remains at  $1456 \text{ mA h g}_{(\text{sulfur})}^{-1}$  after 50 cycles, which is much higher than that of the cathode with unmodified  $\beta$ -CD as binder. Combined with its low cost and environmental benignity, C- $\beta$ -CD is a promising binder for sulfur cathodes in rechargeable lithium batteries with high electrochemical performance.

## 1. Introduction

Recently, “green energy” fields, such as electric vehicles, solar and wind plants, and smart grids, have required batteries working as power sources or as energy storage and conversion devices that exhibit high energy density, long cycle life, low cost, high safety, and nontoxicity.<sup>[1,2]</sup> A conventional lithium ion battery composed of a transitional metal oxide cathode and a carbon-based anode cannot deliver an energy density more than  $300 \text{ W h kg}^{-1}$ . Therefore, rechargeable lithium metal batteries including lithium sulfur (Li/S) and lithium oxygen batteries are expected to boost energy density, even up to  $500\text{--}900 \text{ W h kg}^{-1}$ .<sup>[3]</sup> A Li/S battery composed of an elemental sulfur cathode and lithium metal anode has a theoretical energy density of  $2567 \text{ W h kg}^{-1}$  (based on pure electrochemical active materials). Furthermore, adopting sulfur as the cathode material for rechargeable lithium batteries has other obvious

advantages; there are abundant sulfur resources, and the cathodes are low cost and environmentally friendly.

Despite its considerable advantages, there are many critical problems in having a sulfur cathode in a rechargeable lithium battery; these problems must be properly resolved before practical applications are possible. Firstly, sulfur is highly insulating ( $5 \times 10^{-30} \text{ S cm}^{-1}$  at  $25^\circ\text{C}$ ), which generally causes low utilization of active materials. Another major problem in a rechargeable Li/S battery is the quick capacity decay during the charge–discharge process, which is mainly caused by the high solubility of various forms of intermediate polysulfides. During cycling, polysulfides dissolve into the electrolyte and transfer through the separator to the lithium metal anode where they are reduced to solid precipitates ( $\text{Li}_2\text{S}$  and/or  $\text{Li}_2\text{S}_2$ ),

causing the loss of active materials.<sup>[4–6]</sup> The high solubility of polysulfide causes an additional problem of “sulfur shuttle”, a typical phenomenon in a rechargeable Li/S battery, leading to low coulombic efficiency.<sup>[7]</sup> The main strategies have involved embedding sulfur in conductive polymers<sup>[8–10]</sup> or in carbon of various morphologies including porous carbon,<sup>[11–14]</sup> nanotubes or -fibers,<sup>[15–17]</sup> and graphene,<sup>[18,19]</sup> in order to enhance the electrical conductivity and electrochemical reversibility, and to limit the dissolution of polysulfides. In order to avoid the effects of lithium dendrite,  $\text{Li}_2\text{S}$  has also been reported as a cathode materials with silicon or tin as the anode.<sup>[20,21]</sup>

The binder is undoubtedly an important component in a lithium battery. It functions to bond and keep the active materials in the electrode, to improve electrical contact between the active materials and conductive carbon, as well as to link the active materials with the current collector. For battery technology, a binder should be of low cost and should possess strong bonding strength, high physical and electrochemical stability in the electrolyte, low resistance, and additional functions to buffer the expansion/shrinkage of the cathode during the charge–discharge processes and to maintain the physical structure of the stable electrode.<sup>[22–24]</sup> The ideal binder for the sulfur cathode should have the additional capability to wrap sulfur composite materials and to limit the dissolution of polysulfides. There are already many materials used as sulfur cathode binders in rechargeable lithium batteries. Polyvinyl pyrrolidone (PVP) and polyethyleneimine (PEI) were reported as a mixed binder to modify the morphology of a sulfur cathode.<sup>[25]</sup> Kim et al. reported polytetrafluoroethylene (PTFE) and carboxy

Prof. J. Wang, Z. Yao, Prof. J. Yang, Prof. Y. Nuli  
School of Chemistry and Chemical Engineering  
Shanghai Jiao Tong University  
Shanghai 200240, P. R. China  
E-mail: wangjiulin@sjtu.edu.cn

Prof. C. W. Monroe  
Department of Chemical Engineering  
University of Michigan  
Ann Arbor, MI 48109, USA



DOI: 10.1002/adfm.201201847

methyated cellulose (CMC) as binders, which can alleviate the volume change of the electrode during charge/discharge.<sup>[26]</sup> Choi et al. used polyethylene oxide (PEO) and polyvinylidene fluoride (PVDF) as binders with carbon nanofibers as a conductive additive to improve the cycle performance of sulfur composites.<sup>[27]</sup> In the case of the PEO binder, the PEO is partially soluble in some electrolyte solvents, which may cause poor mechanical strength in the cathode.<sup>[28,29]</sup> Generally, PVDF is dissolved in *N*-methyl-2-pyrrolidone (NMP) which is typically dried at 120 °C under vacuum for complete drying. Under these conditions, sulfur sublimates and vaporizes, causing the loss of active materials and related environmental problems.<sup>[30]</sup>

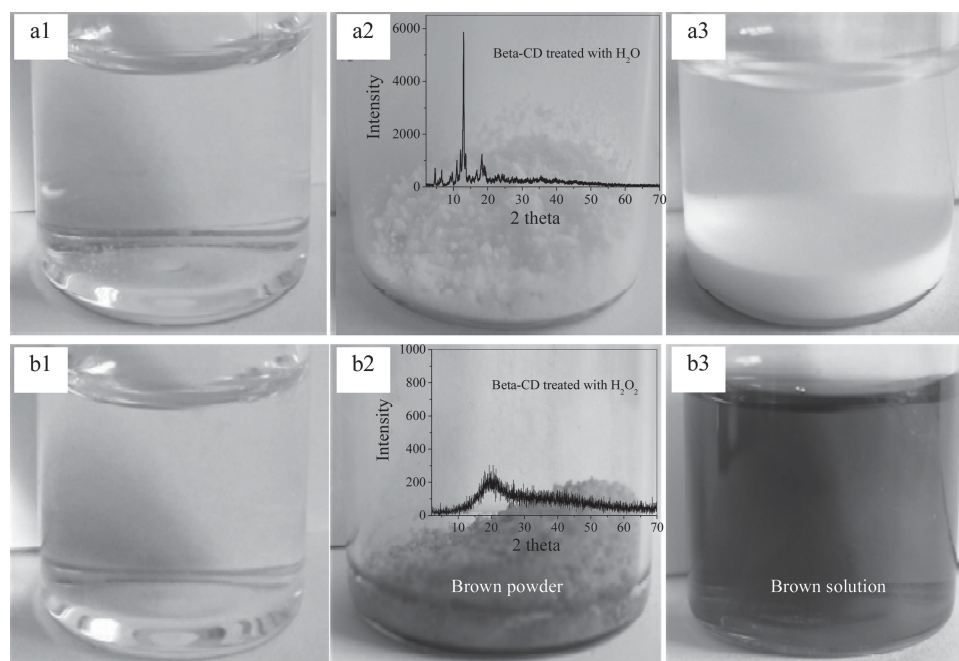
Aqueous binders have attracted a good deal of attention due to the advantages of its low cost, reduced safety concerns, and environmental benignity. Alginate, a natural polysaccharide extracted from brown algae, dramatically stabilized the cycling performance of a nanosilicon and graphite anode.<sup>[24]</sup> Liu et al. modified the elastomeric binder system of styrene butadiene rubber (SBR) and sodium carboxy methyl cellulose (NaCMC) with water as the solvent to enhance the cycle properties of a silicon anode.<sup>[31]</sup> A sulfur cathode prepared at a pH of 10.0 with gelatin binder, a highly adhesive agent, and an effective dispersing agent, exhibited relatively high capacity.<sup>[32–34]</sup> Recently, a Nafion solution neutralized by LiOH was reported as a lithium ionic conductive binder to improve the performance of sulfur cathodes despite its high cost.<sup>[30]</sup>

Cyclodextrins are products of the enzymatic hydrolysis of amylose; structurally, they comprise a series of cyclic oligosaccharides composed of six, seven, or eight D(+)-glucose units

linked by  $\alpha$ -1,4-linkages, named  $\alpha$ -,  $\beta$ - or  $\gamma$ -CD, respectively. The main drawback of cyclodextrins, particularly  $\beta$ -cyclodextrin ( $\beta$ -CD), is its low aqueous solubility, which restricts its application in nanocomposites, medicine, life science, and drug delivery.<sup>[35,36]</sup> Many researchers have focused on improving the solubility of cyclodextrin by modifying it via methylation, hydroxyalkylation, or carbonylation of the hydroxyl groups.<sup>[37–39]</sup> While it is the only large-scale commercialized cyclodextrin and the cheapest derivative,  $\beta$ -CD has a water solubility of only 1.85 g (in 100 g H<sub>2</sub>O) at 25 °C. Its low solubility makes it unsuitable to be used without modification as the aqueous binder in batteries. In this paper,  $\beta$ -CD is partially oxidized to enhance its solubility in water, and then applied as a binder for sulfur-based cathodes. In addition to its bonding function, the modified  $\beta$ -CD is expected to wrap the surface of the sulfur composite cathode to limit the dissolution of soluble polysulfide.

## 2. Results and Discussion

As previously indicated,  $\beta$ -CD—the only large-scale commercialized cyclodextrin and the cheapest cyclodextrin derivative—is composed of seven D(+)-glucose units linked by  $\alpha$ -1,4-linkages, and it has a very poor water solubility (1.85 g in 100 g H<sub>2</sub>O at room temperature). Although its solubility can be enhanced at high temperature (Figure 1a1),  $\beta$ -CD leaves a crystalline solid after the water is evaporated (Figure 1a2), and the solid will not completely dissolve in water at room temperature (Figure 1a3), making it unsuitable to be adopted without modification as an



**Figure 1.** Photos of  $\beta$ -CD treated with pure water (a) and H<sub>2</sub>O<sub>2</sub> (b). a1)  $\beta$ -CD dissolved in pure water at 80 °C; a2) the crystal powder obtained after the sample of (a1) is treated in a sealed bottle for 24 h and then dried at 80 °C; a3) the sample in (a2) is mixed in water at room temperature. b1)  $\beta$ -CD dissolved in H<sub>2</sub>O<sub>2</sub> solution at 80 °C; b2) gel powder obtained after the sample of (b1) is treated in a sealed bottle for 24 h and then dried at 80 °C; b3) the sample of (b2) is dissolved in water at room temperature. The insets in (a2) and (b2) are the X-ray diffraction (XRD) patterns of  $\beta$ -CD treated with pure water and H<sub>2</sub>O<sub>2</sub>, clearly indicating that the materials are crystalline and amorphous powder, respectively.

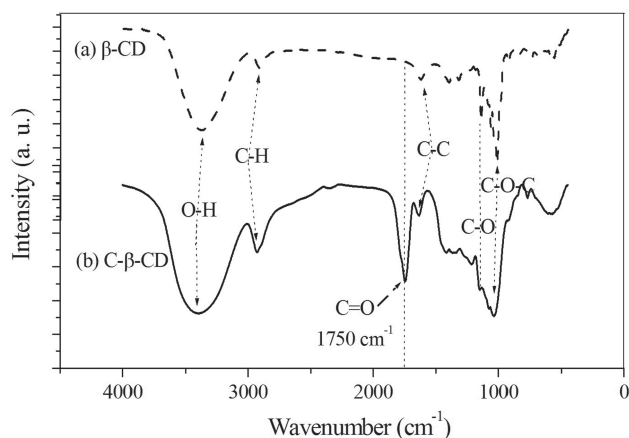


Figure 2. FTIR spectra of  $\beta$ -CD (a) and C- $\beta$ -CD (b).

aqueous binder in batteries. For battery technology, the binder should first completely dissolve in the solvent; after the solvent is completely removed, it should form a network or thin film on the electrochemical active material. Figure 1b1 shows that  $\beta$ -CD can dissolve in  $\text{H}_2\text{O}_2$  solution to form a transparent solution at 80 °C in a sealed bottle. The color of the solution gradually changes from initially being colorless to brown; no further color changes occur after 24 h. Remarkably different from  $\beta$ -CD in  $\text{H}_2\text{O}$  solution, the  $\beta$ -CD hydrogen peroxide solution leaves a gel when the water is evaporated; no crystals are formed during drying process, which results in a dry gel powder (Figure 1b2). This brown dry gel powder can quickly dissolve in water at room temperature (Figure 1b3). It is clear that the  $\text{H}_2\text{O}_2$  treatment modifies  $\beta$ -CD to a soluble form.

Fourier Transform (FT) IR spectra were obtained to investigate the chemical bond changes of  $\beta$ -CD treated with  $\text{H}_2\text{O}_2$  (Figure 2). A new peak at  $1750\text{ cm}^{-1}$  ascribed to the  $\text{C}=\text{O}$  stretching vibration appears after  $\beta$ -CD treated with  $\text{H}_2\text{O}_2$ . Except for this new peak, no other obvious changes exist between the FTIR spectra of  $\beta$ -CD, before and after treatment.

This indicates that the original cyclic oligosaccharide of  $\beta$ -CD has not been destroyed during oxidation. The reaction between  $\beta$ -CD and  $\text{H}_2\text{O}_2$  is proposed to be the following: some of the  $\text{C}-\text{O}-\text{H}$  bonds of  $\beta$ -CD are oxidized by  $\text{H}_2\text{O}_2$  to form  $\text{C}=\text{O}$  as shown in Figure 3, resulting in carbonyl- $\beta$ -cyclodextrin (C- $\beta$ -CD).<sup>[39]</sup> A belt of hydrogen bonds exists around the cyclodextrin side, and the entire  $\beta$ -CD molecule possesses a rather rigid structure, which causes  $\beta$ -CD to barely dissolve in water at room temperature. As some of the  $\text{C}-\text{O}-\text{H}$  bonds are oxidized to carbonyl groups, the strong hydrogen bond network is broken allowing C- $\beta$ -CD to be highly soluble in the water. Most importantly, no crystalline material and only a dry gel is left after the water is completely removed; this is a critical characteristic for the binder in battery technology. It is difficult to get a concrete solubility value for C- $\beta$ -CD because it forms a gel in the concentrated solution during drying. In our experiments, the water solubility of C- $\beta$ -CD is more than 180 g in 100 g  $\text{H}_2\text{O}$  at room temperature, nearly 100 times that of  $\beta$ -CD at 25 °C.

Shearing strength and viscosity are two basic parameters for the binder. The shearing strength of  $\beta$ -CD and C- $\beta$ -CD, along with that of a commercialized randomly methylated  $\beta$ -CD (M- $\beta$ -CD) for comparison, are presented in Table 1.  $\beta$ -CD cannot bond two plastic strips together at all and does not show any bonding capability; however, after carbonylation with  $\text{H}_2\text{O}_2$ , the resulting C- $\beta$ -CD was able to tightly bond an Al foil to a glass dish, and attempts to remove the foil from the glass resulted in the Al foil being torn. Using C- $\beta$ -CD, two plastics were also successfully bonded together after the removal of the solvent water. In this case, the shearing strength of C- $\beta$ -CD is 0.197 MPa. To the best of our knowledge, this is the first report of the excellent bonding capabilities of C- $\beta$ -CD. Although methylation of the hydroxyl groups also results in the more soluble M- $\beta$ -CD, the shear strength of the two strips with the M- $\beta$ -CD coating approaches zero. During the drying process, M- $\beta$ -CD re-crystallized and powder formed, demonstrating a lack of bonding capability—similar to the properties of its precursor  $\beta$ -CD.

The relative viscosities of the C- $\beta$ -CD solutions with different concentrations are shown in Figure 4. The viscosity of water is assumed to be 1.  $\beta$ -CD is barely soluble in water, and

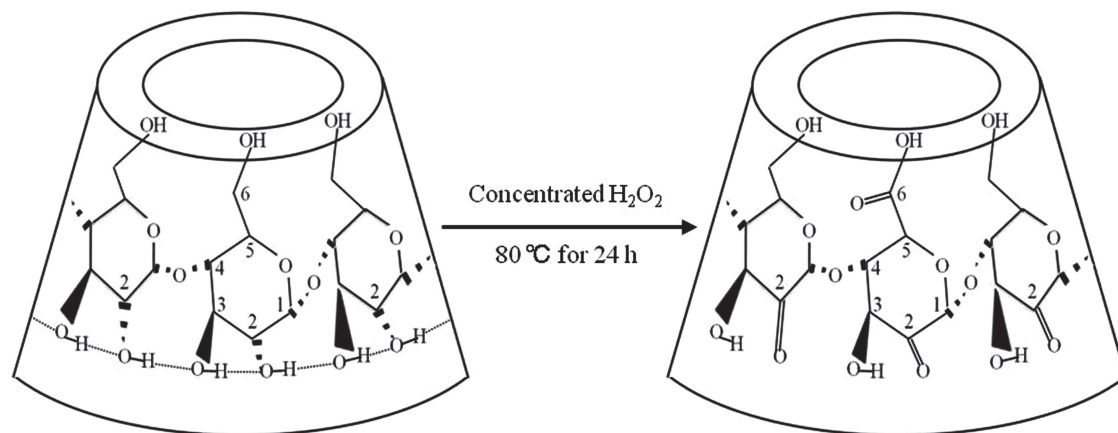


Figure 3. Schematic reaction of  $\beta$ -CD with  $\text{H}_2\text{O}_2$ .

**Table 1.** Properties of  $\beta$ -CD and its derivatives, randomly methylated  $\beta$ -CD (M- $\beta$ -CD) and carbonyl- $\beta$ -CD (C- $\beta$ -CD).

Material	Tension [N]	Bonding strength [MPa]	Solubility [g/(100 g H <sub>2</sub> O)]
$\beta$ -CD	0	0	1.85
M- $\beta$ -CD	0	0	ca. 30
C- $\beta$ -CD	141	0.197	>180

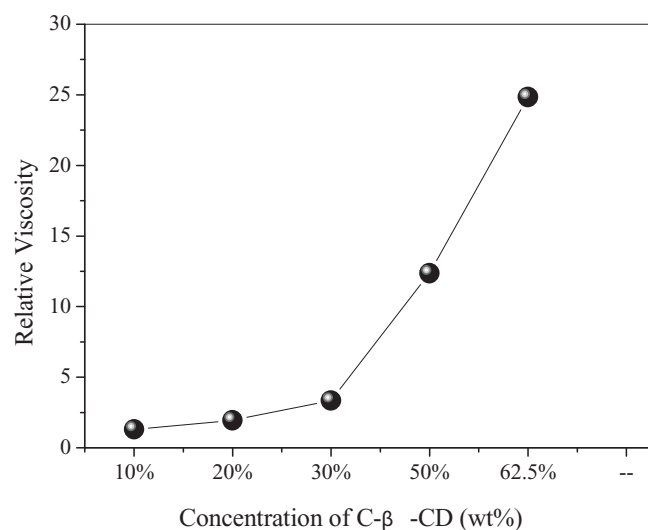
the relative viscosity of its saturated solution is ca. 1.02—very close to that of pure water. After carbonylation with H<sub>2</sub>O<sub>2</sub>, the resulting C- $\beta$ -CD solution demonstrates a considerable change in viscosity, which increases along with its concentration. At a concentration below 20 wt%, the viscosity of the solution is very low, which may be beneficial for the homogeneous mixing of electrochemical active materials with conductive carbon during electrode slurry preparation.

The remarkable differences of solubility and bonding capability between  $\beta$ -CD and C- $\beta$ -CD can be ascribed to the change of molecular structure. In  $\beta$ -CD, all hydroxyl groups at the wider rim of its cyclic structure form intramolecular bonds (dotted bonds in Figure 3). This leads to a belt of hydrogen bonds along the wider rim of  $\beta$ -CD, which gives the entire molecule a rather rigid structure, and thus makes the solubility of  $\beta$ -CD very low.<sup>[39]</sup> When treated with H<sub>2</sub>O<sub>2</sub>, some of the hydroxyl groups are oxidized to form carbonyl functional groups; in particular each C(2)OH (refer to number scheme in Figure 3) is oxidized to a carbonyl group, and the continuous belt of hydrogen bonds is broken, resulting in some “free” hydroxyl groups in C- $\beta$ -CD. As a result, solubility of C- $\beta$ -CD is significantly higher than that of  $\beta$ -CD. The excellent shearing strength property and moderate viscosity of C- $\beta$ -CD are also derived from the existence of the “free” hydroxyl groups in C- $\beta$ -CD. One C- $\beta$ -CD molecule can be connected to another

C- $\beta$ -CD molecule through intermolecular hydrogen bonds, forming a chain- or network-like structure, thus leading to a high bonding capability. In our experiments, the C- $\beta$ -CD solution with a concentration of 30 wt% is weakly acidic, and its pH value is ca. 2. In the reaction of  $\beta$ -CD with H<sub>2</sub>O<sub>2</sub>, some carboxylic acid functional groups, –COOH, may form, and we speculate that they result from the oxidation of some of the C(6)H<sub>2</sub>OH as schematically shown in Figure 3. The detailed reaction mechanism of  $\beta$ -CD with H<sub>2</sub>O<sub>2</sub> will be further investigated via NMR and mass spectrometry (MS) techniques.

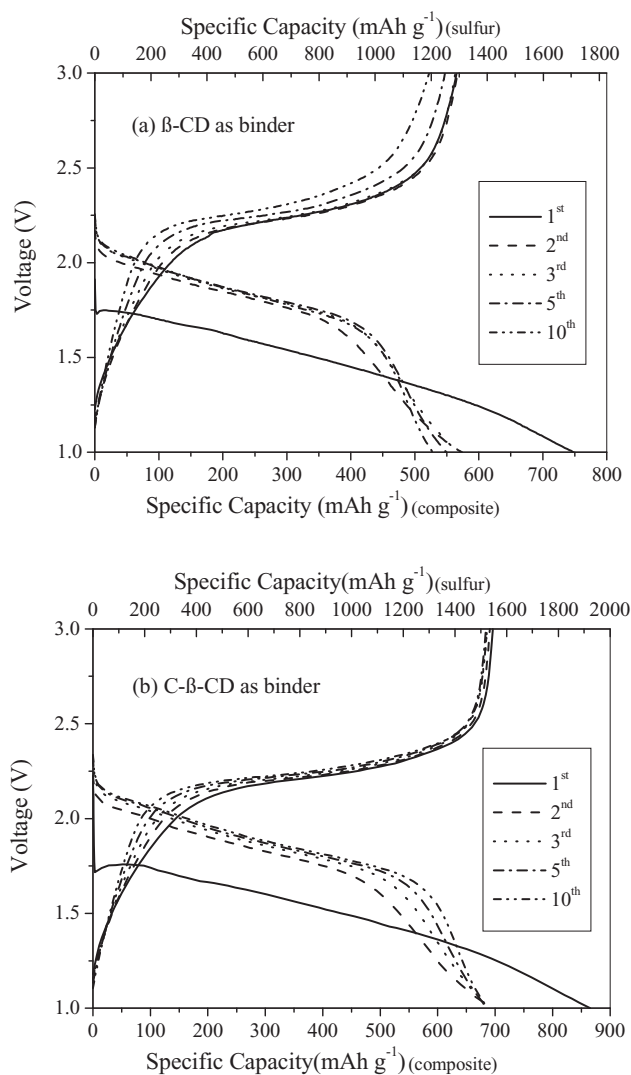
Although C- $\beta$ -CD demonstrates high solubility in the water, it does not dissolve in tetrahydrofuran (THF), propylene carbonate (PC), ethylene carbonate (EC), and their based electrolytes; also, no swelling occurs in any of these solvents. The C- $\beta$ -CD solution is weakly acidic, and the pH value hardly affects its solubility, bonding capability, and viscosity. LiOH or NaOH was used to adjust the pH of C- $\beta$ -CD solution to 6–7. The electrochemical stability window of C- $\beta$ -CD was measured using cyclic voltammetry. The cyclic voltammogram (CV) of the traditional binder PVDF was also obtained for comparison. PVDF is one of the most wide-spread binder materials currently used in the research and manufacturing of lithium ion batteries—with respect to both anode and cathode materials. It is well known that PVDF is stable in the voltage range of 0–5 V. In the electrolytic solution of 1 M LiPF<sub>6</sub> EC/dimethylchloride (DMC), the cathodic peak around 0.75 V arises from the lithium ion intercalating into the conductive carbon Super P, and the anodic peak above 4 V arises from the decomposition of the DMC solvent, as shown in Figure S1 of the Supporting Information. The ionic liquid *N*-methyl-*N*-propylpiperidinium (PP13) with 0.5 M lithium bis(trifluoromethanesulfonyl)imide (TFSI) was used to further confirm the stability of the binders. PP13 was reported to be stable to up to 5.5 V.<sup>[40]</sup> It was found that C- $\beta$ -CD is stable in the voltage range of 0–5 V (Figure S2, Supporting Information).

Sulfur-based cathode materials were adopted to evaluate the electrochemical performance of the C- $\beta$ -CD binder in coin-type cells with a lithium metal anode and 1 M LiPF<sub>6</sub> EC/DMC electrolytic solution. The charge–discharge curves and cycle performance of sulfur-based cathodes with  $\beta$ -CD or C- $\beta$ -CD binders are shown in Figure 5 and 6, respectively. The reversible discharge capacity of the ( $\beta$ -CD-binder)-based cathode is 573.4 mA h g<sup>–1</sup> (calculated based on the entire composite material (composite for short)), while the (C- $\beta$ -CD-binder)-based cathode shows a much higher reversible capacity of 694.2 mA h g<sub>(composite)</sub><sup>–1</sup>. Considering the sulfur content of 45 wt% in the composite, the reversible capacity based on pure sulfur (sulfur for short) is 1542.7 mA h g<sup>–1</sup> with the C- $\beta$ -CD binder, and sulfur utilization approaches to 92.2%. The cycle performance also shows that C- $\beta$ -CD is obviously superior to  $\beta$ -CD and other traditional binders such as PVDF and PTFE. In the case of  $\beta$ -CD, PVDF, and PTFE binders, the capacities faded quickly, and the discharge capacity decreased to ca. 900 mA h g<sub>(sulfur)</sub><sup>–1</sup> after 50 cycles. In the contrast, the (C- $\beta$ -CD)-based cathode demonstrated stable cycling performances, and the discharge capacity remained at 1456 mA h g<sub>(sulfur)</sub><sup>–1</sup> after 50 cycles (Figure 6), which is much higher than that of the three other binder-based cathodes. Considering pure sulfur, the first discharge capacities exceed its theoretical value of 1672 mA h g<sup>–1</sup>.



**Figure 4.** Relation of viscosity to the concentration of C- $\beta$ -CD solutions. The viscosity of water (i.e., 0 wt% C- $\beta$ -CD) is assumed to be 1.

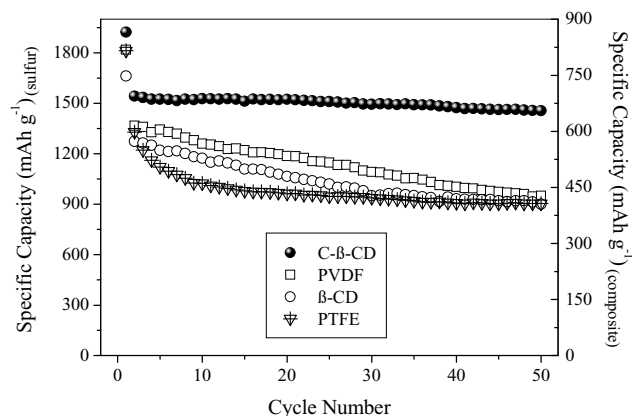




**Figure 5.** Charge–discharge curves of cathodes with a)  $\beta$ -CD and b) C- $\beta$ -CD as binders at 0.2 C with a carbon-coated Al foil current collector.

This phenomenon might arise from irreversible insertion of lithium into an anionic conjugated pyrolyzed polyacrylonitrile (PAN) matrix, as is known for electrical conductive polymers or surface functional groups on nanocomposites during the first discharge process.<sup>[41]</sup>

Sulfur-based composite materials with a particle size of 100–300 nm were prepared by the reaction of PAN and elemental sulfur; their structure possibly comprise sulfur molecules embedded within in the pyrolyzed PAN matrix.<sup>[42,43]</sup> During heat treatment at 300 °C, a certain complexation force formed between the PAN matrix and sulfur, which can be considered as an intermediate state of van der Waals forces and chemical bonds. We speculate that sulfur combines with the PAN matrix at the molecular level of  $S_4$ , of  $S_2$ , or even of the single S atom, rather than by the physical combination of  $S_8$  including absorption and encapsulation. A complex bond between sulfur and the pyrolyzed PAN matrix may form, affecting the reaction of sulfur

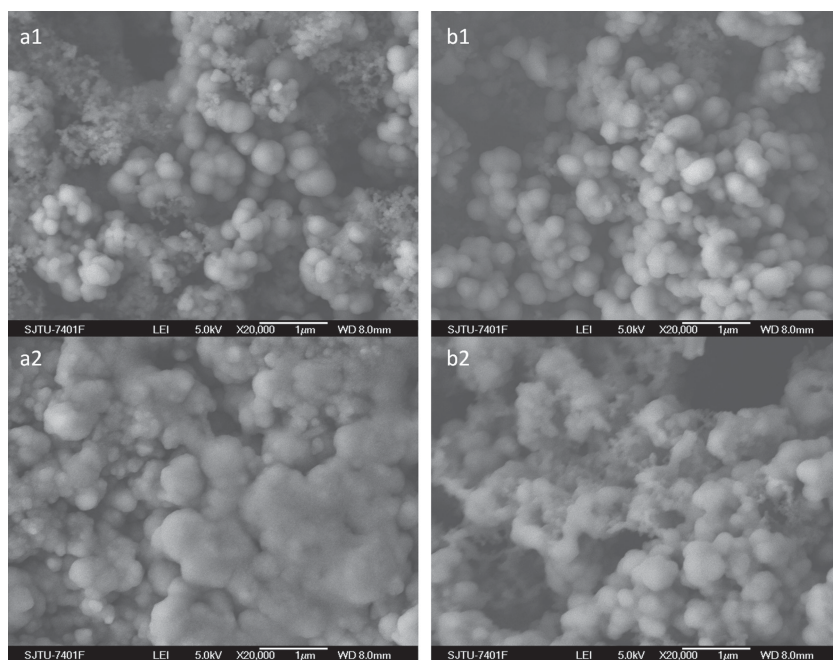


**Figure 6.** Cycle performance of cathodes with  $\beta$ -CD, C- $\beta$ -CD, PVDF, and PTFE binders at 0.2 C with a carbon-coated Al foil current collector.

with lithium—that is, a discharge reaction. Additional energy is needed to dissociate sulfur from the complex bond, resulting in a lower discharge potential than that of the elemental sulfur cathode, which exhibits a main discharge plateau at 2.4 and 2.1 V in ether-based electrolyte.<sup>[42]</sup>

For an elemental sulfur cathode with EC/DMC solvents, there is only a short discharge plateau above 2.3 V, and the main products are  $Li_2S_8$  and  $Li_2S_6$ , both of which exhibit high solubility and strong electron donating ability, react with EC/DMC to form a passivated film, and make the elemental sulfur cathode incompatible with carbonate-based electrolytes.<sup>[44]</sup> For the PAN/S composite with a sulfur content ca. 45 wt% or lower, the discharge products,  $Li_2S_4$ ,  $Li_2S_2$ , or  $Li_2S$  embedded in the pyrolyzed PAN matrix does not react with EC or DMC. If the composite with a sulfur content more than 50 wt%, a plateau at ca. 2.4 V appears during the first discharge process because of more elemental sulfur absorbing on the surface of the composite, leading to poor cycling performance. The sulfur content is a critical parameter for the PAN/S composite. Moreover, strong interactions between the pyrolyzed PAN matrix and sulfur limits discharge products from dissolving into the electrolyte. As a result, there is no “sulfur shuttle” phenomenon, which is typical for elemental sulfur cathodes in dioxalane (DOL)/dimethyl ether (DME) solvents. The coulombic efficiencies of all cathodes with four different binders are ca. 100% except for during the first discharge. The main effort of this paper lies in adopting a  $\beta$ -CD-based binder to further enhance the electrochemical performances of the PAN/S composite materials.

During the discharge/charge process, the sulfur-based composite materials undergo volume expansion/shrinkage along with lithium “intercalates” and “de-intercalates”. The volume change of the sulfur-based composite has been reported to be higher than 22%.<sup>[45]</sup> In addition, for nanoscale electrochemical active materials, aggregation is a typical phenomenon, which is one of the main factors causing capacity degradation.<sup>[46]</sup> To some extent, volume change aggravates aggregation during cycling, leading to serious disconnect between sulfur-based composites and conductive carbon. These two factors markedly deteriorate the electrochemical performance of sulfur



**Figure 7.** Morphologies of the composite cathodes with a1,a2)  $\beta$ -CD and b1,b2) C- $\beta$ -CD binder: a1,b1) as prepared and a2,b2) after 50 cycles.

composite materials. Therefore, the cycling performance of sulfur-based composite materials mainly depend on the physical structure stability of the cathode. The physical structures of sulfur-based cathodes during cycling were investigated through scanning electron microscopy (SEM). **Figure 7** shows the morphology images of cathodes using  $\beta$ -CD or C- $\beta$ -CD binders as prepared and after 50 cycles. It is clear that, in the fresh state, the sulfur composite and acetylene black are well distributed in both ( $\beta$ -CD)- and (C- $\beta$ -CD)-based cathodes. However, obvious differences in the morphologies result after 50 cycles for the cathodes. The sulfur composite materials grew to become large particles in the cathode using  $\beta$ -CD binder (Figure 7a2), resulting in gradual loss of the electrochemical activity and leading to quick capacity degradation. In contrast, the cathode using C- $\beta$ -CD binder showed a homogeneous distribution of the sulfur composite particle even after 50 cycles, which ensures an intimate contact between the sulfur composite and conductive carbon. The even distribution of sulfur and acetylene black leads to important contributions to good electrical conductivity and stable cycling performance. Morphology changes during cycling can be further proven in cathodes with PTFE binder, as shown in Figure S3 of the Supporting Information. PTFE clearly forms nanofibers in the fresh electrode, which comprise the bonding sulfur composite, Super P, and the current collector together. However, after 50 cycles, the PTFE nanofibers were broken because the sulfur cathode volume change during the charge–discharge processes resulted in the electrical disconnect of the sulfur composite materials, resulting in quick capacity fade (Figure 6).

Although its solubility can be enhanced at high temperature,  $\beta$ -CD will re-crystallize from water and form a powder mixed within the cathode during the drying process, and its shear strength approaches to zero. Therefore,  $\beta$ -CD hardly plays the

role of the binder in the cathode. The cathode with  $\beta$ -CD shows good reversible capacity in the first 2 cycles (Figure 5a) but poor cycling performance (Figure 6). The electrolyte directly contacts with the PAN/S composite, and it shows good reversible capacity in the initial cycles. Along with cycling, the PAN/S composite particle expands and shrinks, and aggregates to form large particles as shown in Figure 7a, leading to poor cycling performance. After carbonylation of the hydroxyl groups by  $\text{H}_2\text{O}_2$ , the solubility not only dramatically increased, but a strong bonding capability also appeared—a novel property of C- $\beta$ -CD that is not exhibited by  $\beta$ -CD and its other derivatives. High solubility and strong bonding ensure C- $\beta$ -CD forms a gel film tightly wrapping the surface of the sulfur-based composite after cathode drying. The gel thin film is mechanically strong enough to suppress the aggregation of the sulfur composite during cycling, to ensure the distribution of the sulfur composite and conductive carbon homogeneously, and to ensure a stable cathode structure; this results in excellent cycling performance in

a rechargeable lithium battery. Moreover, C- $\beta$ -CD shows fine compatibility with different types of current collectors, such as Cu foil and Ni foam (Figure S4 of the Supporting Information). There is almost no difference in its capabilities when it is used with various current collectors, except for with Al foil. A carbon coating can improve the contact between the sulfur composite materials and Al current collector; therefore the cathode with a carbon-coated Al current collector shows superior performance to one with a pure Al foil current collector.

### 3. Conclusion

Significantly more soluble derivatives of  $\beta$ -CD are obtained via the partial carbonylation of its hydroxyl groups with  $\text{H}_2\text{O}_2$  in a sealed bottle; the resulting C- $\beta$ -CD demonstrates a high solubility in water that is ca. 100 times that of  $\beta$ -CD at room temperature. Most importantly, C- $\beta$ -CD exhibits a strong bonding capability—a property not demonstrated by  $\beta$ -CD and its other derivatives—and electrochemical stability in the range of 0–5 V. All these characteristics make C- $\beta$ -CD match with the requirements needed for a binder in battery technology. The electrochemical performances of the sulfur-based composite using C- $\beta$ -CD as the binder demonstrates a high reversible capacity of  $694.2 \text{ mA h g}_{(\text{composite})}^{-1}$  and  $1542.7 \text{ mA h g}_{(\text{sulfur})}^{-1}$ , with a sulfur utilization approaching to 92.2% and excellent cycling performance. The discharge capacity remained at  $1456 \text{ mA h g}_{(\text{sulfur})}^{-1}$  after 50 cycles, which is much higher than that of cathodes using  $\beta$ -CD as the binder. High solubility and strong bonding ensure C- $\beta$ -CD forms a gel film that tightly wraps the surface of the sulfur composite after cathode drying, and this gel film is mechanically strong enough to suppress the aggregation of the sulfur composite. The homogeneous distribution of the

sulfur composite and the cathode structure are stable during the charge–discharge process, resulting in excellent cycling performance. Compared to traditional PVDF and PTFE binders, C- $\beta$ -CD has additional advantages, such as low cost, environmental benignity, and wide-ranging electrochemical stability; therefore, C- $\beta$ -CD derived from the simple treatment of  $\beta$ -CD with  $\text{H}_2\text{O}_2$  is a promising binder not only for the sulfur cathode in a rechargeable lithium battery, but also for other electrode materials used in lithium ion batteries.

## 4. Experimental Section

**Preparation of C- $\beta$ -CD:** C- $\beta$ -CD was obtained via a simple procedure; 2 g of  $\beta$ -CD (Sinopharm chemical) was added to 5 mL of  $\text{H}_2\text{O}_2$  solution a concentration of 30%, and kept at 80 °C for 24 h in a sealed bottle, ensuring that the  $\beta$ -CD fully reacts with the  $\text{H}_2\text{O}_2$ . The solution was then dried under vacuum to completely remove all the water and residual  $\text{H}_2\text{O}_2$ . For comparison,  $\beta$ -CD was treated according to a similar procedure using deionized water in place of the hydrogen peroxide solution.

**Measurements of XRD, FT-IR, Shearing Strength, and Viscosity:** XRD patterns were obtained using a Rigaku D/max-2200/PC with a Cu ( $K\alpha$ ) source in the range of 2–70° at a scan speed of 6° min<sup>−1</sup>. FTIR spectra of  $\beta$ -CD and C- $\beta$ -CD were obtained using a PerkinElmer Spectrum 100 FT-IR Spectrometer with KBr pellets. In order to measure shearing strength, pairs of plastic strips were cleaned with alcohol; either the C- $\beta$ -CD or  $\beta$ -CD solution were spread on the strips with a coating area was of 5.5 cm length and 1.3 cm width. After a few minutes of exposure to air, the two coated areas were overlapped and bonded together, and then dried under vacuum at 100 °C for 24 h. The shearing strength was tested using a Tensile Test Machine, and the stretching velocity was set at 10 mm min<sup>−1</sup>. Four C- $\beta$ -CD solutions with concentrations of 10%, 20%, 30%, 50%, and 62.5 wt% were prepared and their viscosities were measured using a Ubbelohde Viscosity Meter. The shearing strength and viscosity of saturated  $\beta$ -CD was also measured using the same procedure.

**Preparation of Sulfur-Based Composite Materials:** The sulfur composite materials were prepared as in our previous papers.<sup>[42,43]</sup> Elemental sulfur and PAN (weight-averaged molecular mass,  $M_w$ , 150 000 g/mol, Aldrich) were mixed and heat treated at 300 °C for 6 h under inert atmosphere, resulting in composite materials with a sulfur content of 45 wt%, as determined by elemental analysis (Perkin Elmer PE 2400 II).

**Preparation of Cathodes and Electrochemical Measurements:** C- $\beta$ -CD and  $\beta$ -CD were adopted separately as binders to investigate the electrochemical properties of sulfur-based composite materials. The cathode was prepared by mixing 80 wt% of the sulfur composite material, 10 wt% acetylene black, and 10 wt% binder with water as dispersant. The slurry was magnetically stirred for 4 h at room temperature, and then spread on a carbon-coated Al foil. Cathodes with a load of ca. 3 mg cm<sup>−2</sup> were dried under vacuum at 80 °C for 2 h. The coin-type 2016 cells were assembled in a glove box filled with the high-purity argon, with lithium foils as anodes, Cellgard 2400 microporous membranes as separators, and 1 M LiPF<sub>6</sub> EC/DMC as the electrolyte (Zhangjiagang Guotai-Huarong New Chemical Materials). The electrochemical performance of the cells were measured galvanostatically using a Land CT2001 battery test system (Wuhan Kingnuo Electronics), with a voltage range of 1.0–3.0 V at room temperature. The morphologies of the cathodes were observed using SEM (JEOL JSM-7401F).

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

## Acknowledgements

This work was supported by the National Natural Science Foundation of China (50902095) and the SJTU-UM joint research project.

Received: July 5, 2012

Revised: August 8, 2012

Published online:

- [1] M. Winter, R. J. Brodd, *Chem. Rev.* **2004**, 104, 4245.
- [2] B. Scrosati, J. Hassoun, Y. K. Sun, *Energy Environ. Sci.* **2011**, 4, 3287.
- [3] P. G. Bruce, S. A. Freunberger, L. J. Hardwick, J. M. Tarascon, *Nat. Mater.* **2012**, 11, 19.
- [4] D. Marmorstein, T. H. Yu, K. A. Striebel, F. R. McLarnon, J. Hou, E. J. Cairns, *J. Power Sources* **2000**, 89, 219.
- [5] X. L. Ji, L. F. Nazar, *J. Mater. Chem.* **2010**, 20, 9821.
- [6] G. He, X. L. Ji, L. F. Nazar, *Energy Environ. Sci.* **2011**, 4, 2878.
- [7] Y. V. Mikhaylik, J. R. Akridge, *J. Electrochem. Soc.* **2004**, 151, A1969.
- [8] F. Wu, J. Z. Chen, R. J. Chen, S. X. Wu, L. Li, S. Chen, T. Zhao, *J. Phys. Chem. C* **2011**, 115, 6057.
- [9] M. M. Sun, S. C. Zhang, T. Jiang, L. Zhang, J. H. Yu, *Electrochem. Commun.* **2008**, 10, 1819.
- [10] L. Xiao, Y. Cao, J. Xiao, B. Schwenzer, M. H. Engelhard, L. V. Saraf, Z. Nie, G. J. Exarhos, J. Liu, *Adv. Mater.* **2012**, 24, 1176.
- [11] X. L. Ji, K. T. Lee, L. F. Nazar, *Nat. Mater.* **2009**, 8, 500.
- [12] N. Jayaprakash, J. Shen, Surya S. Moganty, A. Corona, A. Lynden, *Angew. Chem. Int. Ed.* **2011**, 50, 5904.
- [13] B. Zhang, X. Qin, G. R. Li, X. P. Gao, *Energy Environ. Sci.* **2010**, 3, 1531.
- [14] C. Liang, N. J. Dudney, J. Y. Howe, *Chem. Mater.* **2009**, 21, 4724.
- [15] W. Ahn, K. B. Kim, K. N. Jung, K. H. Shin, C. S. Jin, *J. Power Sources* **2012**, 202, 394.
- [16] L. Ji, M. Rao, S. Aloni, L. Wang, E. J. Cairns, Y. Zhang, *Energy Environ. Sci.* **2011**, 4, 5053.
- [17] G. Zheng, Y. Yang, J. J. Cha, S. S. Hong, Y. Cui, *Nano Lett.* **2011**, 11, 4462.
- [18] H. Wang, Y. Yang, Y. Liang, J. T. Robinson, Y. Li, A. Jackson, Y. Cui, H. Dai, *Nano Lett.* **2011**, 11, 2644.
- [19] L. Ji, M. Rao, H. Zheng, L. Zhang, Y. Li, W. Duan, J. Guo, E. J. Cairns, Y. Zhang, *J. Am. Chem. Soc.* **2011**, 133, 18522.
- [20] Y. Yang, M. T. McDowell, A. Jackson, J. J. Cha, S. S. Hong, Y. Cui, *Nano Lett.* **2010**, 10, 1486.
- [21] J. Hassoun, B. Scrosati, *Angew. Chem. Int. Ed.* **2010**, 49, 2371.
- [22] S. F. Lux, F. Schappacher, A. Balducci, S. Passerini, M. Winter, *J. Electrochem. Soc.* **2010**, 157, A320.
- [23] J. Guo, C. Wang, *Chem. Commun.* **2010**, 46, 1428.
- [24] I. Kovalenko, B. Zdyrko, A. Magasinski, B. Hertzberg, Z. Milicev, R. Burtovyy, I. Luzinov, G. Yushin, *Science* **2011**, 334, 75.
- [25] Y. Jung, S. Kim, *Electrochem. Commun.* **2007**, 9, 249.
- [26] N. Kim, C. Lee, J. Seo, W. Lee, Y. Roh, *J. Power Sources* **2004**, 132, 209.
- [27] Y. J. Choi, K. W. Kim, H. J. Ahn, J. H. Ahn, *J. Alloys Compd.* **2008**, 449, 313.
- [28] S. E. Cheon, S. S. Choi, J. S. Han, Y. S. Choi, B. H. Jung, H. S. Lim, *J. Electrochem. Soc.* **2004**, 151, A2067.
- [29] D. Guy, B. Lestriez, D. Guyomard, *Adv. Mater.* **2004**, 16, 553.
- [30] H. Schneider, A. Garsuch, A. Panchenko, O. Gronwald, N. Janssen, P. Novák, *J. Power Sources* **2012**, 205, 420.
- [31] W. Liu, M. Yang, H. Wu, S. Chiao, N. Wu, *Electrochem. Solid-State Lett.* **2005**, 8, A10.

- [32] J. Sun, Y. Huang, W. Wang, Z. Yu, A. Wang, K. Yuan, *Electrochim. Acta* **2008**, 53, 7084.
- [33] J. Sun, Y. Huang, W. Wang, Z. Yu, A. Wang, K. Yuan, *Electrochem. Commun.* **2008**, 10, 930.
- [34] W. Zhang, Y. Huang, W. Wang, C. Huang, Y. Wang, Z. Yu, H. Zhang, *J. Electrochem. Soc.* **2010**, 157, A443.
- [35] W. Zhao, J. Li, L. Du, C. Tan, Q. Xia, Z. Mao, L. Ji, *Chem. Eur. J.* **2011**, 17, 5171.
- [36] D. Duchene, D. Wouessidjewe, *Drug Dev. Ind. Pharm.* **1990**, 16, 2487.
- [37] A. R. Khan, P. Forgo, K. J. Stine, T. D. S. Valerian, *Chem. Rev.* **1998**, 98, 1977.
- [38] M. Yoshinaga, M. Tanaka, *J. Chromatogr. A* **1994**, 679, 359.
- [39] L. Zheng, L. Xiong, J. Li, X. Li, J. Sun, S. Yang, J. Xia, *Electrochem. Commun.* **2008**, 10, 340.
- [40] J. Xu, J. Yang, Y. Nuli, J. Wang, Z. Zhang, *J. Power Sources* **2006**, 160, 621.
- [41] L. Yin, J. Wang, F. Lin, J. Yang, Y. Nuli, *Energy Environ. Sci.* **2012**, 5, 6966.
- [42] J. Wang, J. Yang, C. Wan, K. Du, J. Xie, N. Xu, *Adv. Funct. Mater.* **2003**, 13, 487.
- [43] J. Wang, J. Yang, J. Xie, N. Xu, *Adv. Mater.* **2002**, 14, 963.
- [44] J. Gao, M. A. Lowe, Y. Kiya, H. D. Abruna, *J. Phys. Chem. C* **2011**, 115, 25132.
- [45] X. He, J. Ren, L. Wang, W. Pu, C. Jiang, C. Wan, *J. Power Sources* **2009**, 190, 154.
- [46] Y. Guo, J. Hu, L. Wan, *Adv. Mater.* **2008**, 20, 2878.