High Performance Lithium-Manganese-Rich Cathode Material with Reduced Impurities

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Abstract

Lithium-manganese-rich transition metal oxides have attracted substantial R&D attention due to their potential for high energy-density lithium-ion batteries. In this work, *in situ* high-energy X-ray diffraction was deployed to investigate the phase evolution during the solid-state synthesis of $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$. A step-wise consumption of the starting materials was observed during the one-step heating process primarily due to the

heterogeneous nature of the precursor. According to observations from *in situ* high-energy X-ray diffraction, a two-step process was adopted to minimize the elemental heterogeneity of the final product. The electrochemical characterization results showed a substantial improvement on the reversible specific capacity for the material synthesized through the two-step process.

Keyword: lithium-manganese-rich transition metal oxide; cathode; lithium-ion battery; heterogeneity; *in situ*; high-energy X-ray diffraction

Introduction

Lithium-rich transition metal oxides are widely considered as layered-layered integrated (M=Ni, Co, Mn) component [1–4]. It is widely accepted that the occupation of excess lithium in the transition metal layer leads to the formation of monoclinic Li_2MnO_3 component that is electrochemical inactive within the normal working potential window (below 4.4 V vs. Li^+/Li). It was found that the integration of inactive Li_2MnO_3 into the active LiMO_2 matrix helps to stabilize the crystal structure of delithiated LiMO_2 and hence substantially improves the capacity retention of lithium-rich transition metal oxides[5]. It was recently reported that the integrated Li_2MnO_3 component could be electrochemically activated at a higher potential, like 4.6 V vs. Li^+/Li [4,6–10]. When increasing the content of Li_2MnO_3 component (latterly referred as lithium-manganese-rich (LMR) transition metal oxides), an extremely high specific reversible capacity, close to the theoretical capacity of stoichiometric LiMO_2 counterpart, was achieved after the electrochemical activation, offering the highest specific energy density among existing

cathode materials for lithium-ion batteries[11–13]. Despite their exceptional high capacity and low cost, the LMR materials suffer from three major disadvantages of low initial coulombic efficiency, voltage fade and poor high rate capability, which bring about great difficulties for practical applications[14–16]. Above all, the voltage fade process creates a big challenge to develop an effective battery management system (BMS) to precisely determine the state of charge (SOC) and state of health (SOH) of the battery packs using this class of materials, triggering serious debate over the suitability of adopting these materials for automobile applications. Nevertheless, this class of materials still holds great promise for applications in single-cell devices, like portable electronics.

In the open literature, lithium-manganese transition metal oxides can be synthesized through various approaches including hydrothermal routes[17–22], co-precipitation process[23–29], spray drying approach[30–35] and solid-state reaction[36–39]. Hydrothermal route is widely used to synthesize nanomaterials at a relatively low temperature with reduced synthesis time[1,3,20,35], generally resulting in materials with substantially higher rate capabilities, but with low loading density and low volumetric energy density. On the other hand, the co-precipitation approach has been widely adopted for industrial application primarily due to its high scalability, ease of control on the particle size and the particle morphology[23], and unique capability to control the elemental distribution of transition metal elements at the particle level[40–43]. However, it is difficult for co-precipitation methods to control precisely the composition of the precursor powders because the precipitation conditions of metal ions are strongly affected by the types of metal components[44]. Comparing to co-precipitation process, solid-state synthesis is expected to have a reduced cost, and reduced synthesis time. However, the

major disadvantage of the solid-state synthesis is the difficulty in controlling the segregation of transition metal elements in the primary particle level[39], which in turn has significant impact on the electrochemical performance of the final cathode materials. In this work, we report our latest effort in developing a low-cost and scalable synthesis route for lithium-manganese-rich transition metal oxides using a combination of ball milling, spray drying and a solid-state synthesis. *In situ* high-energy X-ray diffraction was deployed to investigate the phase evolution during the synthesis of lithium-manganese-rich transition metal oxides, and to guide the material synthesis to reduce the segregation of transition metal elements.

Experimental

Synthesis of lithium-manganese-rich transition metal oxides

1) The Synthesis of sample S1a and S1b

Li_2CO_3 , MnCO_3 , Co_3O_4 and NiO with anatomic molar ratio of 1.2:0.54:0.13:0.13 were used as the starting materials. The mixture powders were ball milled to ground with zirconium dioxide at room temperature with deionized water as dispersant. Then, the suspension of mixture was dried by a spray drying instrument. The precursors were heated to 750°C or 900°C for 10h and cooled down to room temperature in the furnace, to obtain the final lithium-manganese-rich transition metal oxides sample S1a or S1b respectively.

2) The Synthesis of sample S2a and S2b

A mixture containing Li_2CO_3 , MnCO_3 , Co_3O_4 and NiO with an atomic molar ratio of 1.2:0.54:0.13:0.13 was carefully mixed. The mixture powders were preheated at 600°C

°C, then the preheated powders were ball milled to ground with zirconium dioxide at room temperature with deionized water as dispersant. Then, the suspension of mixture was dried by a spray drying instrument. The precursors were heated to 750°C or 900 °C for 10h and cooled down to room temperature in the furnace, to obtain the final lithium-manganese-rich transition metal oxides sample S2a or S2b respectively.

Physical characterization of materials

1) Ex situ high-energy X-ray diffraction (HEXRD)

The HEXRD patterns of synthesized Samples at various conditions were collected at sector 11-ID-C of the Advanced Photon Source (APS) at Argonne National Laboratory. The wavelength of the X-ray beam used was 0.11798 Å.

2) In situ HEXRD

The structural evolution of materials during the solid-state synthesis of $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ was studied using *in situ* high-energy X-ray diffraction. Precursors of $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ were prepared as described above. The precursor was pressed into a 2mm thick pellet with 5mm diameter. The pellet was then placed in a programmable furnace (Linkam TS 1500) vertically with the X-ray beam aiming at the center of the pellet. The sample was then heated from room temperature to 1000°C with a constant heating rate of 2 °C min⁻¹. The in situ HEXRD experiment was carried out at sector 11-ID-C of the APS. The wavelength of the X-ray beam was pre-fixed at 0.11798 Å. The high energy X-ray source was selected for its excellent penetration capability to detect structural changes on bulk part of the sample. During the in situ solid-state synthesis, a 2D X-ray detector was deployed to collect one XRD pattern

every 20 s. Rietveld refinement of interested patterns was then carried out using General Structure Analysis Software (GSAS).

3) Other Physical characterization

The particles morphology and size of the powders were determined using scanning electron microscopy (SEM, Hitachi S4700).

Specific surface area measurements were performed on ST-2000 according to the standard GB/T 13390-2008.

The particle-size distribution of the powders (secondary particles) was measured with Malvern MS3000.

Covariance analysis of in situ HEXRD

The covariance analysis (see Eq. (1)) was applied to calculate the mathematical similarity between two different XRD patterns (r_1 and r_2). Both of which are a series of X-ray intensity at different 2θ values. When two spectra are identical to each other, the covariance value of Eq. (1) equals to 1; a smaller number will be given when two spectra have some difference.

$$\text{CORR}(r_1, r_2) = \frac{\sum_i r_1(i) * r_2(i)}{\sqrt{\sum_i r_1(i) * r_1(i)} * \sqrt{\sum_i r_2(i) * r_2(i)}} \quad (1)$$

Electrochemical Characterization

Electrochemical characterization on synthesized samples $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ were performed by fabricating 2032 coin cells. For making electrode, 80 wt. % of the cathode material was blended with 10wt. % of Super-P, and 10 wt. % of polyvinylidene difluoride (PVDF) dissolved in N-methyl 1-2-pyrrolidene (NMP)

and coated onto Al foil. After drying the electrode overnight at 80 °C in vacuum, the coin cells were assembled in an argon filled glove box (MBraun). 1M LiPF₆ in a 1:1:1 ethylene carbonate (EC) / dimethyl carbonate (DMC) / methyl ethyl carbonate (EMC) was used as electrolyte, lithium foil as anode and Celgard 2400 membrane as separator. The cells were allowed to rest for 10 h and charge-discharged on a battery tester (LAND CT-2001A, China) between 2.0 and 4.8 V (If not specified, vs. Li/Li⁺) at room temperature.

Results and discussion

In order to illustrate the potential impact of the synthesis condition on the structure of the final product (LMR material), *in situ* high-energy X-ray diffraction was carried during the thermal treatment of the precursor materials prepared in different approaches. Figure 1a shows the contour plot of the HEXRD patterns collected during the thermal treatment of the precursor prepared using the one-step process. In Figure 1a, the color of each pixel depicts the measured X-ray intensity at the specific diffraction angle (2θ) and the specific temperature; a red color means a high X-ray intensity and a blue one means a low X-ray intensity. At the beginning of the experiment, the XRD patterns can be fully indexed with the starting materials composing of Co₃O₄ (PDF#74-2120), MnCO₃ (PDF #44-1472), NiO (PDF #44-1159), and Li₂CO₃ (PDF#22-1141) (see Figure 1b). During the initial heating process, all diffraction peaks shifted left with the heating temperature; this is primarily due to the thermal expansion of crystal lattice. One can easily see the disappearance of the diffraction peaks from the raw materials and emergence of a set of new peaks for the layered structure within the temperature window between 300 °C and

450 °C, which is a good indication of ongoing solid-state reaction from the raw materials to the layered cathode material. It can also be seen that the fingerprint peaks of Li_2MnO_3 component at about $1.5\text{-}1.6^\circ$, appeared when the temperature is above about 700 °C. To catch more subtle structural changes during the thermal treatment, a covariance analysis was carried out to calculate the similarity between two HEXRD patterns collected at different time/temperature; the contour plot of the results from covariance analysis is shown in Figure 1c, and the change of the covariance value between adjunct HEXRD patterns is shown in Figure 1d. Both Figure 1c and Figure 1d clearly show three major changes occurred during the heating process, one reaction occurred at about 290 °C, and the other two occurred at about 450 °C and 890 °C, respectively.

Figure 2 shows the areal plot of *in situ* HEXRD data for a better illustration of changes on the XRD pattern with the heating process. Figure 2a shows the intensity of the raw materials started to decrease when the temperature was above 200 °C. However, a synchronized disappearance of the raw materials was not observed. For instance, the diffraction peak at 1.84° , assigned as (012) peak ($d=3.6719 \text{ \AA}$) of MnCO_3 , showed a dramatic decrease at about 315 °C, and completely vanished at about 510 °C. Following the disappearance of MnCO_3 , the diffraction peaks for Co_3O_4 vanished at about 480 °C, and the diffraction peaks for Li_2CO_3 remained visible up to 540 °C. According to literature reports, the reactions occurred below 600 °C may be attributed to (1) the thermal decomposition of MnCO_3 in air to form MnO_2 and the reaction between MnO_2 and Li_2CO_3 that leads to the nucleation of Li_2MnO_3 domains[45]; (2) the reaction between Co_3O_4 and Li_2CO_3 that generates $\text{LiCoO}_2/\text{Li}_2\text{Co}_2\text{O}_4$ [46]. It is also believed that the

integrated layered-layered composite structure ($\text{Li}_2\text{MnO}_3 \cdot \text{LiMO}_2$) was not formed at such a low temperature since the peak intensity for NiO didn't show any significant decrease when the temperature was below 600 °C. Figure 2b clearly shows that a major decrease on intensity of NiO peaks occurred at about 800 °C. However, existence of NiO in the material can be clearly seen even when the temperature was as high as 1000 °C. The step-wise reactions among the raw materials can be reasonably attributed to the heterogeneous nature of the precursor prepared using spray drying process; the secondary particles are composed of loosely packed nanoparticles of various raw materials, and a homogeneous mixing between transition metal elements at the primary particle level was not achieved.

The step-wise reaction mode can be further supported by the evolution of an intermediate phase as shown in Figure 3. The intermediate phase started to appear at about 410 °C and disappeared at about 910 °C. This intermediate showed characteristic peaks at 1.44° , 2.78° , 3.35° , 3.65° , 4.35° , 4.74° , and 4.96° (see Figure 3). Accordingly to the 2θ values of these peaks, the intermediate can be assigned to a manganese-rich phase like MnO_2 (PDF # 44-0992) or $\text{Li}_2\text{Mn}_2\text{O}_4$ (PDF # 84-1524) or a cobalt-based phase like LiCoO_2 (PDF # 70-2685) and $\text{Li}_2\text{Co}_2\text{O}_4$ (PDF # 70-2685). Rietveld refinement was carried out to fit the HEXRD patterns collected at temperatures 600°C using the $\text{Li}_{1.2}(\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54})\text{O}_2$ (R-3m), NiO (Fm-3m) and $\text{Li}_2\text{Mn}_2\text{O}_4$ (I41/amd). A good fit for the sample was obtained (Fig. S1), showing the intermediate is $\text{Li}_2\text{Mn}_2\text{O}_4$. Considering the Co_3O_4 has disappeared completely in 480 °C, the intermediate should also contain element Co, so it should be mainly $\text{Li}_2(\text{Mn}_x\text{Co}_{1-x})_2\text{O}_4$.

The step-wise solid-state reactions discussed above are mostly resulted from the heterogeneous mixing among different ingredients. Unlike the co-precipitation reaction, the secondary particles prepared are physical agglomeration of individual nanoparticles of MnCO_3 , Co_3O_4 , NiO and Li_2CO_3 , and a homogeneous mixing was not achieved. Hence, the formation of the layered-structures and intermixing between transition metal elements was controlled by the mobility of transition metal ions in the oxygen framework, leading to the step-wise disappearance of the raw materials during the solid-state synthesis. One can reasonably speculate that nickel ions, either Ni^{2+} or Ni^{3+} , have lower mobility in the oxygen framework than their manganese and cobalt-based counterparts[47]. Therefore, a small amount of NiO was still visible even when the sample was heated up to 1000°C . In practice, there are two possible approaches to mitigate the intermixing barrier. One is to sinter the materials at an elevated temperature for a higher mobility of transition metal ions and/or with extended period of sintering time. This approach is effective to improve the degree of utilization of NiO raw material, but the migration of highly mobile Mn/Co ions can lead to the substantial growth of the primary particles. The alternative approach, which was adopted for this work, is pre-treating the mixture of the raw materials for a partially completed reaction, followed by a ball-milling, to regenerate the fresh Ni-Co and Ni-Mn interface to shorten the diffusion length for nickel ions during the final sintering step.

Figure 4a shows the contour plot of the *in situ* HEXRD profiles during the heating of a preheated precursor sample. The pre-heated sample appeared like a layered material right at the beginning of the *in situ* experiment, with several minor peaks contributed from the residual NiO from the pre-heating step. The existence of NiO in the pre-heated

sample is clearly supported by extra peaks showing at 3.23° , 4.55° , and 5.32° , respectively (see Figure 4b-d for a better illustration). Figure 4b-d shows that the intensity of diffraction peaks from NiO started to decrease when the temperature was higher than 600°C , and that those peaks completely disappeared at 815°C . This clearly demonstrated that the pre-heating and ball-milling process significantly improves the migration efficiency of nickel ions during the sintering process, will achieve better intermixing between transition metal elements, and making it possible to sinter the material at a reduced temperature to minimize the growth of the primary particles during the sintering process. Uniform elemental distribution is very important. Significant nonuniform Ni distribution of LMR cathodes at atomic level will weaken nickel-manganese interactions, leading to easy reduction of the manganese ions and fast voltage/capacity fade. The samples with uniform atomic level spatial distribution demonstrate much better capacity retention and much smaller voltage fade as compared to those with significant nonuniform Ni distribution [12,15].

Figure 5 shows the evolution of the crystal structure as well as the disappearance of impurities (NiO and a spinel phase) during the solid-state synthesis for both preparation routes. In order to simplify the refinement, the diffraction data within the fingerprint area for Li_2MnO_3 (from 1.5° and 2.2°) were excluded from refinement. Figures 5a-c show that cell parameters (a , b , c , and volume) for both samples increased steadily with the heating temperature. Particularly, the cell parameters for the material prepared with two-step approach showed higher values than those for the material synthesized by one-step approach. This implies that the two-step process can lead to a higher degree of completeness of converting the precursor material into the desired lithium transition

metal oxides than the one-step process. This implication can be further validated with the disappearance of the impurities (NiO and spinel phase) as shown in Figure 5d and 5e. Both Figures 5d and 5e shows that the content of the both impurities decreased steadily with the process of solid-state synthesis. It is shown that the no detectable amount of impurities was observed for the two-step process at a temperature higher than 850°C. However, a small amount of NiO and spinel phase still existed in one-step process even when the temperature is as high as 1000°C. These results indicated that the two-step process can enable us to achieve a maximal completeness of solid-state reaction at a relatively low temperature and in a shorter period of time with a minimal amount of impurities for a better electrochemical performance.

To validate the finding of the *in situ* experiment, four samples were prepared using two approaches without (for sample S1a and S1b) and with (for sample S2a and S2b) pre-heating. Figure 6 shows the scanning electron microscopy (SEM) images of the precursors (see Figure 6a-d) and final powders (see Figure 6e-l) prepared using two different processes. It is demonstrated in Figure 6 that spherical powders, composing of nanometer-sized primary particles, and the spherical morphology was maintained after the sintering process. Particle size analysis of precursors shows that the size of secondary particles for sample S2a&b is slightly smaller than that for sample S1a&b. Table 1 summarizes the results from the basic particle characterization. Average particle size of the samples was determined by measuring the dimension of the particles from the enlarged SEM images. Samples S1a and S2a synthesized at a low temperature have smaller primary particles size: the particle sizes are below 100nm. Increasing temperature leads to larger particles. Sample S2b has smaller particles size than sample

S1b, although they were synthesized at the same temperature, indicating that the size of primary particles was contributed from not only the sintering temperature but also the preparation process. The pre-heating and ball-milling processes are benefiting to controlling the coarsening of particles during the sintering process. The smaller particle sizes are to the benefit of shortening the diffusion pathway of lithium ions [15,48].

High-energy X-ray diffraction characterization on all samples shows that all samples have LiMO_2 (R-3m) component; but substantial difference on the crystallinity of the Li_2MnO_3 (C2/m) component was observed (see Figure 7). Sample S1b and S2b were prepared at a higher temperature, and a set of well-defined superlattice diffraction peaks for Li_2MnO_3 component between $1.5\text{--}2.2^\circ$ was observed and was successfully indexed as shown in Figure 7. However, samples S1a and S2a only showed a poorly resolved broad peak at about 1.6° , indicating that the Li_2MnO_3 component in these samples has a small domain size with a lack of long term ordering, an increase in the amount of stacking faults. From thermodynamics, a material with defects has the higher energy state, which may lower the activation barrier for Li^+ diffusion and allow Li^+ to be extracted at a lower potential [49]. For sample S1a, a weak peak around the two theta of 3.1° are assigned to NiO, show the solid-state reaction is not completed yet. The Rietveld refinement of *ex situ* HEXRD data revealed that the samples prepared with one-step process contained a small amount ($\sim 1\%$) of NiO regardless of the sintering temperature. On the other hand, the samples prepared with the pre-heating step showed no sign of detectable amount of NiO; this can be very beneficial for the electrochemical performance of the cathode material.

Figure 8a shows voltage profiles during the first charge/discharge cycling of half-cells using cathode materials S1a, S1b, S2a and S2b. The current density was 0.1C, assuming that the 1C rate is equivalent to 200mA g⁻¹. During the initial charge up to 4.5 V vs. Li⁺/Li, both samples delivered roughly the same capacity, but the cell containing S1b showed a slightly larger polarization, which might be contributed from the large primary particle size in sample S1b. When the potential was higher than 4.5V vs. Li⁺/Li, the cell containing S2a has the highest initial discharge capacity and coulombic efficiency, while the S1b is the lowest one in both the initial discharge capacity and the coulombic efficiency. The initial discharge capacity of the cell containing S2a was about 40 mAhg⁻¹ higher than that of the cell using S1b, while coulombic efficiency of the cell containing S2a was about 8% higher. Sample S1a, S2a and S2b have higher coulombic efficiencies than S1b, which may be attributed to the smaller particle size. The LMR materials suffer from low initial coulombic efficiency usually. The large initial irreversible capacity loss is considered usually attributed to an irreversible removal of partial lithium as Li₂O along with an elimination of the oxygen vacancies from the crystal lattice produced during the first charge [14,50].

Figures 8b and 8c compare the voltage profiles of Li/S2a cells that were cycled to different upper cutoff potential (from 4.2 V to 4.8 V). It can be seen that the reversible capacity of the material S2a consistently increased with the upper cutoff potential; a substantial jump on the reversible capacity was obtained when the upper cutoff potential was higher than 4.4 V. When the upper cutoff potential was set to 4.8 V vs. Li⁺/Li, the cell delivered a reversible capacity of about 290 mAhg⁻¹.

The rate and cycling performances of the samples with different preparation process were characterized at room temperature as shown in Figure 9. Figure 9a shows the rate capability of samples. Different rates were tested in a sequential manner (0.1C, 0.2C, 0.5C, 1C and 3C) for three cycles at each step between 2-4.8V at room temperature. The material S2a and b show better rate capability than S1a and b. The better rate capability of samples S2a and b is probably due to the smaller primary particles [51] and the absence of the impurity (NiO). Figure 9b shows the discharge capacity of samples during the long term cycling. The cell was initially charged and discharged within the voltage window of 2-4.8 V for activation (1-3 cycles), and then operated between 2 and 2.6 V for the subsequent cycles under 1C rate (1C=200mA g⁻¹). It is clear that the cell using S2a had the highest discharge capacity in those samples, while the cell using S2b had the best cycle performance. The results shown in Figure 9 imply that samples sintered at higher temperature have better cycle performance. The sample S2a though sintered at lower temperature has a much higher discharge capacity and similar cycle performance compared with those of the sample S1b. It is mostly contributed by the higher degree of electrochemical activation during the initial charge/discharge cycling, resulting in more useable sites to store lithium in the activated cathode material, and the absence of NiO impurity that impedes the charge/discharge of the cathode material.

Conclusion

In situ high-energy X-ray diffraction was utilized to investigate the structure evolution during the solid-state synthesis of lithium-manganese-rich transition metal oxides. The results of the *in situ* experiment indicated a step-wise reaction among the raw materials.

It was demonstrated that an extra ball-milling process after the pre-heating effectively reduce the length of diffusion path for transition metal element during the sintering process, and hence a better intermixing between transition metal elements was achieved at a reduced temperature. As a result, phase pure material can be obtained, and a better electrochemical performance was obtained.

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Captions

Tables

Table 1. The results from the basic particle characterization

The name of sample	Secondary particles size (D50, μm)	Specific surface area ($\text{m}^2 \text{g}^{-1}$)	Average primary particle size (nm)	Tap density ($\text{m}^3 \text{g}^{-1}$)
S1a	5.3	6.31	~89	0.7
S1b	5.3	1.47	~280	0.8
S2a	4.5	6.44	~92	1.1
S2b	4.5	2.28	~140	1.2

Figures

Figure 1. (a) The contour plot of in situ HEXRD patterns and (b) The in-situ HEXRD patterns during the thermal treatment of the precursor prepared using the one-step process. (c) Covariance matrix of 2D covariance analysis and (d) 1D covariance analysis of in situ HEXRD profiles.

Figure 2. The areal plot of in-situ HEXRD patterns during the thermal treatment of the precursor prepared using the one-step process

Figure 3. The evolution of an intermediate phase during the thermal treatment of the precursor prepared using the one-step process.

Figure 4. (a) The contour plot of the in-situ HEXRD profiles during the heating of a preheated precursor prepared using the two-step process. (b)-(d) The intensity variation of diffraction peaks from NiO.

Figure 5 Evolution of cell parameters (a) a and b , (b) c , (c) volume of unit cell, (d) content of NiO impurity, and (e) content of spinel phase during the solid state synthesis of cathode materials using two different process.

Figure 6. SEM images of the precursors and final powders.(a) and (b) SEM images of the precursors of S1a&b; (c) and (d) SEM images of the precursors of S2a&b; (e) and (f)

SEM images of the final powders of S1a; (g) and (h) SEM images of the final powders of S1b; (i) and (j) SEM images of the final powders of S2a; (k) and (l) SEM images of the final powders of S2b.

Figure 7. XRD pattern of samples of 2 Theta between 1.2 to 3.4 degree.

Figure 8. (a) Initial charge and discharge curves of samples; (b) and (c) The voltage profiles of Li/S2a cells that were cycled to different upper cutoff potential (from 4.2 V to 4.8 V)

Figure 9. (a) Rate cyclic performance of samples; (b) Cyclic performance of samples (0.1C rate during 1-3 cycles, 1C rate after 3 cycles).

Vitae

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