Facile preparation of core@shell and concentration-gradient spinel particles for Li-ion battery cathode materials

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Abstract
Core@shell and concentration-gradient particles have attracted much attention as improved cathodes for Li-ion batteries (LIBs). However, most of their preparation routes have employed a precisely-controlled co-precipitation method. Here, we report a facile preparation route of core@shell and concentration-gradient spinel particles by dry powder processing. The core@shell particles composed of the MnO2 core and the Li(Ni,Mn)2O4 spinel shell are prepared by mechanical treatment using an attrition-type mill, whereas the concentration-gradient spinel particles with an average composition of LiNi0.32Mn1.68O4 are produced by calcination of their core@shell particles as a precursor. The concentration-gradient LiNi0.32Mn1.68O4 spinel cathode exhibits the high discharge capacity of 135.3 mA h g−1, the wide-range plateau at a high voltage of 4.7 V and the cyclability with a capacity retention of 99.4% after 20 cycles. Thus, the facile preparation route of the core@shell and concentration-gradient particles may provide a new opportunity for the discovery and investigation of functional materials as well as for the cathode materials for LIBs.

Keywords: lithium-ion battery, spinel cathode, mechanical synthesis, core@shell, concentration-gradient

1. Introduction
LIBs have been supporting the development of wide applications from portable electric devices to energy storage systems of renewable energy to build a sustainable society. These offer a high operation voltage and energy density, a low self-discharge rate, flexibility and lightness compared with traditional batteries [1–3]. It is generally accepted that cathode materials for LIBs play a key role in their performance advances [4–6]. Since the discovery of LiCoO2 as a cathode material [7], Li-intercalation oxides with transition metals have been found and investigated over the last few decades. Among oxide-type cathodes, LiMn2O4-based spinel oxides are attractive cathodes for high-power applications such as electric vehicles (EVs), hybrids and plug-in hybrid EVs [8]. In a pure LiMn2O4 spinel, although it has received attention because of its high-power capability and environmental friendliness [9, 10], the dissolution of Mn3+ at a high temperature causes a significant capacity fade [11]. Meanwhile, the Ni-doped LiMn2O4 spinel, LiNi0.5Mn1.5O4, has a better cycling behavior [12–14]. The highest operation voltage of 4.7 V among the transition metal-doped LiMn2O4 spinels is also one of the advantages of LiNi0.5Mn1.5O4 [15]. This high operation voltage leads to an increase in the energy density of LIBs. However, the electrochemical and physicochemical properties of cathodes roughly depend on their crystal structures and the transition metal ions, so there is a limitation of the characteristics in the active cathode material of a single component.

Recently, the particle design for cathode materials has become a hot topic in the field of LIBs [16]. In particular, a
core@shell structure, which has the expected synergistic effects of a core and shell, has attracted much attention [17]. A significant breakthrough of cathode materials with the core@shell structure has been energetically reported by Sun’s group [18–20]. The first designed core@shell particle was demonstrated in the layered cathode materials and is composed of the Li(Ni0.8Co0.1Mn0.1)O2 core with a high capacity and the Li(Ni0.6Mn0.4)O2 shell with an excellent thermal stability [18]. In the spinel-type cathode materials, the particle composed of the Li1.1Mn1.9O4 core and the LiNi0.5Mn1.5O4 shell has been delivered [21]. This core@shell spinel cathode showed an excellent cyclic performance because the LiNi0.5Mn1.5O4 shell protects the dissolution of Mn3+ from the Li1.1Mn1.9O4 core. However, a structural mismatch and a difference in volume change between the core and shell encounter the unfavorable problem of void formation at the interface [19, 20], which leads to a diffusion barrier of Li+.

To overcome the structural mismatch, concentration-gradient approaches in the shell [22–24] or the entire particle [25–27] have been proposed in terms of the improvement of their performances for the above layered and spinel-type core@shell cathodes. The interfacial barrier between the core and shell can be mitigated by the gradient design, which makes possible the stepwise tuning of material properties. Usually, the preparation of the core@shell and concentration-gradient cathode particles can be attained by a precisely controlled co-precipitation route [18–27]. Although the tailored synthesis of the particles with high quality and a uniform size are successfully conducted via the co-precipitation method, the reaction conditions (pH and concentration of the solutions, temperature, agitation speed, aging time, etc.) should be carefully controlled. For the development and investigation of the core@shell and concentration-gradient cathode materials, the development of a simple and effective method to prepare these particles is of much interest from a viewpoint of the practical applications as well as the fundamental material sciences. Here, we report on a facile preparation route of the core@shell and concentration-gradient spinel particles by dry powder processing. The core@shell particle was prepared by mechanical treatment using an attrition-type mill, and the concentration-gradient spinel particle was produced by calcination of the core@shell particle, which was used as the precursor. The resultant concentration-gradient spinel cathode with an average composition of LiNi0.32Mn1.68O4 exhibited the favorable electrochemical performances. The method presented in this paper provides a new approach to the particle design of cathode materials for LIBs.

2. Experimental

2.1. Preparation of a MnO2@Li(Ni,Mn)2O4 core@shell and of concentration-gradient spinel particles

Firstly, we prepared MnO2@Li(Ni,Mn)2O4 core@shell particles by a mechanical process. MnO2 (>85% purity, Kanto Chemical, Japan) sieved to obtain the particle size of 45–100 μm, Li2CO3 (>99% purity, Sigma-Aldrich, USA) and NiO (99.8% purity, Sigma-Aldrich, USA) powders were used as the raw materials. These raw materials at a molar ratio of Li:Ni:Mn = 2:1:3 (total amount of their powders, 60 g) were put into the chamber of an attrition-type mill. The milling apparatus has been illustrated elsewhere [28]. Mechanical treatment using the attrition-type mill was conducted for 18 min at room temperature, where the rotation speed of the rotor was controlled below 4500 rpm. The obtained MnO2@Li(Ni, Mn)2O4 core@shell particles were collected and used as the precursor of concentration-gradient spinel particles. Preparation of the concentration-gradient spinel particles was carried out by calcination of the MnO2@Li(Ni,Mn)2O4 core@shell particles at 600–800 °C for 2 h in air.

2.2. Characterization

The products were characterized by powder x-ray diffraction (XRD, D2 PHASER, Bruker AXS, Germany) using Cu Kα radiation at room temperature. The operating voltage and current were maintained at 30 kV and 10 mA, respectively. The lattice parameters of the concentration-gradient product were calculated by the least square method using silicon (99.999% purity, Sigma-Aldrich, USA) as an internal standard material. The morphology and elemental distribution of the products were observed via scanning electron microscopy-energy dispersive x-ray spectrometry (SEM-EDS, JSM-6010LA, JEOL, Japan). To obtain the cross-sectional image, the powder samples were mounted in carbon and polished to a mirror-like surface. The particle size distribution was determined by the laser diffraction-scattering method (Microtrac MT3300EXII, NIKKISO, Japan). Small amounts of the sample were dispersed in 0.05 wt% sodium hexametaphosphate (Kishida Chemical, Japan) solution using an ultrasonic bath and a homogenizer. Nitrogen adsorption-desorption measurements (3Flex, micromeritics, Japan) were performed to obtain the specific surface area (S BET) and pore size distribution of the products. Prior to each measurement, the powder samples were outgassed under vacuum at 120 °C for 3 h. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method in a relative pressure range of 0.12–0.20. The equivalent BET diameter (d BET) was estimated from the following equation: d BET = 6/ρ × S BET, where ρ is a theoretical density. For the pore size distribution, the adsorption branch was used in the BJH method. The average chemical composition of the products was analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, SPS5100, SII nanotechnology, Japan). The samples were dissolved in a mixture of HNO3 and H2O2, and then diluted with ultrapure water.

2.3. Electrochemical measurements

The electrochemical performances of the concentration-gradient spinel cathodes were evaluated using CR2032 coin-type half-cells with Li metal as the anode. The prepared concentration-gradient spinel powders were mixed with acetylene black (DENKA, Japan) and polyvinylidene fluoride (Kishida...
Chemical, Japan) (80:15:5 wt%) in N-methylpyrrolidone (Kishida Chemical, Japan). The obtained homogeneous slurry was coated onto Al foil by the doctor blade method and dried at 100 °C in a vacuum. The dried cathode was uniaxially-pressed and punched out. The coin-type half-cells were assembled in a glovebox filled with dry argon. A polypropylene membrane (Celgard #2400, Celgard, USA) and 1 M LiPF6 (Kishida Chemical, Japan) in a mixture of ethylene carbonate and diethyl carbonate (1:1 vol %) were used as a separator and an electrolyte, respectively. The galvanostatic charge and discharge tests were performed on a VMP system.

MnO2 phase as the core is predicted. Hence, the MnO2 particles with the median size of 43 μm estimated from the cross-sectional view of the particles. The starting powder consisted of the micrometer-sized MnO2 particles with an irregular shape and the primary particles of Li2CO3 and NiO (figures 2(a), (b)). The product with a spherical shape was obtained by mechanical treatment of the starting powder using an attrition-type mill (figure 2(c)). A cross-sectional observation of the product revealed the deposition of nanometer-sized particles onto the surface (figure 2(c), inset figure). The EDS maps of oxygen, nickel and manganese clearly exhibited that the mechanically treated product had a core@shell structure and that the shell was constructed by the deposited particles (figures 2(d)–(f)). Nickel was detected in the surface layer of the product particles, while oxygen and manganese were homogeneously distributed. Thus, the core is attributed to a MnO2 phase. The XRD pattern of the product, which is shown later, indicated a Ni-doped LiMn2O4 phase, i.e. a Li(Ni,Mn)2O4 spinel. Consequently, the MnO2@Li(Ni,Mn)2O4 core@shell particles could be prepared by the simple mechanical process without external heating.

The powder properties of the resultant MnO2@Li(Ni, Mn)2O4 core@shell particle were compared with those of the MnO2 raw material to discuss the formation of the core@shell particles. The particle size distribution after mechanical treatment shifted to a smaller size. The median size of the core@shell particles was 21 μm and decreased from 43 μm of the MnO2 raw particles. The nitrogen adsorption-desorption isotherms shown in figure 3 revealed microstructure of the particles. Both the MnO2 and core@shell powders showed a hysteresis loop at a relative pressure from 0.45 to 0.99. According to the pore size distributions calculated from the adsorption branches (figure 3, inset figure), the average pore diameter increased from 5.4 nm to 10.1 nm after mechanical treatment. On the other hand, the specific surface area and the pore volume decreased from 41.1 m² g⁻¹ and 0.056 cm³ g⁻¹ of the MnO2 raw material to 19.3 m² g⁻¹ and 0.049 cm³ g⁻¹ of the core@shell particles, respectively. These powder property changes are due to the formation of the Li(Ni,Mn)2O4 particles as the shell. The primary particle size of the MnO2 raw material, which was estimated from the specific surface area, was 29 nm. That is, the MnO2 raw material consists of the nanometer-sized primary particles. The formation of Li(Ni, Mn)2O4 particles arises at the nanometer-sized particle of the MnO2 surface through mechanical treatment. However, the shearing process of an attrition-type mill scrapes the synthesized LiNi0.5Mn1.5O4 nanoparticles, and the fresh surfaces are created at the MnO2 particles. By repeating the formation and abrasion of LiNi0.5Mn1.5O4 particles, the product particles are made more round in shape. Meanwhile, the synthesized Li(Ni,Mn)2O4 nanoparticles are progressively deposited on the particle surface of MnO2, and the core@shell structure is
formed during mechanical treatment. This deposition process of the Li(Ni,Mn)2O4 nanoparticles onto MnO2 leads to the increase of the pore diameter and the decrease of the specific surface area. The mechanical treatment using an attrition-type mill allows surface coating of the larger species in the case of an obvious difference in particle size between reactants [30]. In this study, the synthesis of the shell particles and the formation of the core@shell structure were achieved by a one-step dry process.

The concentration-gradient spinel particles were prepared by calcination of the MnO2@Li(Ni,Mn)2O4 core@shell powder at 600–800 °C for 2 h. The superimposed EDS maps and elemental profiles of the cross-sectional view for the obtained particles are shown in figure 4. The distribution of nickel, which existed in the shell, spread into the core with the increasing calcination temperature (figures 4(a), (b)). After calcination at 800 °C, manganese and nickel were distributed to all the regions of the particles (figure 4(c)). The relative atomic ratio of manganese and nickel from the center to the surface was measured by EDS point analysis, which selected particles with a diameter of ≈50 μm (figure 4(d)). Comparing the atomic ratios in the MnO2@Li(Ni,Mn)2O4 core@shell particle and the concentration-gradient particle obtained by calcination at 600 °C, the nickel ratio slightly increased in the shell part. The product possessing a concentration gradient of manganese and nickel in the entire particle was obtained by calcination at 700 °C. In the case of calcination at 800 °C, the atomic ratio of manganese and nickel was about 80% and 20%, respectively, all through the particle. The formation approaches of the concentration-gradient shell or particle were achieved by changing a calcination temperature of the core@shell particles as a precursor. An elemental analysis of the concentration-gradient particles was conducted by ICP-AES. The total average chemical composition was determined to be LiNi0.32Mn1.68O4 in all the concentration-gradient particles prepared by calcination at 600–800 °C. The doped
amount of nickel in this average composition was higher than that in the concentration-gradient spinel particle prepared by Wei et al. [27].

The XRD patterns of the MnO2@Li(Ni,Mn)2O4 core@shell powder and the concentration-gradient powders prepared by calcination at various temperatures are shown in figure 5. Although a broad XRD pattern was obtained for the core@shell powder, the diffraction peaks were attributed to a cubic spinel structure with a space group of Fd-3m. This broad XRD pattern is due to the low crystalline MnO2 phase of the core and the unreacted NiO phase. By calcination of the core@shell powder, the sharp XRD patterns were obtained, and the separation of (311) and (222) diffraction peaks became clear. A tiny diffraction peak at 17° is due to a Kβ peak of the strongest (111) diffraction. The expanded XRD patterns in the 2θ regions of 17°–20° and 43°–46° show the (111) and (400) diffraction peaks of their spinel phases, respectively (figure 5(b)). These diffraction peaks for the Li(Ni,Mn)2O4 shell of the core@shell powder were located between the LiMn2O4 and LiNi0.5Mn1.5O4 phases as a reference. Consequently, the formation of a Ni-doped LiMn2O4 phase by mechanical treatment was confirmed by XRD analysis. Both (111) and (400) diffraction peaks shifted to a higher angle by calcination. This peak shift suggests that the MnO2 phase of the core decreased with increasing the formation ratio of the spinel phase. The lattice parameter of the concentration-gradient LiNi0.5Mn1.5O4 particles obtained by calcination at 700 °C was calculated by the least square method using silicon as an internal standard material. The calculated lattice parameter of 8.181(1) Å was in agreement with the linear relation estimated from the reported values of the LiNi0.5−xMn1.5+xO4 spinels [15].

The electrochemical performances of the concentration-gradient spinel powders were tested using a coin-type half-cell employing Li metal as the anode. Figure 6 shows the first charge-discharge curves of the concentration-gradient spinel cathodes, measuring at a constant current density of
14.6 mA g⁻¹ (0.1 C rate for LiNi₀.₃₂Mn₁.₆₈O₄) in a voltage range of 3.0–5.0 V. There are two noteworthy features in our concentration-gradient spinels compared with the reported core@shell and concentration-gradient spinels [21, 27]. One is a high specific discharge capacity. The theoretical values for the LiNi₀.₅ₓMn₁.₅ₓO₄ (0 ≤ x ≤ 0.5) spinels are 146.7–148.2 mA h g⁻¹. The concentration-gradient spinel prepared by calcination at 700 °C provided the highest discharge capacity of 135.3 mA h g⁻¹, whereas that at 600 °C was 120.2 mA h g⁻¹. The low discharge capacity at 600 °C is caused by a remaining MnO₂ phase. This high capacity will lead to an increase of the energy density on the practical applications. The other feature is the presence of an electrochemically active region at a high voltage of 4.6–4.7 V. A capacity of about 90 mA h g⁻¹ was delivered by this high-voltage region. The operation voltages of LiMn₂O₄ and LiNi₀.₅Mn₁.₅O₄ spinels are 4.1 V and 4.7 V, which are attributed to the redox couples of Mn³⁺/Mn⁴⁺ and Ni²⁺/Ni⁴⁺, respectively [9, 15]. Therefore, the concentration-gradient LiNi₀.₃₂Mn₁.₆₈O₄ spinels had a close property to the LiNi₀.₅Mn₁.₅O₄ spinel.

From the results of the first charge-discharge curves, the concentration-gradient LiNi₀.₃₂Mn₁.₆₈O₄ spinel prepared by calcination at 700 °C was selected to evaluate the further electrochemical performances. Although the obvious difference between the spinel cathodes prepared at 700 °C and 800 °C were not found in the first charge-discharge curves, calcination at a high temperature may lead to the formation of a Li₁₋ₓNiₓO phase [15]. The cycle behavior and cyclic voltammograms (CVs) during the initial 20 cycles and rate properties are summarized in figure 7. There was no change in the charge-discharge curves during 20 cycles at a constant current density of 14.6 mA g⁻¹ (figure 7(a)). Accordingly, the discharge capacities during the cycles were recorded at around 135 mA h g⁻¹ (figure 7(b)). The capacity retention after 20 cycles was 99.4%. If the discharge capacity decreases with increasing a cycle number, the capacity retention after 100 cycles extrapolated from the 20 cycles data shows 91.0%. However, the degradation by oxidation of an electrolyte at a high-voltage region is not negligible [31, 32], so it is necessary to further increase the cycle number. The CV curves recorded at a scan rate of 0.2 mV s⁻¹ indicated the three redox peaks (figure 7(c)). A small hump centered at about 4.1 V corresponds to the redox couple of Mn⁵⁺/Mn⁴⁺, which is referred from the Mn⁵⁺ constituent in the concentration-gradient LiNi₀.₃₂Mn₁.₆₈O₄ spinel. The partially overlapped peaks at about 4.7 and 4.8 V correspond to the redox couples of Ni²⁺/Ni³⁺ and Ni³⁺/Ni⁴⁺, respectively. These redox couples showed the reversibility and the cyclability. The rate properties of the concentration-gradient LiNi₀.₃₂Mn₁.₆₈O₄ spinel cathode were tested up to 1.46 A g⁻¹ (10 C rate) (figure 7(d)). The charge rate was equal to the discharge rate, and the constant-voltage charge for 5 h was conducted after achieving maximum voltage of 5 V. The first discharge capacities over 125 mA h g⁻¹ were recorded until reaching a 1 C rate. Although the discharge capacity gradually decreased with
increasing the applied current densities, 68.4 mA h g$^{-1}$ was yielded at a 10 C rate. The discharge capacities at each rate were almost the same after 3 cycles. The concentration-gradient LiNi$_{0.32}$Mn$_{1.68}$O$_4$ spinel showed favorable cathode properties in the initial electrochemical performances.

4. Conclusions

We have demonstrated a facile method to prepare the core@shell and concentration-gradient spinel particles. The preparation method of the concentration-gradient spinels with an average composition of LiNi$_{0.32}$Mn$_{1.68}$O$_4$ consists of the mechanical synthesis of the MnO$_2$@Li(Ni,Mn)$_2$O$_4$ core@shell particles using an attrition-type mill and the calcination step of those as a precursor. The core@shell and concentration-gradient structures were confirmed by EDS elemental maps and profiles. According to the cell tests using a coin-type half-cell employing Li metal as the anode, the concentration-gradient LiNi$_{0.32}$Mn$_{1.68}$O$_4$ spinel cathode prepared by calcination at 700 °C exhibited the high discharge capacity of 135.3 mA h g$^{-1}$, the wide-range plateau at a high voltage of 4.7 V and the cyclability with a capacity retention of 99.4% after 20 cycles. These concentration-gradient LiNi$_{0.32}$Mn$_{1.68}$O$_4$ spinel particles are expected to be used as a cathode for high-energy LIBs, though a further examination of its cyclability is necessary. Additionally, the facile preparation route of the core@shell and concentration-gradient particles demonstrated in this study may provide a new opportunity for the discovery and investigation of functional materials as well as for the cathode materials for LIBs.

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References

[1] Tarascon J-M and Armand M 2001 Issues and challenges facing rechargeable lithium batteries Nature 414 359–67
[2] Armand M and Tarascon J-M 2008 Building better batteries Nature 451 652–7
[3] Song Z, Ma T, Tang R, Cheng Q, Wang X, Krishnaraju D, Panat R, Chan C K, Yu H and Jiang H 2014 Origami lithium-ion batteries Nat. Commun. 5 3140
[4] Whittingham M S 2004 Lithium batteries and cathode materials Chem. Rev. 104 4271–301
[5] Ellis B L, Lee K T and Nazar L F 2010 Positive electrode materials for li-ion and li-batteries Chem. Mater. 22 691–714
[6] Goodenough J B and Park K-S 2013 The Li-Ion rechargeable battery: a perspective J. Am. Chem. Soc. 135 1167–76
[7] Mizushima K, Jones P C, Wiseman P J and Goodenough J B 1980 Li4CoO4 (0 < x ≤ 1): a new cathode material for batteries of high energy density Mater. Res. Bull. 15 783–9
[8] Krätschmer A and Ein-Eli Y 2012 Higher, stronger, better... a review of 5 volt cathode materials for advanced lithium-ion batteries Adv. Energy Mater. 2 922–39
[9] Tarascon J M, Wang E, Shokoohi F K, McKinnon W R and Colson S 1991 The spinel phase of LiMn2O4 as a cathode in secondary lithium batteries J. Electrochem. Soc. 138 2859–64
[10] Thackeray M M 1997 Manganese oxides for lithium batteries Prog. Solid State Chem. 25 1–71
[11] Xia Y, Zhou Y and Yoshio M 1997 Capacity fading on cycling of 4 V Li/LiMn2O4 cells J. Electrochem. Soc. 144 2593–600
[12] Kanamura K, Hoshikawa W and Umegaki T 2002 Electrochemical characteristics of LiNi0.5Mn1.5O4 cathodes with Ti or Al current collectors J. Electrochem. Soc. 149 A339–45
[13] Shaju K M and Bruce P G 2008 Nano-LiNi0.5Mn1.5O4 spinel: a high power electrode for Li-ion batteries Dalton Trans. 5471–5
[14] Zhu Z, Zhang D, Yan H, Li W and Qiu 2013 Precise preparation of high performance spherical hierarchical LiNi0.5Mn1.5O4 for 5 V lithium ion secondary batteries J. Mater. Chem. A 1 5492–6
[15] Zhong Q, Bonakdarpour A, Zhang M, Gao Y and Dahn J R 1997 Synthesis and electrochemistry of LiNi4Mn2−xO4 J. Electrochem. Soc. 144 205–13
[16] Liu C, Li F, Ma L P and Cheng H M 2010 Advanced materials for energy storage Adv. Mater. 22 E28–62
[17] Su L, Jing Y and Zhou Z 2011 Li ion battery materials with core–shell nanostructures Nanoscale 3 3967–83
[18] Sun Y-K, Myung S-T, Kim M-H, Prakash J and Amine K 2005 Synthesis and characterization of Li[(Ni0.5Co0.5)0.8(Ni0.5Mn0.5)0.2]O2 with the microscale core–shell structure as the positive electrode material for lithium batteries J. Am. Chem. Soc. 127 13411–8
[19] Sun Y-K, Myung S-T, Shin H-S, Bae Y C and Yoon C S 2006 Novel core–shell-structured Li[(Ni0.5Co0.5)0.8(Ni0.5Mn0.5)0.2]O2 via coprecipitation as positive electrode material for lithium secondary batteries J. Phys. Chem. B 110 6810–5
[20] Sun Y-K, Myung S-T, Park B-C and Amine K 2006 Synthesis of spherical nano–microscale core–shell particles Li[(Ni0.5Co0.5)0.8(Ni0.5Mn0.5)0.2]O2 and their applications to lithium batteries Chem. Mater. 18 5159–63
[21] Myung S-T, Lee K S, Kim D-W, Scrosati B and Sun Y-K 2011 Spherical core-shell Li[(Li0.8Mn0.2)x(Ni0.5Mn0.5)1−x]O2 spinels as high performance cathodes for lithium batteries Energy Environ. Sci. 4 935–9
[22] Sun Y-K, Myung S-T, Park B-C, Prakash J, Belharouak I and Amine K 2009 High-energy cathode material for long-life and safe lithium batteries Nat. Mater. 8 320–4
[23] Sun Y-K, Kim D-H, Yoon C S, Myung S-T, Prakash J and Amine K 2010 A novel cathode material with a concentration-gradient for high-energy and safe lithium batteries Adv. Funct. Mater. 20 485–91
[24] Sun Y-K, Lee B-R, Noh H-J, Wu H, Myung S-T and Amine K 2011 A novel concentration-gradient Li[(Ni0.5Co0.5)0.8(Ni0.5Mn0.5)0.2]O2 cathode material for high-energy lithium-ion batteries J. Mater. Chem. 21 10108–12
[25] Koenig G M, Belharouak I, Deng H, Sun Y-K and Amine K 2011 Composition-tailored synthesis of gradient transition metal precursor particles for lithium-ion battery cathode materials Chem. Mater. 23 1954–63
[26] Sun Y-K, Chen Z, Noh H-J, Lee D-J, Jung H-G, Ren Y, Wang S, Yoon C S, Myung S-T and Amine K 2012 Nanostructured high-energy cathode materials for advanced lithium batteries Nat. Mater. 11 942–7
[27] Wei Q et al 2013 Spherical concentration-gradient LiMn1.87Ni0.13O4 spinel as a high performance cathode for lithium ion batteries J. Mater. Chem. A 1 4010–6
[28] Hosokawa K, Kondo A, Okumiya M, Abe H and Naito M 2014 One-step mechanical processing to prepare LSM/ScSZ composite particles for SOFC cathode Adv. Powder Technol. 25 1430–4
[29] Kozawa T, Kondo A, Nakamura E, Abe H, Naito M, Koga H, Nakaniishi S and Iba H 2014 Rapid synthesis of LiNi0.5Mn1.5O4 by mechanical process and post-annealing Mater. Lett. 132 218–20
[30] Abe H, Abe I, Sato K and Naito M 2005 Dry powder processing of fibrous fumed silica compacts for thermal insulation J. Am. Ceram. Soc. 88 1359–61
[31] Arora P, White R E and Doyle M 1998 Capacity fade mechanisms and side reactions in lithium-ion batteries J. Electrochem. Soc. 145 3647–67
[32] Li Y, Ravdel B and Lucht B L 2010 Electrolyte reactions with the high voltage LiNi0.5Mn1.5O4 cathodes for lithium-ion batteries Electrochem. Solid-State Lett. 13 A95–7