Glycine/sucrose-based solution combustion synthesis of high-purity LiMn_2O_4 with improved yield as cathode materials for lithium-ion batteries

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Abstract: Single-phase, high-purity nanosized LiMn_2O_4 powders, which are employed as cathode materials for lithium-ion batteries, were produced by solution combustion synthesis using glycine, sucrose, and nitrate, followed by calcination. Phase structure and morphology of the powders were characterized by X-ray diffraction and scanning electron microscopy. The electrochemical performance was measured by galvanostatic charge-discharge cycling in a voltage range of 3.2–4.4 V. The analysis of yield, morphology, and electrochemical performance mainly focused on the influence of different glycine/sucrose ratios. Compared to the sample obtained using 100% glycine, the yields of powders obtained by adding sucrose to the fuel were remarkably improved, from around 50% to over 90%. The highest discharge capacity at 1 C was obtained for the sample with 2% added sucrose, which retained a capacity of 116.6 mAh/g after 80 cycles.

Keywords: LiMn_2O_4 , Cathode material, Solution combustion synthesis

1. Introduction

Rechargeable lithium-ion batteries (LIBs) are the most attractive energy storage devices. They display promising applications in the automotive field, such as in electric vehicles (EVs) and hybrid EVs (HEVs), because of their high power and energy density [1–5]. LIBs consist of an anode and a cathode separated by a separator soaked with electrolyte solution [6,7]. However, the comparatively low storage capacity of the cathode materials have limited their overall performances and hampered wider applications in the next generation of high-energy LIBs [7]. Although LIBs with a high-energy/density LiCoO_2 cathode have been commercialized, the toxicity and high cost of Co pose a challenge to further broad applications. This has forced researchers to explore nontoxic and low-cost new materials. The manganese-based material LiMn_2O_4 is being considered one of the most promising cathode materials owing to its low cost, abundance, environmental friendliness, nontoxicity, and high capacity [8–10]. Various synthesis techniques have been employed to prepare LiMn_2O_4 cathode materials, such as solid-state reaction [11,12], hydrothermal synthesis [13–15], microwave synthesis [16], sol-gel processing [17,18], co-precipitation [19,20], and so on. Among these techniques, a novel solution combustion

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synthesis (SCS) method, based on a highly exothermic and self-sustaining reaction, has been attracting particular interest because it allows homogeneous doping of elements in trace amounts, and yields nano-sized particles with high specific areas [21,22]. The SCS approach, heating sol-gels mixed with metal salt nitrates and fuels such as glycine, urea, and glucose, has been widely used to prepare various oxides[23-25]. However, only few studies have employed SCS to target the superior electrochemical performance of LiMn_2O_4 cathodes. An initial discharge capacity of 127 mAh/g at 0.1 C between 3.0 and 4.3 V was measured for LiMn_2O_4 obtained by SCS with a mixed triethanolamine/starch (in a molar ratio of 1) fuel, combined with calcination at 800 °C for 10 h [26]. An initial discharge capacity of 110 mAh/g and capacity retention of 80% after 40 cycles at 1/3 C between 3.5 and 4.3 V were measured for LiMn_2O_4 obtained by urea-assisted SCS along with calcination at 800 °C for 12 h [27]. In our previous work, an initial discharge capacity of 115.6 mAh/g and a capacity retention of 93% after 50 cycles at 1 C in the 3.2-4.4 V range were obtained for LiMn_2O_4 produced by glycine-assisted SCS followed by calcination at 900 °C for 10 h [28]. High discharge capacity and good cyclability can be achieved in LiMn_2O_4 produced by SCS using glycine as a fuel, which the glycine molecule can participate in the complexation of metal cations of various ionic sizes through its carboxylic acid and amino groups [29]. However, low yields of only around 50% for the final LiMn_2O_4 powders represent an obstacle to both the laboratory testing and industry production, due to the intensive combustion reaction. A high yield of around 96% along with moderate reaction was achieved by tuning the ratio of sucrose fuel to nitrate in the SCS production of Ni-doped LiMn_2O_4 spinels [30].

In this work, glycine/sucrose based SCS is used to improve not only the yields but also the electrochemical properties of LiMn_2O_4 as cathode material for lithium ion batteries. The effect of the glycine/sucrose mole ratio on yields, morphology, and electrochemical performances are also examined.

2. Experimental

Preparation and characterization of cathode materials. For producing LiMn_2O_4 in a theoretical amount of 2 g, an appropriate amount of lithium nitrate (LiNO_3 , 99.0%, Kishida Chemical Co., Ltd., Japan) was dissolved in a manganese nitrate aqueous solution ($\text{Mn}(\text{NO}_3)_2$, 50% w/w aqueous solution, Alfa Aesar) in a Li/Mn molar ratio of 1.05/2 (5% excess weight of lithium). Glycine ($\text{C}_2\text{H}_5\text{NO}_2$, 99.0%, Chameleon Reagent, Japan) and sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$, Chameleon Reagent, Japan) fuels in different molar ratios and 5 ml distilled water were mixed with the above substances with a fuel/nitrate ratio of 1, to form a homogenous solution in a crucible. The reaction can be written as follows:

Seven samples labeled G100%, G98%, G95%, G90%, G80%, G50%, and G0% were designed, with the G value indicating the glycine molar percentage. The above solutions were magnetically stirred in the crucible at 350 rpm and 90 °C for 5-10 h to form sol-gels. The sol-gel was put into a home-made combustion synthesis apparatus, which mainly consisted of the stainless metal bin and a

mesh chimney [28]. This apparatus was placed into a constant temperature lab electric jacket preheated and maintained at 400 °C. The sol-gel mixture in the crucible self-ignited under heating, and released smokes that passed through the meshes into the surrounding air atmosphere, leaving behind the reactant residuum to be collected from the apparatus. The electric jacket was switched off once the combustion reaction associated with gas emission was observed. In order to obtain highly crystalline and high-purity LiMn_2O_4 , the collected powders were further calcined in a muffle furnace under air atmosphere at 800 °C for 24 h at a 5 °C/min rate after grinding in an agate mortar for 10 min.

The phase structure was characterized by powder X-ray diffraction (XRD, Cu $K\alpha$, Rigaku Miniflex). The morphology and size of the powders were determined by scanning electron microscopy (SEM, JEOL, JSM-7001FA). The particle size distributions were analyzed by a particle size analyzer (LA-920, Horiba). The decomposition and thermal behavior of the sol-gels before the combustion reaction were studied by a combined thermogravimetric and differential scanning calorimetry (TG-DSC, Mettler Toledo) analyzer.

Cell assembly and electrochemical measurement. A two-electrode Swagelock-type cell was assembled in an Ar-filled glove box, just as described in our previous reports [28]. The cell consisted of a working electrode, a lithium metal anode, and an electrolyte solution, that was adsorbed in a celgard polypropylene membrane as separator. The working electrode contained the LiMn_2O_4 active powders, a polymer binder (polyvinylidene fluoride (PVDF)), and conductive carbon (acetylene black) in a weight ratio of 80:10:10. Furthermore, an N-methyl-2-pyrrolidone (NMP) solution was also added to the above mixture to form a homogenous slurry under continuous magnetic stirring. The slurry mixture was cast on an aluminum foil current collector and then dried in a vacuum oven at 110 °C for >12 h. The dried electrode on the aluminum foil was punched into disks with a diameter of 10 mm and thickness of 0.1 mm. Meanwhile, a lithium metal disk of 10 mm diameter was chosen as the counter and reference electrode. A solution of 1 M lithium hexafluorophosphate (LiPF_6) in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 in volume) was used as electrolyte. The electrochemical measurements were carried out galvanostatically at a voltage of 3.2-4.4 V and a current density of 1 C (a rate of 1 C corresponding to a full charge/discharge of 150 mAh/g in 1 hour) at room temperature in a battery tester (Arbin Instrument, MSTAT4, USA). The cyclic voltammetry (CV) was carried out by using a potentiostat/galvanostate apparatus (Autolab, PGSTAT128N) at a scan rate of 0.1mV/s.

3. Results and discussion

Fig. 1 shows a schematic diagram of the SCS process along with the yields and images of the products for each sample. The precursor powders of sample G100% were scraped from the metal mesh; only few powders were left in the crucible after SCS in this case, because of an explosive reaction accompanied by large amounts of smoke and loud explosion. In the case of sample G98%, fine powders were found in the crucible and many powders were found on the metal mesh, while for sample G95% we observed aggregated powders in the crucible and few powders on the metal mesh. Sponge-like growth ashes were observed in samples G90%, G80% and

G50%. The precursor powders of sample G0% displayed a large bulk, ascribed to incomplete reaction in the short reaction time. With increasing amounts of sucrose, the explosive reaction gradually turned into a moderate reaction. This effect can be attributed to both the decreased amounts of glycine used for the combustion reaction, corresponding to the weaker exothermic peak at around 260 °C in Fig. 2a-d, and the reduced reaction heat absorbed by the additional sucrose. The yield of produced powders was remarkably enhanced, from only around 50% to >90%, via the 76.4% of sample G98%, owing to the gradual moderate reaction that developed with increasing sucrose amounts.

In order to highlight the occurrence of an increasingly more moderate combustion reaction, a TG-DSC analysis of the sol-gels was carried out. Fig. 2 shows the TG-DSC curves of sol-gels consisting of fuel and nitrate for sample G95% (a), G90% (b), G50% (c), and G0% (d), together with the curves of the glycine (e) and sucrose (f) reagents. The TG-DSC analysis of samples G100% and G98% was not performed in order to protect the equipment, because of the violent reactions involving these samples. Weak endothermic peaks around 130 °C in the (a)-(d) DSC curves are observed for all sol-gels; these peaks are related to the decomposition of combined water in nitrate gels. Sharp exothermic peaks at 260 °C are observed in the DSC curves of samples G95% and G90%, along with a TG weight loss of about 36.5% and 43.8%, indicating the typical combustion synthesis between glycine and nitrates. The subsequent weak exothermic peak from 300 °C to 400 °C in the DSC curves and small weight losses in the TG ones are due to the combustion and decomposition of residual carbides in the following temperature rise process. A low exothermic peak and a weight loss of 12.5% at around 260 °C can be noticed in sample G50%, denoting a weak combustion reaction between glycine and nitrate. With a further increase in temperature, a broader (compared to the former) exothermic peak is observed at 385 °C, together with about 28.1% weight loss in TG curve, which can be attributed to the sluggish combustion of carbonaceous materials with air derived from the pyrolysis of sucrose. A small exothermic peak between 300-350 °C appearing in sample G0%, also shown in Fig. 2f, is attributed to the carbonization of sucrose. Finally, the subsequent evident exothermic peak at around 380 °C, along with a 23.5% weight loss, denotes combustion of carbides in air. The commercial glycine reagent (Fig. 2e) shows an endothermic peak around 260 °C and a weight loss of 44.8%, ascribed to the combustion of glycine in air. A weak endothermic peak at 170 °C occurs for the pure sucrose sample owing to the melt of sucrose, while the weight loss of 61.8% shown in the TG curve arises from the carbonization and combustion of sucrose under air atmosphere. An increasingly more moderate combustion reaction between glycine and nitrate is thus achieved by increasing the amount of sucrose in the fuel, as reflected by the weaker exothermic peak around 260 °C in the DSC curves.

Fig. 3 presents the XRD patterns of SCS-treated powders with different glycine/sucrose ratios. The main diffraction peaks of samples G100% and G98% match well with the standard peaks of the MnO phase, whereas Li is possibly combined with other organics and shows non-characteristic diffraction peaks because of the explosive combustion reaction. However, all diffraction peaks of samples G95%, G90%, G80%, and G50% correspond to the standard peaks of spinel-structure LiMn_2O_4 , indicating the formation of LiMn_2O_4 precursor powders during the SCS process. No diffraction peaks are detected for sample G0%, denoting that the powders

are amorphous because of the incomplete reaction. These SCS-treated powders need to be further calcined in order to obtain better crystallization, which can contribute to the improved electrochemical properties.

Fig. 4 shows the SEM images of SCS-treated powders, with higher magnification pictures shown in the insets. Primary particles with 0.5-1 μm size and agglomerated secondary particles of 1-3 μm can be noticed in sample G100%. Inflated primary and secondary particles with a size of around 5 μm are observed in sample G98%. An increasing amount of fine particles can be seen in sample G95%. Fine primary particles and downy secondary particles with loosened structure are observed in samples G90%, G80% and G50%. Large particles with size $>10 \mu\text{m}$ are observed in sample G0% owing to the incomplete reaction during the SCS process.

Fig. 5 displays the XRD patterns of powders with different glycine/sucrose ratios calcined in air at 800 $^{\circ}\text{C}$ for 24 h. The diffraction peaks of all samples match well with the standard patterns of the LiMn_2O_4 phase without any second phase detected, indicating the complete synthesis of single-phase LiMn_2O_4 powders after calcination. Compared to the SCS-treated powders, an increase in the grain size and a higher degree of crystallization can be deduced from the narrow half-peak width and sharp diffraction peak, which enhance the electrochemical performances.

Fig. 6 shows the SEM images of powders calcined in air at 800 $^{\circ}\text{C}$ for 24 h, with the primary particles displayed in the insets. The particle size distributions of samples G100%, G98%, and G95% are appended in the figure to distinguish the particle sizes. The size of the primary particles for all samples ranges from 100 nm to 200 nm, and decreases slightly upon sucrose addition. Primary particles of around 200 nm are observed in sample G100%, however, slight decreasing sizes of 100-200 nm for primary particles are found for sample G98%. Undifferentiated sizes of secondary particles between samples G100% and G98% are shown in SEM images. In the figure of the particle size distributions, a wide particle size distribution and average particle size of 6.228 μm are displayed in sample G100%. But a narrow particle size distribution and average particle size of 3.620 μm and 3.371 μm are given in samples G98% and G95%, respectively. This effect of decreasing particle sizes can be attributed to the stable binding of metal ions with more polyfunctional-COOH and -OH groups from the sucrose molecule [31]. Increasing pulverization, loosened structure, and finer particles are observed going from sample G95%, to sample G90%, up to samples G80% and G50%. An inhomogeneous distribution of secondary particles is observed in sample G0%, owing to the large size of SCS-treated powders.

Fig. 7 displays the discharge capacity at 1 C between 3.2 and 4.4 V for LiMn_2O_4 samples with different glycine/sucrose ratios. Initial discharge capacities of 123.0, 126.9, 121.2, 121.4, 118.8, 120.9, and 115.8 mAh/g were obtained for samples G100%, G98%, G95%, G90%, G80%, G50%, and G0%, respectively, while the corresponding final discharge capacities of 113.3, 116.6, 114.0, 110.5, 110.5, 109.1, 108.2 mAh/g were still maintained after 80 cycles. The capacity retention of all samples is $>90\%$, namely, 92.1%, 91.9%, 94.1%, 91.0%, 93.0%, 90.2%, and 93.4% for samples G100%, G98%, G95%, G90%, G80%, G50%, and G0%, respectively. Nondecreasing discharge capacity were obtained for sample G98% compared to sample G100%, which can be attributed to the shortened diffusion length of Li ions during cycling confirmed by CV curves of Fig. 9. Charge-discharge curves of the first cycle and

the 80th cycle for LiMn_2O_4 samples with different glycine/sucrose ratios are shown in Fig 8. Two plateaus around 3.9 V and 4.1 V are observed in the discharge curves at the first and 80th cycle for all the samples, indicating a two-steps redox reaction of $\text{Mn}^{3+}/\text{Mn}^{4+}$ during cycling. Fig. 9 shows the CV curves of initial three cycles for sample G100% (a), and sample G98% (b) together with the compared CV curves of the first cycle for samples G100% and G98% (c) at a scan rate of 0.1 mV/s. Table 1 lists the peak parameters of CV curves at the first cycle for samples G100% and G98%. In Fig. 9 (a) and (b), two pairs of well-separated redox peaks are obviously observed for samples G100% and G98%, indicating two-step reversible intercalation/deintercalation of Li ions corresponding two plateaus of charge-discharge curves in Fig. 8. The minor reduced peak currents and areas indicate the slight decrease of capacity from the first cycling to the third cycling. In Fig. 9 (c), the redox peaks of the first cycle in CV curves locate at 4.089/4.216 V, 3.922/4.049 V for sample G100%, and 4.079/4.207 V, 3.922/4.057 V for sample G98%, respectively. The large ΔE_p away from the ideal condition ($\Delta E_p=0$) indicates that the $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox reaction is predominated by the intercalation and deintercalation of Li ions [32]. Compared to sample G100%, the smaller ΔE_p of sample G98% indicated the faster intercalation and deintercalation process of Li ions, reflecting the shortened diffusion length of Li ions. The solution combustion synthesis based on glycine-sucrose could thus provide a new route for the production of nano-sized electrode materials with high performances.

4. Conclusions

The vigorous and explosive nitrate-glycine combustion reaction was mitigated by the addition of sucrose, resulting in improved production yields, from 50% using 100% glycine fuels to over 90% by adding sucrose, passing through 76.4% for sample G98%. Single-phase and high-purity LiMn_2O_4 oxide cathode materials were synthesized by SCS followed by calcination in air at 800 °C for 24 h. The high discharge capacity, 116.6 mAh/g, was obtained for sample G98% during cycling, with a capacity retention of 91.9% after 80 cycles.

Figures

Fig.1 Schematic representation of the SCS process along with the yields and pictures of the products corresponding to each sample. With increasing sucrose amounts, the explosive reaction gradually turned into a moderate reaction.

Fig. 2 TG-DSC of sol-gels consisting of fuels and nitrates for samples G95% (a), G90% (b), G50% (c), and G0% (d), as well as pure glycine (e) and sucrose (f).

Fig. 3 XRD patterns of SCS-treated powders with different glycine/sucrose ratios. The mixed peaks of LiMn₂O₄ and MnO phases are observed in samples G100% and G98%. The main diffraction peaks match well with those of the LiMn₂O₄ phase in the case of samples G95%, G90%, G80%, and G50%. No obvious peaks are observed in sample G100% owing to incomplete reaction.

Fig. 4 SEM images of SCS-treated powders, with the insets showing higher-magnification images.

Fig. 5 XRD patterns of powders with different glycine/sucrose ratios calcined in air at 800 °C for 24 h. All the diffraction peaks match well with those of the LiMn_2O_4 phase.

Fig. 6 SEM images of powders calcined in air at 800 °C for 24 h, with their higher-magnification images shown in the insets. The particle size distributions of samples G100%, G98%, and G95% are appended to distinguish the particle sizes.

Fig. 7 Discharge capacity at 1 C between 3.2 and 4.4 V, measured for LiMn_2O_4 samples with different glycine/sucrose ratios.

Fig. 8 Charge-discharge curves of the first cycle and the 80th cycle for LiMn_2O_4 samples with different glycine/sucrose ratios.

Fig. 9 CV curves of initial three cycles for sample G100% (a), and sample G98% (b) together with the compared CV curves of the first cycle for samples G100% and G98% (c) at a scan rate of 0.1 mV/s.

Table 1 Peak parameters of CV curves at the first cycle for samples G100% and G98%. ΔE_p is the separation between the anodic peak potential E_{pa} and the cathodic peak potential E_{pc} .

Sample	E_{pa1} (V)	E_{pa2} (V)	E_{pc1} (V)	E_{pc2} (V)	ΔE_{p1} (mV)	ΔE_{p2} (mV)
G100%	4.089	4.216	3.922	4.049	167	167
G98%	4.079	4.207	3.922	4.057	157	150

References

- [1] M.-J. Lee, S. Lee, P. Oh, Y. Kim, J. Cho, High performance LiMn₂O₄ cathode materials grown with epitaxial layered nanostructure for Li-Ion batteries, *Nano Lett.* 14 (2014) 993–999.
- [2] B. Stiaszny, J.C. Ziegler, E.E. Krauss, J.P. Schmidt, E. Ivers-Tiffée, Electrochemical characterization and post-mortem analysis of aged LiMn₂O₄-Li(Ni_{0.5}Mn_{0.3}Co_{0.2})O₂/graphite lithium ion batteries. Part I: cycle aging, *J. Power Sources* 251 (2014) 439–450.
- [3] Y.L. Ding, J. Xie, G.S. Cao, T.J. Zhu, H.M. Yu, X.B. Zhao, Enhanced elevated-temperature performance of Al-doped single-crystalline LiMn₂O₄ nanotubes as cathodes for lithium ion batteries, *J. Phys. Chem. C* 115 (2011) 9821–9825.
- [4] A.S. Arico, P. Bruce, B. Scrosati, J.M. Tarascon, W. Van Schalkwijk, Nanostructured materials for advanced energy conversion and storage devices, *Nat. Mater.* 4 (2005) 366–377.
- [5] J. Maier, Nanoionics: ion transport and electrochemical storage in confined systems, *Nat. Mater.* 4 (2005) 805–815.
- [6] R. Pitchai, V. Thavasi, S.G. Mhaisalkar, S. Ramakrishna, Nanostructured cathode materials: a key for better performance in Li-ion batteries, *J. Mater. Chem.* 21 (2011) 11040–11051.
- [7] C.M. Hayner, X. Zhao, H.H. Kung, Materials for rechargeable lithium-ion batteries, *Annu. Rev. Chem. Biomol. Eng.* 3 (2012) 445–471.
- [8] J.M. Tarascon, E. Wang, F.K. Shokoohi, W.R. McKinnon, S. Colson, The spinel phase of LiMn₂O₄ as a cathode in secondary lithium cells, *J. Electrochem. Soc.* 138 (1991) 2859–2864.

- [9] E. Hosono, T. Kudo, I. Honma, H. Matsuda, H. Zhou, Synthesis of single crystalline spinel LiMn_2O_4 nanowires for a lithium ion battery with high power density, *Nano Lett.* 9 (2009) 1045–1051.
- [10] Z. Xiao, Y. Zhou, L. Song, F. Zhang, J. Gao, J. Zeng, Z. Cao, Thermal-electrochemical behaviors of LiMn_2O_4 lithium-ion cell studied by electrochemical-calorimetric method, *J. Alloys Compd.* 592 (2014) 226–230.
- [11] B. Ju, X. Wang, C. Wu, Q. Wei, X. Yang, H. Shu, Y. Bai, Excellent cycling stability of spherical spinel LiMn_2O_4 by Y_2O_3 coating for lithium-ion batteries, *J. Solid State Electrochem.* 18 (2014) 115–123.
- [12] T. Kakuda, K. Uematsu, K. Toda, M. Sato, Electrochemical performance of Al-doped LiMn_2O_4 prepared by different methods in solid-state reaction, *J. Power Sources* 167 (2007) 499–503.
- [13] G.H. Waller, S.Y. Lai, B.H. Rainwater, M. Liu, Hydrothermal synthesis of LiMn_2O_4 onto carbon fiber paper current collector for binder free lithium-ion battery positive electrodes, *J. Power Sources* 251 (2014) 411–416.
- [14] P. Ragupathy, H.N. Vasan, N. Munichandraiah, Microwave driven hydrothermal synthesis of LiMn_2O_4 nanoparticles as cathode material for Li-ion batteries, *Mater. Chem. Phys.* 124 (2010) 870–875.
- [15] D. Guo, Z. Chang, B. Li, H. Tang, X.-Z. Yuan, H. Wang, Synthesis of high-purity LiMn_2O_4 with enhanced electrical properties from electrolytic manganese dioxide treated by sulfuric acid-assisted hydrothermal method, *J. Solid State Electrochem.* 17 (2013) 2849–2856.
- [16] H. Zhang, D. Liu, X. Zhang, C. Zhao, Y. Xu, Microwave synthesis of $\text{LiMg}_{0.05}\text{Mn}_{1.95}\text{O}_4$ and electrochemical performance at elevated temperature for lithium-ion batteries, *J. Solid State Electrochem.* 18 (2014) 569–575.
- [17] C.L. Chen, K.F. Chiu, Y.R. Chen, C.C. Chen, H.C. Lin, H.Y. Chiang, High rate performance of LiMn_2O_4 cathodes for lithium ion batteries synthesized by low temperature oxygen plasma assisted sol-gel process, *Thin Solid Films* 544 (2013) 182–185.
- [18] X.-M. Liu, Z.-D. Huang, S. Oh, P.-C. Ma, P.C.H. Chan, G.K. Vadam, K. Kang, J.-K. Kim, Sol-gel synthesis of multiwalled carbon nanotube- LiMn_2O_4 nanocomposites as cathode materials for Li-ion batteries, *J. Power Sources* 195 (2010) 4290–4296.
- [19] H.W. Chan, J.G. Duh, S.R. Sheen, LiMn_2O_4 cathode doped with excess lithium and synthesized by co-precipitation for Li-ion batteries, *J. Power Sources* 115 (2003) 110–118.
- [20] R. Thirunakaran, R. Ravikumar, S. Gopukumar, A. Sivashanmugam, Electrochemical evaluation of dual-doped LiMn_2O_4 spinels synthesized via co-precipitation method as cathode material for lithium rechargeable batteries, *J. Alloys Compd.* 556 (2013) 266–273.
- [21] K.C. Patil, S.T. Aruna, S. Ekambaram, Combustion synthesis, *Curr. Opin. Solid State Mater. Sci.* 2 (1997) 158–165.
- [22] A.S. Mukasyan, P. Epstein, P. Dinka, Solution combustion synthesis of nanomaterials, *Proc. Combust. Inst.* 31 (2007) 1789–1795.
- [23] C. Zhu, A. Nobuta, I. Nakatsugawa, T. Akiyama, Solution combustion synthesis of LaMO_3 (M=Fe, Co, Mn) perovskite nanoparticles and the measurement of their electrocatalytic properties for air cathode, *Int. J. Hydrogen Energy* 38 (2013)

- [24] K. Tahmasebi, M.H. Paydar, The effect of starch addition on solution combustion synthesis of $\text{Al}_2\text{O}_3\text{-ZrO}_2$ nanocomposite powder using urea as fuel, *Mater. Chem. Phys.* 109 (2008) 156–163.
- [25] R. Ianos, A. Taculescu, C. Pacurariu, I. Lazau, Solution combustion synthesis and characterization of magnetite, Fe_3O_4 , nanopowders, *J. Am. Ceram. Soc.* 95 (2012) 2236–2240.
- [26] G.T.-K. Fey, Y.-D. Cho, T. Prem Kumar, A TEA-starch combustion method for the synthesis of fine-particulate LiMn_2O_4 , *Mater. Chem. Phys.* 87 (2004) 275–284.
- [27] K.-M. Lee, H.-J. Choi, J.-G. Lee, Combustion synthesis of spinel LiMn_2O_4 cathode materials for lithium secondary batteries, *J. Mater. Sci. Lett.* 20 (2001) 1309–1311.
- [28] C. Zhu, A. Nobuta, G. Saito, I. Nakatsugawa, T. Akiyama, Solution combustion synthesis of LiMn_2O_4 fine powders for lithium ion batteries. *Adv. Powder Technol.* 25 (2014) 342–347.
- [29] L.A. Chick, L.R. Pederson, G.D. Maupin, J.L. Bates, L.E. Thomas, G.J. Exarhos, Glycine-nitrate combustion synthesis of oxide ceramic powders, *Mater. Lett.* 10 (1990) 6–12.
- [30] M.G. Lazarraga, L. Pascual, H. Gadjov, D. Kovacheva, K. Petrov, J.M. Amarilla, R.M. Rojas, M.A. Martin-Luengo, J.M. Rojo, Nanosize $\text{LiNi}_y\text{Mn}_{2-y}\text{O}_4$ ($0 < y \leq 0.5$) spinels synthesized by a sucrose-aided combustion method. Characterization and electrochemical performance, *J. Mater. Chem.* 14 (2004) 1640–1647.
- [31] M.T. Makhlof, B.M. Abu-Zied, T.H. Mansoure, Direct fabrication of cobalt oxide nanoparticles employing sucrose as a combustion fuel, *J. Nanopart.* 2013 (2013) 1–7.
- [32] M.A. Kiani, M.F. Mousavi, M.S. Rahmanifar, Synthesis of nano- and micro-particles of LiMn_2O_4 : electrochemical investigation and assessment as a cathode in Li battery, *Int. J. Electrochem. Sci.* 6 (2011) 2581–2595.