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Flash microwave synthesis of Mn_3O_4-hausmannite nanoparticles

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Today's world of modernization and miniaturization lays a greater emphasis on more power from smaller and lighter battery packs (portable electronic devices), which explains the various and extensive investigations in this field. Following on from lithium primary cells (introduced into the market about 25 years ago), research is currently going on to improve the secondary lithium battery (or storage battery) technology. Significant improvements involve the replacement of the lithium-metal negative electrode by lithium-storing materials, while the positive electrode is a lithium-containing compound [1–9].

The spinel structure compounds provide suitable host lattices for the insertion of electron donor elements such as lithium, because of the presence of many vacant sites. The different oxidation states of the metallic elements that may be present in these solids allow the electron transfer process to take place during the redox insertion reactions. Thus, several interesting candidates for applications as electrode in lithium and rocking-chair batteries have been found among solids with spinel-related structures [10–12].

The structural formula of an idealized spinel phase is commonly written $(A)_{Td}[B_2]_{Oh}X_4$. It consists of a cubic close-packed array of X anions with one-eighth of the tetrahedral interstices (Td) and one-half of the octahedral ones (Oh) filled by cations. In a *normal spinel*, A cations are placed on Td sites and B cations on the Oh sites. In the *inverse spinel*, the A cations are now randomly placed on Oh sites, half of the B cations are on the Td sites, and the rest of the B cations are on the Oh sites.

During the few last decades, a lot of effort has been focused on manganese because of its low cost, low toxicity, and familiarity to the battery field. In fact, the synthesis of the spinel and layered types of manganese oxides and their lithium insertion reactions have been studied for possible applications as cathode materials for rechargeable batteries [13, 14].

We chose to study manganese oxide, the compound Mn_3O_4 named *hausmannite* [15].

Mn_3O_4 exists in two ordered rock-salt polymorphs: above 1273 °C, a cubic high temperature phase (space group Fd3m) exists, and below this temperature, the compound has tetragonal symmetry (space group $I4_1/amd$). This one, named hausmannite, is a distorted spinel structure, with O atoms on position (16 h), Mn^{2+} ions on (4a) tetrahedral sites ans Mn^{3+} ions on weakly distorted (8d) octahedral sites, as shown in the following formula:

$$({Mn^{2+}}_1)_{\mathbf{4a}}[{Mn^{3+}}_2]_{\mathbf{8d}}{O_4^{2-}}_{\mathbf{16h}}.$$

Mn_3O_4 is only stable at high temperature (in the range of 900 to 1700 °C). So, it is very difficult to stabilize Mn oxidation degrees, and so to synthesize stable Mn_3O_4 below 900 °C, by the usual route [16]. We present here a new way to obtain stable hausmannite at 190 °C, using microwave heating. A microwave method is usually used for synthesis of organic and inorganic materials [17, 18]. Microwave irradiation enhances the reaction speed significantly and reduces the reaction temperature. Energy transfer from the microwaves to the material occurs through resonance, which results in rapid heating. Microwave heating is a core heating process [19]. Moreover, nanocrystalline materials with average grain size of less than 50 nm have attracted considerable scientific interest because of their unusual physical and chemical properties [20–23]. In our case, previous investigations have shown that the microwave synthese route leads to nanoparticles [24, 25], favoring the sintering step.

Most of the papers describe the use of laboratory devices deriving from domestic ovens. We have designed an original microwave reactor, the RAMO system (french acronym of **R**eacteur **A**utoclave **M**icro**O**nde). This experimental system consists of a microwave applicator associated with an autoclave. The microwave oven and the reactor are specially designed by the authors. Compared to domestic ovens, our microwave oven allows higher electric field strengths for heating samples. By varying the position of a plunger, we can control the resonant frequency of the cavity and we can increase the effective cavity power by three orders of magnitude. The microwave generator used was operated at 2.45 GHz, with a power of 1 KW. This instrument is a monomodal cavity. The autoclave is made with polymer materials which are microwave transparent, chemically inert, and sufficiently strong to accommodate induced pressures. The required quantity of $KMnO_4$ was dissolved in ethanol under magnetic stirring, in order to obtain a 0.1 M solution [26]. Then the reactant was placed in a Teflon flask inserted within a polyetherimide flask. A pressure transducer and a manometer allowed the pressure within the

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reactor to be measured. We adjusted the microwave power to allow constant pressure within the vessel. An incorporated pressure release valve permitted the use of this experimental device routinely and safely. Moreover, we introduced inert gas within the reactor to avoid sparking risk with flammable solvents. In our case, microwave irradiation was performed under argon atmosphere. The heated volume was approximatively 20 cm^3. Solutions were heated under a pressure of 10–11 bars, which corresponds to a temperature of 190 °C. An irradiation of 5 min was applied. After the treatment, the samples were cooled to room temperature, then washed with distilled water and alcohol. After drying at room temperature, we obtained a brownish black powder. The results of the microwave heating experiments show that a solution of $KMnO_4$ in ethanol can absorb microwave radiation efficiently.

The phase identification was performed by X-ray powder diffraction (XRD) using a diffractometer SIEMENS Kristalloflex type F, with Fe K_α radiation. A typical XRD pattern of microwave synthesized Mn_3O_4 is given in Fig. 1. All the diffraction lines can be indexed on a body-centered tetragonal unit cell with $a = b = 5.7858$ Å, and $c = 9.1916$ Å, which is in good agreement with literature. Furthermore, we applied the following Scherrer formula in order to calculate the diameter d (Å) of the particles:

$$d = \frac{k \cdot \lambda}{H \cdot \cos \Theta}$$

where k is the shape factor (respectively 0.9 and 1 for a Lorentz or Gauss line), λ, the radiation Fe K_α wavelenght (Å), and H, the half-width of line for a considered Θ-peak (radians).

After calculation, we obtained a particle size equal to 30.7 nm. So, the microwave heating allowed us to synthesize nanoparticles of well-crystallized hausmannite-Mn_3O_4. The size distribution of the particles was obtained by photon correlation spectroscopy (PCS) using a MALVERN 4700 apparatus with a 25 mW He-Ne laser ($\lambda = 633$ nm). This system allows measurement of particles in the range 3 nm–3 μm. The sample temperature was 25 °C. Generally, particles are subject to the Brownian motion; the frequency and amplitude of this movement depends on the particle size. The application of the Stokes-Einstein equation allowed us to infer the average size of particles and the size distribution [27–30]. Experimentally, powder was dispersed in distilled water under ultrasound. Fig. 2 describes a typical narrow size distribution. We can conclude that this one was monomodal and the average size was roughly 600 nm. This result showed that the 30 nm particles were agglomerated, probably by ultrasonic application. The morphology of the particles was examined by transmission electron microscopy (TEM) in a Jeol JEM 100 C model. The powder was dispersed in ethanol, and the suspension was deposited on carbon-coated grids and further evaporated. Fig. 3 shows the morphology of hausmannite-Mn_3O_4. Agglomerated particles can be observed (confirming the PCS results) with a distribution size averaging from 30–40 nm, according to the previous Scherrer calculation.

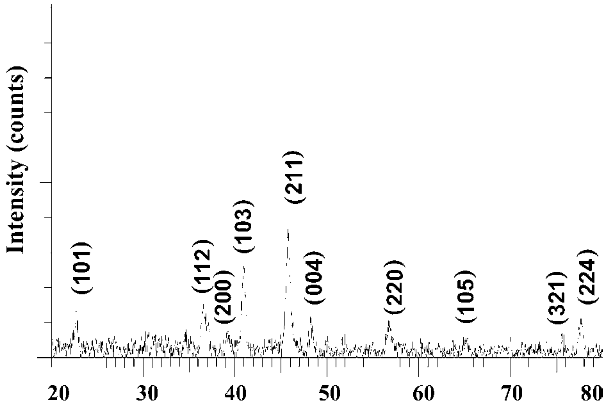

Figure 1 XRD pattern (using Fe K_α) of hausmannite-Mn_3O_4 synthesized by microwave heating.

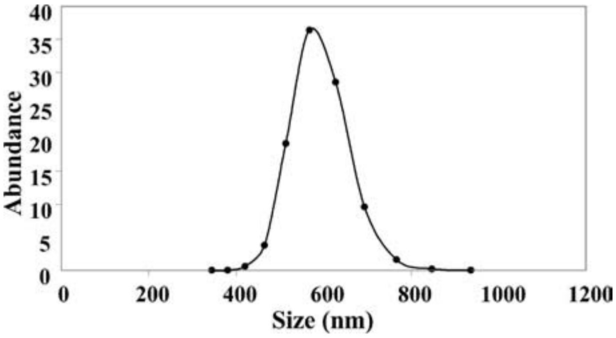

Figure 2 Size distribution obtained by PCS for Mn_3O_4 solution.

Finally, the BET (Brunauer-Emmet-Teller) method allowed us to calculate specific areas. It consists of studying gas adsorption (or desorption) by the sample solid with an AUTOSORB 1 device. The absorbed gas was nitrogen. The determinate specific area value was about 43.11 m^2/g. Moreover, the averaged diameter d' of the hausmannite particles using the following relation was calculated:

$$d' = \frac{6}{\rho \cdot S}$$

with ρ as Mn_3O_4 density, and S as specific area.

Applying the above formula with $\rho = 4.856$ g/cm^3, the particle size was found to be about 28.7 nm. This value is close to the one found using the Scherrer formula, and so confirms the XRD and TEM results.

In conclusion, single-phase tetragonal Mn_3O_4 called hausmannite can be synthesized very quickly (a few minutes only) by microwave heating at a temperature close to 190 °C. The powder was well crystallized and the particles were nanometric, with a size of about 30 nm (evidenced by Scherrer calculation, TEM, and BET method). Photon correlation spectroscopy (PCS) showed that after ultrasonic treatment, Mn_3O_4 grains were agglomerated to form bigger particles (of about 600 nm). The use of a microwave process offers a new way for the synthesis of nanometer particles with a high crystallinity. In the future, hausmannite-Mn_3O_4

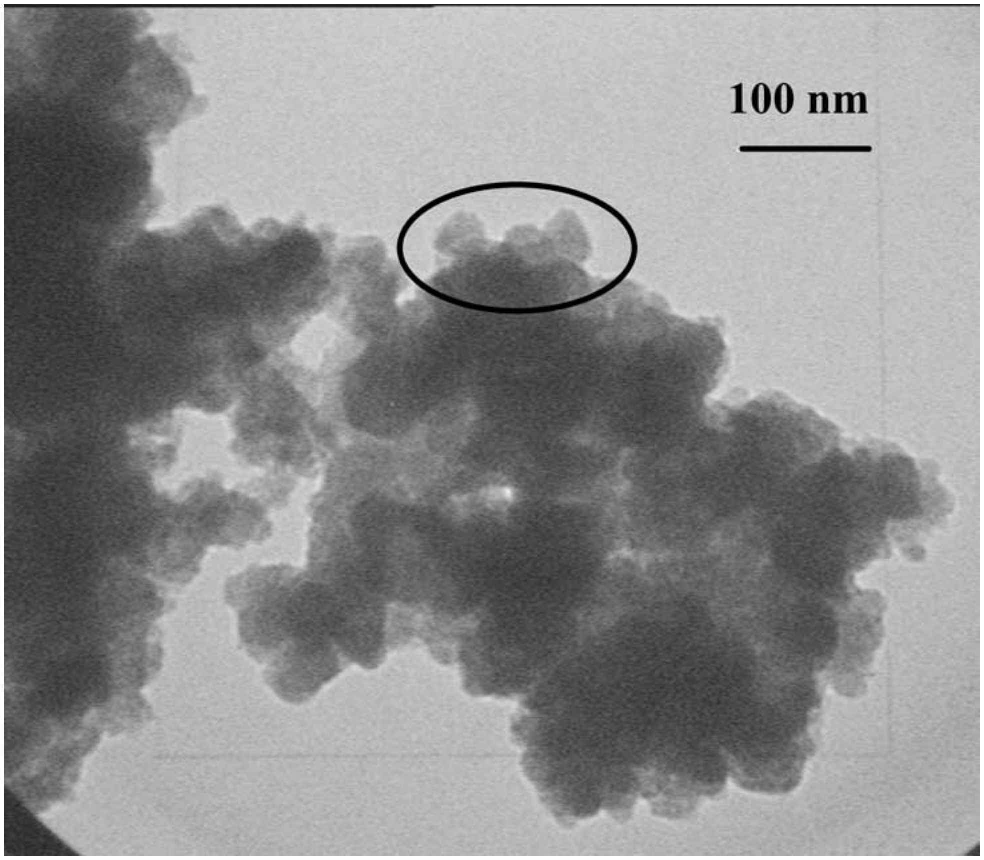

Figure 3 Morphology of haunsmannite-Mn_3O_4.

will be electrochemically intercalated (with lithium) and then tested as cathode material for rechargeable batteries.

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References

1. C. VINCENT, *IEE Rev.* **45**(2) (1999) 65.
2. *Idem.*, *Solid State Ion.* **134** (2000) 159.
3. Y. NISHI, *J. Power Sources* **100** (2001) 101.
4. M. BROUSSELY, P. BIENSAN and B. SIMON, *Electrochemica Acta* **45** (1999) 3.
5. C. BOUSQUET, A. KRÄMER, C. PEREZ-VICENTE, J. L. TIRADO, J. OLIVIER-FOURCADE and J. C. JUMAS, *J. Solid State Chem.* **134** (1997) 238.
6. C. BOUSQUET, C. PEREZ-VICENTE, A. KRÄMER, J. L. TIRADO, J. OLIVIER-FOURCADE and J. C. JUMAS, *J. Mater. Chem.* **8**(6) (1998) 1399.
7. G. MAURIN, C. BOUSQUET, F. HENN, P. BERNIER, R. ALMAIRAC and B. SIMON, *Chem. Phys. Lett.* **312**(1) (1999) 14.
8. J. XIE, X. ZHAO, G. CAO, Y. ZHONG and M. ZHAO, *J. Mater. Sci. Lett.* **22**(3) (2003) 221.
9. H. CHEN, X. QIU, W. ZHU and P. HAGENMULLER, *Electrochem. Comm.* **4** (2002) 488.
10. M. EISENBERG, *J. Electrochem. Soc.* **127** (1980) 2382.
11. A. C. W. P. JAMES, B. ELLIS and J. B. GOODENOUGH, *Solid State Ion.* **27** (1988) 45.
12. J. MORALES, J. L. TIRADO, M. L. ELIDRISSI MOUBTASSIM, J. OLIVIER-FOURCADE and J. C. JUMAS, *J. Alloys Comp.* **217** (1995) 176.
13. M. S. WHITTINGHAM and P. Y. ZAVALIJ, *Solid State Ion.* **131** (2000) 109.
14. M. M. THACKERAY, W. I. F. DAVID, P. G. BRUCE and J. B. GOODENOUGH, *Mater. Res. Bull.* **18**(4) (1983) 461.
15. V. BARON, J. GUTZMER, H. RUNDLÖF and R. TELLGREN, *Amer. Miner.* **83** (1998) 786.
16. E. R. STOBBE, B. A. DE BOER and J. W. GEUS, *Catal. Today* **47** (1999) 161.
17. Y. YANG, J. L. ONG and J. TIAN, *J. Mater. Sci. Lett.* **21**(1) (2002) 67.
18. S. DAS, A. K. MUCKHOPADHYAY, S. DATTA and D. BASU, *ibid.* **22**(22) (2003) 1635.
19. D. STUERGA and P. GAILLARD, *Tetrahedron* **52**(15) (1996) 5505.
20. W. H. QI and M. P. WANG, *J. Mater. Sci. Lett.* **21**(22) (2002) 1743.
21. J. CHEN, L. SHAO, C. ZHANG, J. CHEN and G. CHU, *ibid.* **22**(6) (2003) 437.
22. X. WANG, B. I. LEE, M. Z. HU, E. A. PAYZANT and D. A. BLOM, *ibid.* **22**(7) (2003) 557.
23. Y. XING, T. P. KOLE and J. L. KATZ, *ibid.* **22**(11) (2003) 787.
24. D. S. WU, C. Y. HAN, S. Y. WANG, N. L. WU and I. A. RUSAKOVA, *Mater. Lett.* **53** (2002) 155.
25. P. RIGNEAU, K. BELLON, I. ZAHREDDINE and D. STUERGA, *The Europ. Phys. J. (Appl. Phys.)* **7** (1999) 41.
26. Z. WEIXIN, W. CHENG, Z. XIAOMING, X. YI and Q. YITAI, *Solid State Ion.* **177** (1999) 331.
27. K. J. RANDLE, *Chem. Ind.* **19** (1980) 74.
28. N. DE JAEGER, H. DEMEYERE, R. FINSY, R. SNEYERS, J. VANDERDEELEN, P. VAN DER MEEREN and M. VAN LAETHEM, *Part. Part. Syst. Charact.* **8** (1991) 179.
29. R. FINSY and N. DE JAEGER, *ibid.* **8** (1991) 187.
30. R. FINSY, N. DE JAEGER, R. SNEYERS and E. GELADE, *ibid.* **9** (1992) 125.

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