Engineering Cationic Vacancies in Nanosized Mo-Substituted Fe₂O₃ towards Better Electrochemical Cationic Insertion †

Chérazade Haouari [1,2,3,*]**, Lorenzo Stievano** [1,3]**, Romain Berthelot** [1,3] **and Damien Dambournet** [2,3]

[1] Institut Charles Gerhardt Montpellier, ICGM, (UMR 5253 CNRS), Université Montpellier, Place Eugène Bataillon, 34095 Montpellier, France; lorenzo.stievano@umontpellier.fr (L.S.); romain.berthelot@umontpellier.fr (R.B.)

[2] Physico-Chimie des Electrolytes et Nano-Systèmes Interfaciaux, PHENIX, (UMR 8234 CNRS), Sorbonne Université, 4 place Jussieu, F-75005 Paris, France; damien.dambournet@upmc.fr

[3] RS2E, FR 3459 CNRS, HUB de l'Energie, 15 rue Baudelocque, 80039 Amiens, France

* Correspondence: cherazade.haouari@upmc.fr

† Presented at the 2nd International Online-Conference on Nanomaterials, 15–30 November 2020; Available online: https://iocn2020.sciforum.net/.

Abstract: The search for high-energy density batteries especially stimulates the design of electrode materials with enhanced electrochemical storage properties. Downsizing the material to extend its electrochemically active surface as well as creating vacancies to create more available insertion sites are common approaches to improve the performance of electrode materials (1,3). In this work, our strategy is to maximize the cationic vacancies into nano-sized spinel Fe2O3 through substituting iron by molybdenum, with the final objective of extending the electrochemical insertion domain and accessing higher specific capacities. Our electrode materials were prepared by a simple solvothermal route which allows a carefully tuning of the cationic precursors.[2] The stabilization of molybdenum cations inside the spinel structure, and consequently the creation of cationic vacancies, were characterized by a wide range of complementary techniques, including pair distribution function analysis, X-ray absorption spectroscopy and 57Fe Mössbauer spectroscopy. Interestingly, it is possible to tune both size and crystallinity of such nanomaterials by modifying the iron precursors and the synthesis conditions. The positive influence of this nanoscale engineering was firstly verified by evaluating the synthesized materials as positive electrodes in lithium batteries, with a significant enhancement of the initial specific capacity (from 40 to 100 mAh/g) for Li insertion. As magnesium-ion batteries are emerging electrochemical storage systems that are still facing lack of positive electrode materials, we are also currently evaluating the magnesium insertion inside the Mo-substituted nanosized Fe2O3.

The search for high-energy density batteries especially stimulates the design of electrode materials with enhanced electrochemical storage properties. Downsizing the material to extend its electrochemically active surface as well as creating vacancies to create more available insertion sites are common approaches to improve the performance of electrode materials [1,2].

In this work, our strategy is to maximize the cationic vacancies into nano-sized spinel Fe₂O₃ through substituting iron by molybdenum, with the final objective of extending the electrochemical insertion domain and accessing higher specific capacities.

Our electrode materials were prepared by a simple solvothermal route which allows a carefully tuning of the cationic precursors [3]. Interestingly, it is possible to tune both size and crystallinity of

such nanomaterials by modifying the synthesis conditions. The stabilization of molybdenum cations inside the spinel structure, and consequently the creation of cationic vacancies (Figure 1), were characterized by a wide range of complementary techniques, including pair distribution function analysis, X-ray absorption spectroscopy and ^{57}Fe Mössbauer spectroscopy. From the position of the Bragg peaks, the iron oxide phases present in the as-prepared samples were identified to be magnetite (Fe_3O_4) or maghemite (γ-Fe_2O_3) with no impurity (Figure 2a). Mössbauer spectroscopy is a powerful tool to discriminate between the two phases and understanding the iron local environment. These spectra measured at room temperature were refined with a doublet and a sextuplet distribution. As Fe is replaced with Mo, the paramagnetic doublet component increases in the central part of the spectra. This indicates that nanoparticles undergo the transition from the magnetic order to the paramagnetic state.

The positive influence of this nanoscale engineering was firstly verified by evaluating the synthesized materials as positive electrodes in lithium batteries, with a significant enhancement of the initial specific capacity (from 40 to 100 mAh/g) for Li insertion (Figure 3). As magnesium-ion batteries are emerging electrochemical storage systems that are still facing lack of positive electrode materials, we are also currently evaluating the magnesium insertion inside the Mo-substituted nanosized Fe_2O_3.
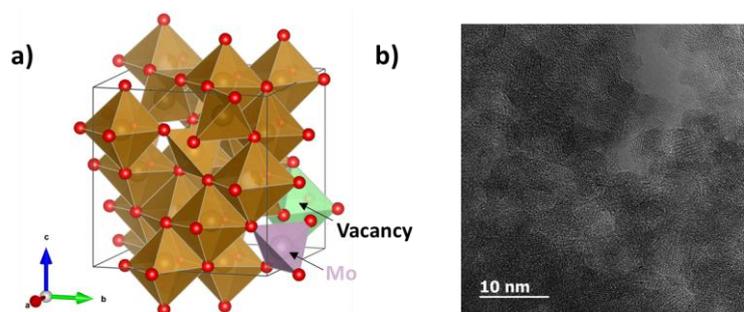

Figure 1. Structure and morphology representation of Mo-substituted nanosized Fe_2O_3. (**a**) Representation of the crystallographic structure of Fe_2O_3 spinel with the P4₃32 space group: red, brown and purple balls represent oxygen, iron and molybdenum atoms respectively. This Mo substitution creates a vacancy represented with a green empty polyedra which is the location of the missing Fe atom. No distorsion was taking into account. (**b**) TEM images of Mo-substituted nanosized Fe_2O_3.
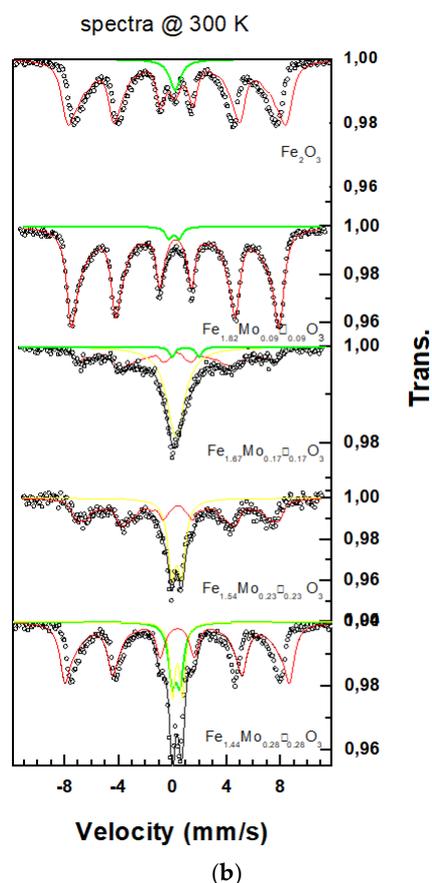

(**a**)
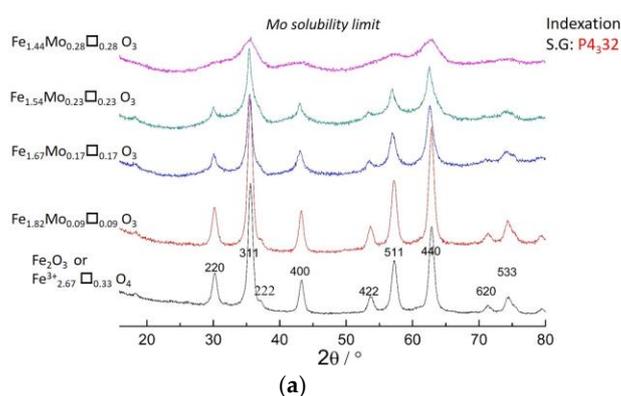
Figure 2. Caracterisation of Mo-substituted iron oxide samples prepared by varying the Mo quantity (**a**) X-ray diffraction patterns (**b**) Mössbauer spectra at 300 K.
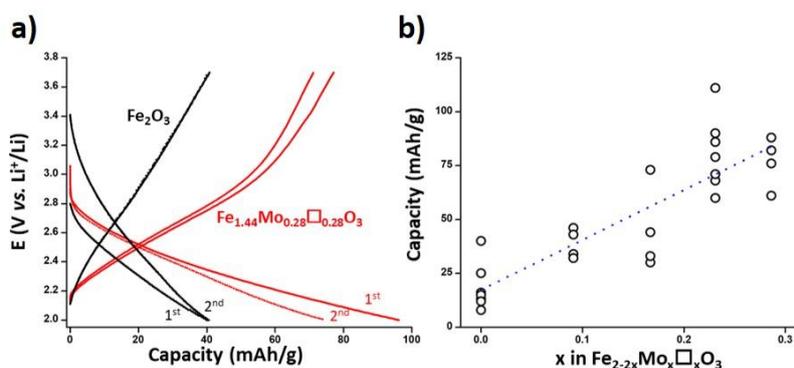

Figure 3. Electrochemical performances of Mo-substituted iron oxide electrodes at current density of 20 mA/g. (**a**) Galvanostatic charges and discarges curves of nano-sized spinel Fe_2O_3 and maximum Mo-substituted nanosized Fe_2O_3. (**b**) Evolution of initial and second discharges capacities with increasing Mo substitution.

References

1   Hahn, B.P.; Long, J.W.; Rolison, D.R. *Acc. Chem. Res.* **2013**, *46*, 1181.

2   Kanzaki, S.; Inada, T.; Matsumura, T.; Sonoyama, N. *J. Power Sources* **2005**, *146*, 323.

3   Hahn, B.P.; Long, J.W.; Mansour, A.N.; Pettigrew, K.A.; Osofsky, M.S.; Rolison, D.R. *Energy Environ. Sci.* **2011**, *4*, 1495.