Article

A New, Friendlier Methodology to Determine the Average Manganese Valence in $Li_xMn_2O_4$ Spinels Using Atomic Absorption Spectrometry and Molecular Absorption Spectrophotometry

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An alternative, friendlier methodology for the determination of the average manganese valence (ν) of manganese oxides (mainly pure and doped spinels) is presented. This methodology is based on the facile determination of the concentration of Mn^{2+} and Fe^{2+} ions by atomic absorption spectrometry (AAS) and molecular absorption spectrophotometry (MAS), respectively. Prior to this determination, the manganese oxides are reacted with an acidic solution containing Fe^{2+} ions, when all $Mn^{\nu+}$ ions are reduced to Mn^{2+}. Then, the concentration of Mn^{2+} ions is obtained directly by AAS, whereas that of Fe^{2+} ions is obtained by MAS after their complexation with *o*-phenanthroline. Using this methodology, the obtained mean (n = 3) ν values for the stoichiometric oxides Mn_2O_3 and Mn_3O_4 are 2.98 ± 0.01 and 2.66 ± 0.01, respectively; their precision is a clear evidence of the suitability of the here-proposed methodology. Additionally, a precise mean ν value (3.46 ± 0.01; n = 3) is also obtained for the spinel $Li_{1.05}Mn_2O_4$, whereas a higher ν value (3.52 and 3.53; n = 2) is obtained for the doped spinel $Li_{1.05}Mn_{1.98}Al_{0.02}O_{3.98}S_{0.02}$, evidencing that effective doping has been indeed attained. This novel methodology is easily applicable for Mn oxides in electrode materials of many energy storage devices.

Keywords: manganese oxides, Mn valence spectroscopic determination, $Li_{1.05}Mn_2O_4$ spinel, doped spinel $Li_{1.05}Mn_{1.98}Al_{0.02}O_{3.98}S_{0.02}$

Introduction

In the last decade, the popularization of portable electronic devices has increased, leading to a growing demand for lithium ion batteries (LIBs). In this scenario, some oxides have been targeted for studying and testing as cathode materials in LIBs; the spinel lithium manganese oxide ($Li_xMn_2O_4$) is one of these oxides.[1,2] The use of this spinel is favored by factors such as the manganese abundance, non-toxicity, and low cost, as well as the possibility of insertion of two lithium ions *per* formula unit.[3] When $0 \leq x \leq 1$, $Li_xMn_2O_4$ provides a theoretical specific capacity of 148 mA h g^{-1} and a potential of

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4 V *vs*. Li/Li$^+$, related to the insertion/extraction processes of Li$^+$ ions into/from the spinel structure. When $1 \leq x \leq 2$, the theoretical specific capacity is 296 mA h g^{-1} and the potential is 3 V *vs*. Li/Li$^+$.[4] Furthermore, the preparation of the spinel $Li_xMn_2O_4$ is easy, being usually done by solid-state reaction[5,6] between compounds containing Li (LiOH, LiCO$_3$) and Mn (MnO$_2$, Mn$_2$O$_3$, Mn$_3$O$_4$, MnCO$_3$).

On the other hand, the spinel $Li_xMn_2O_4$ presents some disadvantages and the most important among them is the specific capacity loss that occurs during successive charge-discharge cycles, particularly at temperatures higher than 55 °C.[7] This capacity loss is usually correlated with the (*i*) Jahn-Teller effect, which occurs mainly during charge-discharge at 3 V *vs*. Li/Li$^+$,[3,8] (*ii*) manganese dissolution caused by the disproportionation reaction $2Mn^{3+}(s) \rightarrow Mn^{4+}(s) + Mn^{2+}(slv)$,[3,9] and (*iii*) instability of the spinel structure at the end of the charging process due

to oxygen loss.[3] Different experimental strategies have been employed to minimize these possible problems: change of precursors and synthesis conditions,[10,11] change of size and morphology of the spinel particles,[12,13] coating of the spinel particles to prevent manganese dissolution,[14-16] trapping of the Mn cation,[17] and doping of the spinel Li$_x$Mn$_2$O$_4$ with different cations and anions.[3,7,18] This last strategy is one of the most employed and cited in the current literature.

Cationic doping replaces small amounts of Mn^{3+} ions (responsible for the Jahn-Teller effect) and thus minimizes the distortions that occur in the crystal structure of the spinel Li$_x$Mn$_2$O$_4$ during charging-discharging processes. Usually, Mn^{3+} ions are replaced by other trivalent cations like Co^{3+},[3,19-21] Ga^{3+},[3,22] Al^{3+},[3,7,22-25] and Fe^{3+}.[26] The excess of Li$^+$ ions in the spinel structure also promotes its doping.[27,28] Additionally, anionic doping replaces small amounts of O^{2-} ions in the spinel framework and therefore minimizes the disproportionation reaction of Mn^{3+} ions and the instability of the spinel structure due to oxygen loss (as mentioned above). Commonly, O^{2-} ions are replaced by anions such as F$^-$,[3,4,29] S^{2-},[3,30] and Br$^-$.[31]

Cationic doping promotes variations in the amount of Mn^{3+} ions and therefore causes changes in the values of the average manganese valence, ν, in the Li$_x$Mn$_2$O$_4$ spinels. For stoichiometric LiMn$_2$O$_4$, $\nu = 3.5$; the substitution of Mn^{3+} ions by other trivalent cations leads to increased ν values, as reported, e.g., by Amaral *et al.*[3] Therefore, the average manganese valence of doped spinels is a useful parameter because it can provide information on their effective doping and structural changes.

As far as we could ascertain, the most common approach to determine the average manganese valence of manganese oxides has been the Vetter and Jaeger's method,[32] essentially based in potentiometric titrations involving the MnO$_4^-$/Mn^{2+}, Fe^{3+}/Fe^{2+}, and Mn^{3+}/Mn^{2+} redox couples. The main drawback of this method is the long time (hours or even days) needed to reach the equilibrium conditions, making it very laborious. Methodologies involving iodometry and titration with ethylenediaminetetraacetic acid (EDTA) have also been proposed. The one proposed by Tung *et al.*[33] employs an acid solution of potassium iodide to reduce all Mn ions in the manganese oxides to Mn^{2+} ions. In this process, iodine is formed and quantified by titration with a sodium thiosulfate solution, while Mn^{2+} ions are determined by titration with an EDTA solution. Titration of iodine was also proposed by Licci *et al.*[34] to determine the average manganese valence in Mn-La complexes. Firstly, after the Mn-La complex is dissolved in dilute H$_2$SO$_4$, the Mn ions are oxidized to permanganate ions by adding an excess of solid bismuthate, followed by the addition of an iodide solution (also in excess) that converts

all permanganate ions into Mn^{2+} ions, yielding iodine. In a parallel step, the Mn-La complex is reacted directly with an iodide solution, also yielding iodine. In both cases, the iodine is amperometrically titrated with a thiosulfate solution, detecting the equivalent point by the dead-stop method. However, titrations involving the I$_2$ and I$^-$ species require total elimination of dissolved oxygen and refined pH control, as I$^-$ ions react with oxygen to form I$_2$; indeed, this reaction is the main source of error in iodometry.[35] Another methodology, which uses vanadium sulfate solutions,[36] has also been proposed to determine the average manganese valence of various cations in transition-metal oxides, including the spinel Li$_x$Mn$_2$O$_4$, as reported by Okubo *et al.*[37] However, some materials are so difficult to dissolve that they have to be boiled in the vanadium solution for several days under reflux to attain their complete dissolution. Very recently, a new reaction headspace gas chromatographic (HS-GC) technique has been proposed to quantify the average valence of manganese in manganese oxides.[38] This method is based on the reaction between manganese oxides and sodium oxalate under acidic condition, when the CO$_2$ formed as a reaction product can be quantitatively analyzed by HS-GC.

Therefore, the main purpose of this article is to report on an alternative, friendlier methodology to determine the average manganese valence in manganese oxides (mainly pure and doped spinels) using atomic absorption spectrometry (AAS) and molecular absorption spectrophotometry (MAS). This novel methodology is based on the fact that the concentrations of Mn^{2+} and Fe^{2+} ions are easily quantified by the AAS and MAS techniques, respectively.

Experimental

The spinel Li$_{1.05}$Mn$_2$O$_4$ and the doped spinel Li$_{1.05}$Mn$_{1.98}$Al$_{0.02}$O$_{3.98}$S$_{0.02}$ used in the present work were in-house produced by a microwave-assisted solid-state reaction; details on the experimental setup as well as on the effects of synthesis parameters (e.g. precursor reactants, temperature, and time) can be found elsewhere.[39] In that process, Mn$_3$O$_4$, LiOH·H$_2$O (Riedel-de Haen, 98%), Li$_2$S (Aldrich), and Al$_2$O$_3$ (Aldrich) were used as precursors. To obtain the reactant Mn$_3$O$_4$, ε-MnO$_2$ (also synthesized according to a procedure previously optimized in our laboratory)[40] was microwave-calcined during 5 min using the same experimental setup employed for the preparation of pure and doped spinels.[39] To prepare these spinels, the respective reactants were mixed in the same molar proportion of their stoichiometric formulas (Li$_{1.05}$Mn$_2$O$_4$ and Li$_{1.05}$Mn$_{1.98}$Al$_{0.02}$O$_{3.98}$S$_{0.02}$, respectively), amounting to a total

mass of ca. 150 mg. The resulting mixture was homogenized by grinding in an agate mortar for 10 min, then placed in an Al_2O_3 (97%)-CeO_2 (3%) crucible and, finally, submitted to microwave irradiation for 2.5 min in a domestic microwave oven (Panasonic, Piccolo NN-ST359WRU), operating at a frequency of 2.45 GHz and maximum power of 800 W. This oven was also used to prepare Mn_2O_3 from ε-MnO_2, by calcining the latter for 4 min. Since both Mn_2O_3 and Mn_3O_4 present well-defined stoichiometry, they were used to validate the here-proposed methodology to determine the average manganese valence of pure and doped spinels.

The structure of all reaction products was characterized by X-ray diffraction (XRD), using a RIGAKU diffractometer with CuKα radiation at 0.02° min^{-1}.

The procedure to determine the average manganese valence consisted in directly transferring 10-25 mg of the manganese oxide (Mn_2O_3 or Mn_3O_4, or $Li_{1.05}Mn_2O_4$ or $Li_{1.05}Mn_{1.98}Al_{0.02}O_{3.98}S_{0.02}$) to a beaker containing 50 mL of an aqueous 0.01 mol L^{-1} $Fe(NH_4)_2(SO_4)_2.6H_2O$ (PanReac, 99%) and 0.07 mol L^{-1} H_2SO_4 (Synth, 98%) solution; this acidified Fe^{2+} solution was previously standardized by potentiometric titration using a standard aqueous 0.0100 mol L^{-1} $K_2Cr_2O_7$ (Aldrich) solution. The resultant mixture was stirred for 1 h, a time that was sufficient for complete dissolution of the manganese oxide to be attained. Then, depending on the nature of the manganese oxide, different volumes were transferred to two 50 mL volumetric flasks. One flask was completed with deionized water and used in the Mn^{2+} determination by AAS. Volumes of 10 mL of aqueous 10% (m/m) $NaCH_3COO$ (Synth) and 0.1% (m/m) 1,10-phenanthroline (Synth) solutions were added to the other flask, which was then completed with deionized water; the resulting solution was used in the Fe^{2+} determination by MAS. An aqueous 1000 mg L^{-1} Mn^{2+} (Merck) standard solution was used to obtain the analytical curve in the concentration range of 4.5-36.3 µmol L^{-1}. Due to the high dilution factors, deionized water was used as the blank solution. For the Fe^{2+} ions analyses, the analytical curve was obtained using an aqueous Fe^{2+} standard solution containing $NaCH_3COO$ and 1,10-phenanthroline in the same concentrations of the real samples. The Fe^{2+} standard solution was added in volumes varying from 100 to 500 µL, to obtain concentrations in the range of 20.0-100.0 µmol L^{-1}. In this case, the blank was a solution containing only $NaCH_3COO$ and 1,10-phenanthroline, obtained by adding 10 mL of aqueous 10% (m/m) $NaCH_3COO$ and 0.1% (m/m) 1,10-phenanthroline solutions to a 50 mL volumetric flask and completing its volume with deionized water. The AAS analyses were carried out using a Varian spectrometer (model spectrAA 50), operating with a Mn hollow cathode lamp

at 279.5 nm. The MAS analyses were carried out using a Shimadzu spectrophotometer (model UV-1800), operating in the visible spectral region.

Results and Discussion

Structural analyses of the microwave-assisted reaction products

The XRD profiles obtained for the in-house synthesized manganese oxides are presented in Figure 1. The diffractograms for Mn_2O_3 and Mn_3O_4 (Figure 1a), as well for $Li_{1.05}Mn_2O_4$ and $Li_{1.05}Mn_{1.98}Al_{0.02}O_{3.98}S_{0.02}$ (Figure 1b), are consistent with their respective crystallographic patterns, indicating that these manganese oxides were obtained in their pure single phases.
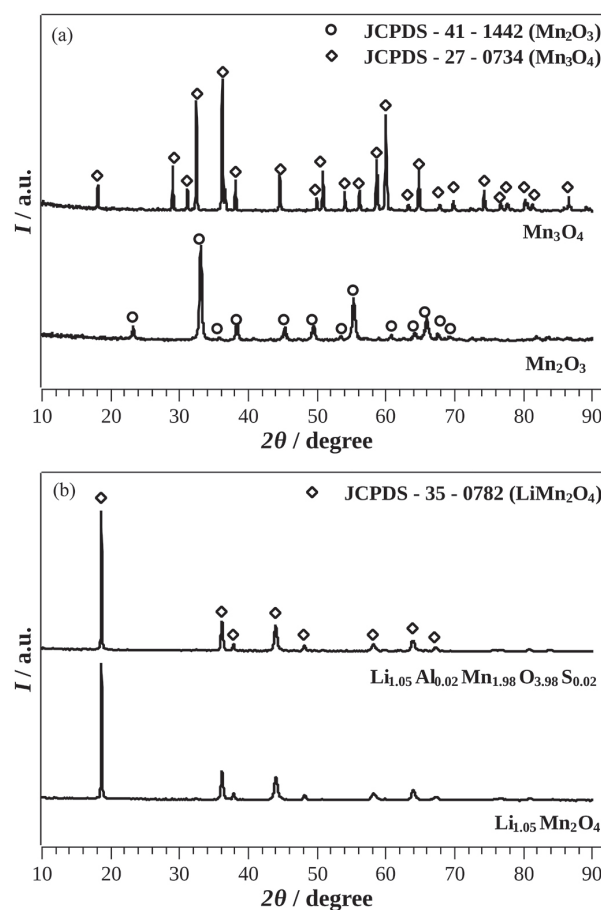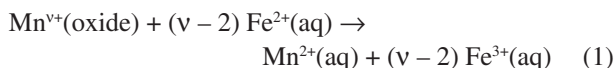

Figure 1. X-ray diffractograms obtained for the in-house synthesized manganese oxides: (a) Mn_2O_3 and Mn_3O_4; (b) $Li_{1.05}Mn_2O_4$ and $Li_{1.05}Mn_{1.98}M_{0.02}O_{3.98}S_{0.02}$.

Determination of the average manganese valence

Considering a manganese oxide in which the Mn oxidation state is "+ν", its Mn ions can be written as $Mn^{\nu+}$,

with $2 \leq v \leq 4$. When this manganese oxide is allowed to react with an acidic solution containing Fe^{2+} ions, all the Mn^{v+} ions are reduced to Mn^{2+} ions according to the equation 1:

$$Mn^{v+}(oxide) + (v-2)\,Fe^{2+}(aq) \rightarrow$$
$$Mn^{2+}(aq) + (v-2)\,Fe^{3+}(aq) \quad (1)$$

Then, the Mn oxidation state (or average valence) can be determined by determining the amounts of Fe^{2+} ions consumed and Mn^{2+} ions produced. Taking into account the stoichiometry of the reaction represented in equation 1, the following relationship is easily inferred.

$$v = \frac{n(Fe^{2+})}{n(Mn^{2+})} + 2 \quad (2)$$

where $n(Fe^{2+})$ is the amount of Fe^{2+} ions and $n(Mn^{2+})$ the amount of Mn^{2+} ions.

As described in detail in the Experimental section, the concentration of Mn^{2+} ions was obtained using AAS, whereas that of Fe^{2+} ions was obtained using MAS, employing the specific reaction between Fe^{2+} and 1,10-phenanthroline, also known as *o*-phenanthroline (*o*-phen), according to the equation 3:

$$Fe^{2+}(aq) + 3\,o\text{-phen}(aq) \rightarrow [Fe(o\text{-phen})_3]^{2+}(aq) \quad (3)$$

The Fe^{3+} ions resulting from this chemical reaction also react with *o*-phen forming $[Fe(o\text{-phen})_3]^{3+}$.[41] However, the $[Fe(o\text{-phen})_3]^{3+}$ and $[Fe(o\text{-phen})_3]^{2+}$ complex ions present maximum absorbance at different wavelengths (λ), as can be seen in the respective UV-Vis spectra shown in Figure 2. While the $[Fe(o\text{-phen})_3]^{2+}$ complex ions present a maximum absorbance at 510 nm, the $[Fe(o\text{-phen})_3]^{3+}$ complex ions do not absorb any radiation at this wavelength; therefore, the presence of Fe^{3+} ions does not interfere in the quantification of Fe^{2+} ions by MAS.
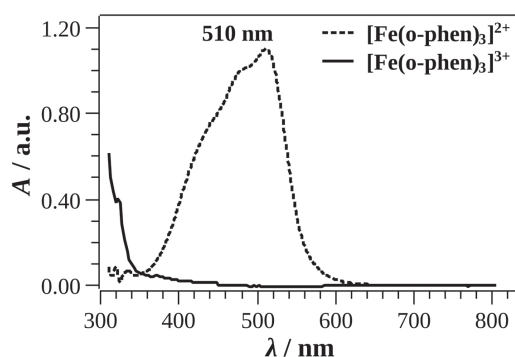

Figure 2. UV-Vis absorbance spectra for 10^{-4} mol L^{-1} aqueous solutions of the $[Fe(o\text{-phen})_3]^{3+}$ and $[Fe(o\text{-phen})_3]^{2+}$ complex ions.

The value of $n(Fe^{2+})$ can be calculated using the following equation:

$$n(Fe^{2+}) = c(Fe^{2+})\,V - n([Fe(o\text{-phen})_3]^{2+}) \quad (4)$$

where $c(Fe^{2+})$ is the initial concentration of Fe^{2+}, V the volume of the standardized Fe^{2+} solution used to reduce the Mn^{v+} ions from the manganese oxide, and $n([Fe(o\text{-phen})_3]^{2+})$ the amount of $[Fe(o\text{-phen})_3]^{2+}$. The values of $n(Mn^{2+})$ and $n([Fe(o\text{-phen})_3]^{2+})$ were calculated from their respective concentrations, which were obtained using the analytical curves presented in Figures 3a and 3b, respectively; both curves are linear, with excellent correlation coefficients (R^2):

$$A(\lambda = 279.5\ nm) = -0.001 + 3.371 \times 10^{-3}\ L\ \mu mol^{-1}\ c(Mn^{2+}),$$
$$R^2 = 0.9998 \quad (5)$$

$$A(\lambda = 510\ nm) = 0.002 + 1.100 \times 10^{-2}\ L\ \mu mol^{-1}\ c([Fe(o\text{-phen})_3]^{2+}),$$
$$R^2 = 0.9999 \quad (6)$$

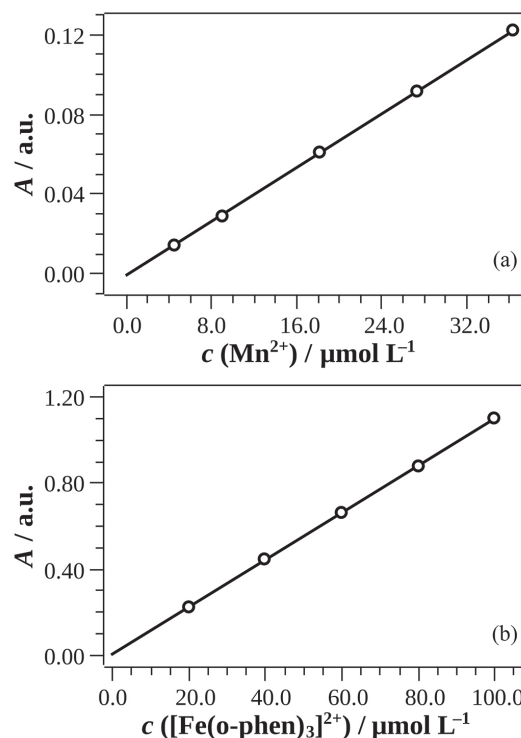**Figure 3.** Analytical curves obtained for the analysis of (a) Mn^{2+} ions by AAS and (b) $[Fe(o\text{-phen})_3]^{2+}$ complex ions by MAS.

To check whether the here-proposed methodology works well, firstly the average manganese valence (v) of Mn_2O_3 and Mn_3O_4 were determined, since both oxides present well-defined stoichiometry[42] and known theoretical values of v; the same was done for the spinel $Li_{1.05}Mn_2O_4$. In these oxides, Mn is present in three different oxidation

states: +2, +3, and +4;[43] in Mn_2O_3 the oxidation state of Mn is +3, while in Mn_3O_4 the oxidations states are +2 and +3 in a proportion that yields an average manganese valence of ca. +2.67 (or exactly +8/3). The determination of the ν values was carried out in triplicate, yielding values practically identical to those expected for Mn_2O_3 and Mn_3O_4, as shown in Table 1. This precision is indicative that the here-proposed methodology is indeed suitable to determine the average Mn valence in manganese oxides. For the spinel $Li_{1.05}Mn_2O_4$, the determination of ν values was also performed in triplicate, yielding the results presented in Table 1. For the stoichiometric spinel $LiMn_2O_4$, ν = 3.50; in the synthesis of the spinel $Li_{1.05}Mn_2O_4$ the molar proportion of Mn:Li was 2.00:1.05 and, therefore, the expected (theoretical) value of ν is 3.48. As the proposed methodology also yielded a precise mean value of the average manganese valence ($ν_{mean}$) for $Li_{1.05}Mn_2O_4$ (see Table 1), its methodological suitability is once again evidenced.

Table 1. Mean values (n = 3) of the average manganese valence ($ν_{mean}$) obtained for different manganese oxides by applying the here-proposed methodology (see text)

Manganese oxide	$ν_{theoretical}$	$ν_{exp}$	$ν_{mean}$
Mn_2O_3	3.00	2.98	2.98 ± 0.01
		2.98	
		2.99	
Mn_3O_4	2.67	2.66	2.66 ± 0.01
		2.65	
		2.67	
$Li_{1.05}Mn_2O_4$	3.48[a]	3.46	3.46 ± 0.01
		3.46	
		3.47	

[a]Theoretical average manganese valence of the spinel taking into account the proportion 2.00Mn:1.05Li.

Secondly, the here-proposed methodology was also applied in the determination of ν for the doped spinel $Li_{1.05}Mn_{1.98}Al_{0.02}O_{3.98}S_{0.02}$ (the same molar proportion of Mn and Li was employed in the preparation of this spinel doped with Al^{3+}). The analyses were carried out for two samples of this material, yielding ν values of 3.52 and 3.53. The relevant result to be here emphasized is the increase in the ν value when compared to that for $Li_{1.05}Mn_2O_4$ (3.46 ± 0.01), since this increase in ν provides information on the effectiveness of the doping process. Therefore, the replacement of small amounts of Mn^{3+} by Al^{3+} did cause an increase in the ratio $Mn^{4+}:Mn^{3+}$, leading to a greater ν value, which is indicative that effective doping was indeed attained in the synthesis of the doped spinel. Here it should be noted

that the determination of the average manganese valence of Mn spinels is sufficient when one needs solely an indication of their effective doping and possible associated structural changes. Moreover, that determination, associated with XRD data, is also sufficient to verify the stoichiometry and purity of Mn oxides (such as Mn_2O_3 and Mn_3O_4) and spinels. On the other hand, when one needs quantitative information on the proportion of Mn^{3+} and Mn^{4+} in those materials, other techniques such as X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) are required. One example is the employment of XPS to obtain the surface Mn valence for the $Li_{3.5}Ti_5O_{12}$-coated-$LiMn_2O_4$ increased after annealing,[44] or to seek the optimum composition of a $LiSn_{x/2}Mn_{2-x}O_4$ spinel to enhance the cycling performance of the material in a lithium ion battery.[45] In the case of XAS, one possible example is its use in the determination of the average manganese oxidation of a fluorine-doped lithium manganese spinel oxide.[46]

Finally, possible interferences in the here-proposed analyses need to be discussed. First, the presence of metallic ions, such as[41] Ag^+, Bi^{2+}, Co^{2+}, Cu^{2+}, and Ni^{2+}, or Zn^{2+} and Cd^{2+}, in manganese oxides can interfere in the reaction between Fe^{2+} ions and *o*-phen (equation 2). However, this interference can be eliminated using liquid-phase extraction, when the complex ions $[Fe(o\text{-phen})_3]^{2+}$ are easily extracted with nitrobenzene.[35] Second, in the analysis of Mn^{2+} ions by AAS, only Mg^{2+} ions can interfere, as these ions present one absorption line at 279.55 nm,[47] identical to the principal absorption line of Mn^{2+} ions. However, in the presence of Mg^{2+} ions, another absorption line of Mn^{2+} ion at 403.1 nm can be used as an alternative.[47] Although the presence of any of those ions could decrease the accuracy of the analyses, the actual interference would be minimal as their quantity in doped spinels is significantly lower than that of manganese. Otherwise, the here-proposed methodology can be directly applied (without any interferential restrictions) in the analysis of the pure spinel $Li_xMn_2O_4$ and spinels commonly doped with ions such as Al^{3+}, Ga^{3+}, and Fe^{3+}.

Conclusions

The here-proposed methodology to determine the average manganese valence (ν) of manganese oxides, using spectrometric (AAS) and spectrophotometric (MAS) techniques, has been shown to be simpler and faster than those commonly employed. From the obtained mean (n = 3) value of ν for the stoichiometric oxides Mn_2O_3 and Mn_3O_4 (2.98 ± 0.01 and 2.66 ± 0.01, respectively), which are very precise, it can be unequivocally stated that this novel methodology, besides being friendly, is highly

suitable for the determination of ν. The methodology was also applied for a pure ($Li_{1.05}Mn_2O_4$) and a doped ($Li_{1.05}Mn_{1.98}Al_{0.02}O_{3.98}S_{0.02}$) spinel oxide, yielding ν values of 3.46 ± 0.01 (n = 3) and 3.52/3.53 (n = 2), respectively; the precision of the mean value of ν obtained for the spinel $Li_{1.05}Mn_2O_4$ also attests to the suitability of the here-proposed methodology, whereas the higher ν value obtained for the doped spinel $Li_{1.05}Mn_{1.98}Al_{0.02}O_{3.98}S_{0.02}$ is a clear evidence that effective doping was indeed attained. Moreover, this new methodology is easily applicable for Mn oxides used as electrode materials in many energy storage devices.

Acknowledgments

References

1. Guo, D.; Chang, Z.; Li, B.; Tang, H.; Yuan, X.-Z.; Wang, H.; *Solid State Ionics* **2013**, *237*, 34.

2. Du, K.; Hu, G. R.; Peng, Z. D.; Qi, L.; *Electrochim. Acta* **2010**, *55*, 1733.

3. Amaral, F. A.; Bocchi, N.; Brocenschi, R. F.; Biaggio, S. R.; Rocha-Filho, R. C.; *J. Power Sources* **2010**, *195*, 3293.

4. Whitfield, P. S.; Davidson, I. J.; *J. Electrochem. Soc.* **2000**, *147*, 4476.

5. Ferracin, L. C.; Amaral, F. A.; Bocchi, N.; *Solid State Ionics* **2000**, *130*, 215.

6. Liu, Q.; Yu, L.; Wang, H.; *J. Alloys Compd.* **2009**, *486*, 886.

7. Yuan, A.; Tian, L.; Xu, W.; Wang, Y.; *J. Power Sources* **2010**, *195*, 5032.

8. Ragavendran, K.; Xia, H.; Mandala, P.; Arof, A. K.; *Phys. Chem. Chem. Phys.* **2017**, *19*, 2073.

9. Bhandari, A.; Bhattachary, J.; *J. Electrochem. Soc.* **2017**, *164*, A106.

10. Fang, H.; Li, L.; Yang, Y.; Yan, G.; Li, G.; *J. Power Sources* **2008**, *184*, 494.

11. He, X.; Wang, J.; Jia, H.; Kloepsch, R.; Liu, H.; Beltrop, K.; Li, J.; *J. Power Sources* **2015**, *293*, 306.

12. Bazito, F. F. C.; Torresi, R. M.; *J. Braz. Chem. Soc.* **2006**, *17*, 627.

13. Xiao, L.; Guo, Y.; Qu, D.; Deng, B.; Liu, H.; Tang, D.; *J. Power Sources* **2013**, *225*, 286.

14. Yang, Z.; Yang, W.; Evans, D. G.; Zhao, Y.; Wei, X.; *J. Power Sources* **2009**, *189*, 1147.

15. Qing, C.; Bai, Y.; Yang, J.; Zhang, W.; *Electrochim. Acta* **2011**, *56*, 6612.

16. Waller, G. H.; Brooke, P. D.; Rainwater, B. H.; Lai, S. Y.; Hu, R.; Ding, Y.; Alamgir, F. M.; Sandhage, K. H.; Liu, M. L.; *J. Power Sources* **2016**, *306*, 162.

17. Banerjee, A.; Ziv, B.; Luski, S.; Aurbach, D.; Halalay, I. C.; *J. Power Sources* **2017**, *341*, 457.

18. Zhao, H.; Liu, X.; Cheng, C.; Li, Q.; Zhang, Z.; Wu, Y.; Chen, B.; Xiong, W.; *J. Power Sources* **2015**, *282*, 118.

19. Elumalai, P.; Vasan, H. N.; Munichandraiah, N.; *J. Power Sources* **2004**, *125*, 77.

20. Zheng, C.-H.; Wu, Z.-F.; Li, J.-C.; Liu, X.; Fang, D.-L.; *Ceram. Int.* **2014**, *40*, 8455.

21. Kim, K. J.; Lee, J. H.; Koh, T. Y.; Kim, M. H.; *Electrochim. Acta* **2016**, *200*, 84.

22. Amaral, F. A.; Santana, L. K.; Campos, I. O.; Fagundes, W. S.; Xavier, F. F. S.; Canobre, S. C.; *Mater. Res.* **2015**, *18(Suppl 2)*, 250.

23. Lee, Y.-S.; Kumada, N.; Yoshio, M.; *J. Power Sources* **2001**, *96*, 376.

24. Yang, Y.; Xie, C.; Ruffo, R.; Peng, H.; Kim, D. K.; Cui, Y.; *Nano Lett.* **2009**, *9*, 4109.

25. Asakura, D.; Nanba, Y.; Makinose, Y.; Matsuda, H.; Hosono, E.; *Phys. Chem. Chem. Phys.* **2017**, *19*, 16507.

26. Mateyshina, Y. G.; Lafont, U.; Uvarov, N. F.; Kelder, E. M.; *Solid State Ionics* **2008**, *179*, 192.

27. Chan, H. W.; Duh, J. G.; Sheen, S. R.; *J. Power Sources* **2003**, *115*, 110.

28. Prabu, M.; Reddy, M. V.; Selvasekarapandian, S.; Rao, G. V. S.; Chowdari, B. V. R.; *Electrochim. Acta* **2013**, *88*, 745.

29. Li, H.; Luo, Y.; Xie, J.; Zhang, Q.; Yan, L.; *J. Alloys Compd.* **2009**, *639*, 346.

30. Bakierska, M.; Świętosławski, M.; Gajewska, M.; Kowalczyk, A.; Piwowarska, Z.; Chmielarz, L.; Dziembaj, R.; Molenda, M.; *Materials* **2016**, *9*, 366.

31. Huang, Y.; Jiang, R.; Bao, S.-J.; Cao, Y.; Jia, D.; *Nanoscale Res. Lett.* **2009**, *4*, 353.

32. Vetter, K. J.; Jaeger, N.; *Electrochim. Acta* **1966**, *11*, 401.

33. Tung, M. T.; Thuy, H. T. B.; Hang, L. T. T.; *J. Nanosci. Nanotechnol.* **2015**, *15*, 6949.

34. Licci, F.; Turilli, G.; Ferro, P.; *J. Magn. Magn. Mater.* **1996**, *164*, L268.

35. Jeffery, G. H.; Bassett, J.; Mendhan, J.; Denney, R. C.; *Vogel's Textbook of Quantitative Chemical Analysis*, 5th ed.; Longman: Harlow, 1989.

36. Wickham, D. G.; Whipple, E. R.; *Talanta* **1963**, *10*, 314.

37. Okubo, M.; Mizuno, Y.; Yamada, H.; Kim, J.; Hosono, E.; Zhou, H.; Kudo, T.; Honma, T.; *ACS Nano* **2010**, *4*, 741.

38. Xie, W. Q.; Gong, Y. X.; Yu, K. X.; *J. Chromatogr. A* **2017**, *1511*, 138.

39. Silva, J. P.; Biaggio, S. R.; Bocchi, N.; Rocha-Filho, R. C.; *Solid State Ionics* **2014**, *268*, 42.

40. Laurindo, E. A.; Amaral, F. A.; dos Santos, M. L.; Ferracin, L. C.; Carubelli, A.; Bocchi, N.; Rocha-Filho, R. C.; *Quim. Nova* **1999**, *22*, 600.

41. Marczenco, Z.; *Spectrophotometric Determination of Elements*, John Wiley & Sons: Warsaw, 1976, p. 309.

42. Amankwah, R. K.; Pickles, C. A.; *J. Therm. Anal. Calorim.* **2009**, *98*, 849.

43. Jacob, K. T.; Kumar, A.; Rajitha, G.; Waseda, Y.; *High Temp. Mater. Processes* **2011**, *30*, 459.

44. Yao, J.; Shen, C.; Zhang, P.; Ma, C. A.; Gregory, D. H.; Wang, L.; *Electrochem. Commun.* **2013**, *31*, 92.

45. Shin, D. W.; Choi, J. W.; Choi, W. K.; Cho, Y. S.; Yoon, S. J.; *Electrochem. Commun.* **2009**, *11*, 695.

46. Lee, H. R.; Lee, B.; Chung, K. Y.; Cho, B. W.; Lee, K.-Y.; Oh, S. H.; *Electrochim. Acta* **2014**, *136*, 396.

47. Parsons, M. L. In *Analytical Instrumentation Handbook*; Ewing G. W., ed.; Marcel Dekker: New York, 1997, p. 276.