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# Lithium manganese oxides as high-temperature thermal energy storage system



### Francesca Varsano\*, Carlo Alvani, Aurelio La Barbera, Andrea Masi, Franco Padella

ENEA-Casaccia Research Center, 00123 Via Anguillarese 301, Rome, Italy

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#### ABSTRACT

The reversible oxidation of LiMnO<sub>2</sub> to LiMn<sub>2</sub>O<sub>4</sub> and Li<sub>2</sub>MnO<sub>3</sub> coexisting phases has been investigated in view of its possible application as high temperature energy storage system. By means of thermoanalytical techniques information regarding the heat exchanged during both oxidation and reduction reactions have been collected and the temperature range for cyclic reduction–oxidation has been explored. Initial tests regarding the cyclical operation highlight the optimal thermal stability of the mixture confirming the exploitability of the system for high temperature thermal energy storage applications. Preliminary information concerning the kinetic behavior of the powder during the reduction stage evidences a two-step mechanism. The reaction can be described through a first stage characterized by oxygen depletion from the spinel phase, followed by a major oxygen loss concomitant with the depleted LiMn<sub>2</sub>O<sub>4</sub> and Li<sub>2</sub>MnO<sub>3</sub> solid state transformation into LiMnO<sub>2</sub>.

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#### 1. Introduction

The development of thermal energy storage systems, which will store heat during the sunshine period and release it during the stages of scarce solar irradiation is essential for the growth of efficient and cost effective concentrated solar power plants [1,2] allowing the overcoming of the intermittence of the primary energy source. The utilization of reversible chemical reactions occurring at high temperature as thermal energy storage system is a recent application born under the boost of solar towers plants development, for which it is necessary a thermal storage system operating at temperatures such that conventional systems based on sensible or latent heat are inadequate. Several systems based on redox chemical reactions, that reversibly loose and gain oxygen, have been proposed as particularly suited for the high temperature range (700–1000 °C) operated in solar tower centrals [3–7]. The search for suitable redox couples is targeted to chemical compounds that can be reversibly reduced and oxidized under air atmosphere to contain costs associated to inert gas utilization or vacuum pumping and separate heat exchangers. Among the proposed couples one of the most promising is the redox cycle of manganese oxides  $(Mn_2O_3/Mn_3O_4)$ , being this material the less expensive and more abundant among proposed pairs. Laboratory tests [8] have proved

\* Corresponding author. E-mail address: francesca.varsano@enea.it (F. Varsano).

http://dx.doi.org/10.1016/j.tca.2016.07.018 0040-6031/© 2016 Elsevier B.V. All rights reserved. the reaction to be reversible during long-term cyclability although sintering processes led to a serious decrease of the oxidation rate. Addition of metal dopants [6] in various amounts in some cases improved the energy storage performance: the addition of iron [9], in particular, was found beneficial to enhance the oxidation kinetics and improve the cyclability.

In this work the possibility of utilizing lithium-manganese oxides as thermal energy storage materials is explored. Lithiummanganese oxides have been the object of numerous studies owing to their application as cathode materials for advanced lithium batteries. In particular the compounds LiMnO<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub> and more recently Li<sub>2</sub>MnO<sub>3</sub> have been considered promising candidates with respect to lithium intercalation de-intercalation reactions [10,11]. Solid-state synthesis of the materials has been accomplished starting from different reacting systems and according to several synthetic routes. At the same time thermal stability of some Li-Mn oxide phases has been examined in different working atmosphere in a wide temperature range [12–16]. From literature data it appears that  $LiMnO_2$  can be reversibly oxidized to a mixture of Li<sub>2</sub>MnO<sub>3</sub> and LiMn<sub>2</sub>O<sub>4</sub> coexisting phases with an increase of mean manganese oxidation state from 3 to 3.66. Such reaction operates in the useful temperature range (700–1000 °C). Aim of the work is to assess the exploitability of the LiMnO<sub>2</sub>/Li<sub>2</sub>MnO<sub>3</sub>/LiMn<sub>2</sub>O<sub>4</sub> based thermochemical cycle as thermal energy storage system. To this end, information regarding the heat exchanged during both oxidation and reduction reactions has been collected, the temperature range for cyclic reduction-oxidation has been determined and cyclical operation of the system has been tested. In addition, preliminary information about the kinetic behavior of the reduction reaction has been collected.

#### 2. Materials and methods

Each experiment consisted in the following sequence: in-situ synthesis of LiMnO<sub>2</sub> starting from Li<sub>2</sub>O<sub>2</sub> and MnO (Riedel-de Haën 99%) precursors (Fig. S1 in supporting information) immediately followed by cyclical thermal treatments. Small pellets (~1 mm<sup>3</sup>) have been utilized for the scope. In a typical run about 60 mg of precursor material is placed inside a compact alumina open crucible. The sample is heated to 1000 °C at 10 °C/min in Ar/O<sub>2</sub> (80/20 v/v) at a constant total gas flow of 60 ml/min; an isothermal step of 2h followed to allow complete LiMnO<sub>2</sub> synthesis. After the *in-situ* synthesis has been completed. 5 or more consecutive oxidation/reduction cycles have been performed in Ar/O<sub>2</sub> (80/20) atmosphere between 1000 °C and 500 °C without dwell. Heating and cooling rates varied between 1 °C/min and 20 °C/min. TG (Thermogravimetric Analysis) and DSC (Differential Scanning Calorimetry) experiments were performed in a STA 409C (Netzsch, Germany). Blank runs have been performed in order to correct the baseline. Repeatability of the measurement was checked for all the scans. For data analysis the Netzsch software Proteus 4.3 was utilized. Oxidation enthalpies were determined integrating the area under the heat flow signal obtained from the DSC analysis, utilizing sigmoidal tangent peak integration. Integration of reduction reaction heat flow signal is less straightforward because, as it will be explained in the paper, the main reduction peak follows a preceding oxygen release whose broad peak does not allow an accurate integration. In this case a tangential baseline type was found more appropriate.

Powder X-ray diffraction (XRD) analysis was carried out employing a simultaneous  $120^{\circ}$  angular dispersion X-ray Diffractometer (XRD 3000 Italstructure, curved Position Sensitive Detector from INEL) equipped with a Fe K $\alpha_1$  radiation. A heating reactive chamber (Anton Paar Gmbh XRK900) was mounted on the apparatus for the in situ high temperature measurements carried out in inert helium atmosphere (60 ml/min).

Peak profile analysis was performed on differential thermogravimetric (DTG) scans associated to reduction phenomena. Every thermogram was considered as composed by the sum of two asymmetric peak contributions. In order to simulate the single constituents different mathematical functions have been adopted. The first (lower temperature) peak, due to the linearity observed at a first sight and clearly noticed in all the DTG curves was simulated by considering the phenomenon as composed by the sum of a straight line (in the lower temperature range) and a Pearson VII semi-peak profile (in the higher temperature range). A split Gaussian function simulates the second peak i.e. the main contribution to the differential thermogravimetric trace. The function is composed by two Gaussian semi-equations having in common the center and the height. Fityk software (1.3.0 version) [17] was utilized to perform a non-linear minimization of the weighted square sum of residuals (WSSR) as defined in [17] to obtain the best values of the selected functions parameters. The minimization process is repeated up to a constant value of WSSR. More details can be found in supporting information.

#### 3. Results and discussion

#### 3.1. The thermochemical cycle

Thermal analyses of the cyclical oxidation/reduction of LiMnO<sub>2</sub> to LiMn<sub>2</sub>O<sub>4</sub> + Li<sub>2</sub>MnO<sub>3</sub> are reported in Fig. 1. In (a) the thermogravimetric behavior is shown, in (b) the associated calorimetric flow is reported. The reported measurement has been performed in Ar/O<sub>2</sub> (20% v/v) scanning the temperature at 1 °C/min. The redox cycle starts with the oxidation step (see segment 1 in Fig. 1a) right after LiMnO<sub>2</sub> synthesis (completed at 1000 °C) cooling the sample down to 500 °C. The high temperature phase LiMnO<sub>2</sub> gains oxygen during cooling and forms a mixture of LiMn<sub>2</sub>O<sub>4</sub> and Li<sub>2</sub>MnO<sub>3</sub> coexisting compounds according to the global Reaction (1):

$$3LiMnO_2 + 1/2O_2 = Li_2MnO_3 + LiMn_2O_4$$
(1)



**Fig. 1.** (a) Thermogravimetric curve of LiMnO<sub>2</sub> pellet cooled (1) and successively heated (2) at  $1 \circ C/\min$  in Ar/O<sub>2</sub> (80/20 v/v) atmosphere. Mass signal is normalized to LiMnO<sub>2</sub> weight. During temperature cooling LiMnO<sub>2</sub> is oxidized to LiMn<sub>2</sub>O<sub>4</sub> and Li<sub>2</sub>MnO<sub>3</sub>. Successively, reversing the temperature scan, the oxide mixture releases oxygen, reproducing LiMnO<sub>2</sub>. In (b) the corresponding DSC signal is reported.

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