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Fabrication and electrochemical characterization of amorphous lithium iron silicate thin films as positive electrodes for lithium batteries

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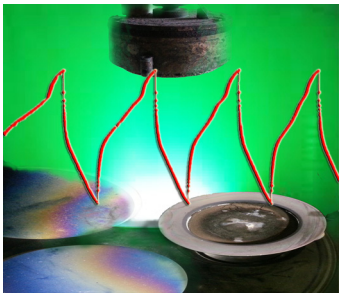
HIGHLIGHTS

- Thin film deposition of amorphous Li/M(Fe,Mn)/Si/O by r.f. sputtering.
- Good electrochemical performances: 50 mAh g^{-1} at 2.5 C.
- The films were able to sustain about 300 cycles of charge–discharge.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work we reported, for the first time, the preparation by radio frequency sputtering and the electrochemical characterization of Li/M/Si/O thin films (M = Fe, Mn), as positive electrodes for lithium microbatteries. The deposited films were amorphous both in case of pure iron and mixed iron/manganese compositions. The electrochemical performances, in terms of capacity values and coulombic efficiency, were comparable to those currently reported for the corresponding crystalline bulk materials. In particular, capacities of the order of 50 mAh g^{-1} were obtained at 2.5 C with coulombic efficiency near 90% by using a standard liquid electrolyte. Our preliminary electrochemical results, together with the easiness of preparation, suggested that Li/M/Si/O thin films could be interesting candidates as cathodes in lithium microbatteries.

1. Introduction

The development of thin-film lithium batteries as power sources for new generation micro-devices was rapidly growing over these last years. Such microsystems show several advantages, e.g. lightness, low cost and easy integration in micro-devices owing to their miniaturization [1,2]. A wide area of applications may be foreseen, ranging from microelectronics to sensors in medical and

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military fields, smart cards and other micro-devices (MEMS, NEMS), and also Radio Frequency Identification (RFID) tags, and this represents a very topical target. Large-scale applications in the next future are chiefly expected for food and drug control. During the last years, many efforts on the optimization of lithium microbatteries were discussed in the literature, regarding both flat [Ref. [3] and references therein] and 3D configurations [4].

Many materials were suggested in the past as microbattery components, such as V_2O_5 [5], $LiCoO_2$ [6,7] or $LiMn_2O_4$ [8,9] as high voltage cathodes, lithium oxide or sulphide compounds (crystals and glasses) as solid electrolytes [10], and Li metal or vanadates [11] as the anodes. The use of thin film electrodes to shorten diffusion paths of Li ions seems to be an effective solution to enhance the rate capability of a battery, but the energy density still remains a challenge. A recently proposed solution encompassing both high energy and high power densities is the development of three-dimensional (3D) nanostructured architectures and design with large surface area [12–14]. However, there are still two major obstacles for wider applications of the 3D electrodes. The first one is the complex and high-cost fabrication process, that limits the large-scale production. The other is that the energy density of the whole device is still low, due to the extremely thin active material layer as compared with the much thicker substrate.

Moreover, increasingly important safety and toxicity issues should be considered, which are chiefly relevant in case of $LiCoO_2$ and $LiMn_2O_4$, the most used compounds for thin film cathode preparation. Therefore, more environmentally friendly compounds are required for these applications. In this frame, $LiFePO_4$ belonging to the family of polyanion compounds is important because, among other fundamental properties such as the good cycling stability, it is highly safe and non-toxic. Thin films of $LiFePO_4$ have been prepared by different deposition techniques such as r.f. sputtering [15], electrophoretic deposition [16] and pulsed laser deposition [17], and the effects of deposition temperature and kind of substrate on the crystal structure and morphology of the resulting thin films have been already addressed.

Recently, low toxic, low cost and highly available cathode materials belonging to the orthosilicate family with formula Li_2MSiO_4 (M = Fe, Mn) were proposed as bulk materials [18–20]. Several works were devoted to their structural and computational characterization [21–24], as well as to the optimization of their electrochemical performances [25]. The importance of these compounds chiefly resides in their high theoretical capacity (up to 330 mAh g^{-1} for two lithium ions insertion/extraction) that justifies the efforts devoted to the preparation of new architectures such as nano- and mesoporous forms [26–28]. In case of standard Li-ion cells, orthosilicates (e.g. Li_2MnSiO_4) are generally prepared and used in crystalline form, but they can undergo amorphization on repeated cycling [29]. This crystalline-to-amorphous transition, in turn, leads to a progressive worsening of the electrochemical performances. So far, the preparation of orthosilicate thin films was never reported, likely due to the difficulty to deposit with the right stoichiometry a ternary oxide, differently from binary compounds such as vanadium [30], titanium [31] and iron oxides [32].

In this work, for the first time to our knowledge, we reported the radiofrequency (r.f.) magnetron sputtering preparation and the physico-chemical characterization of Li/M/Si/O (M = Fe, Mn) amorphous films with nominal composition $Li_2Fe_{1-x}Mn_xSiO_4$ (x = 0, 0.5). The structural and microstructural properties of the thin films were investigated by means of XRD, SEM and XPS techniques. The electrochemical properties were addressed by performing cyclic voltammetry and preliminary battery tests on a lithium cell with a standard liquid electrolyte.

2. Experimental

2.1. Synthesis

Thin films with nominal composition $Li_2Fe_{1-x}Mn_xSiO_4$ ($x = 0, 0.5$) were deposited in a high vacuum (10^{-3} Pa) r.f. magnetron sputtering system, which consists of three confocal cathodes at 40–50 mm from the substrate center. As the deposition substrates, we used stainless steel (s.s.) disks with a diameter of 10 mm (Good Fellow, SS-AISI304 Fe/Cr18/Ni10 annealed), previously coated by a 150 nm-thick layer of gold as current collector. $Li_2Mn_{0.5}Fe_{0.5}SiO_4$ and Li_2FeSiO_4 powders, prepared by sol–gel synthesis [20,21], were used as the target. The depositions were performed by a procedure made of two consecutive steps without sample extraction: 1) at 60 W for 1 h; 2) at 100 W for 2 h. The pressure was kept at $3 \cdot 10^{-2}$ mbar, with a substrate temperature of 700 °C and 20 sccm of Ar flow. At the end of the deposition, the samples were kept at the same temperature (700 °C) for additional 1 h inside the r.f. sputtering chamber, and then cooled down to ambient temperature under vacuum. The thickness of both the films was about 390 nm, as determined by profilometry. The samples were named FeMn or Fe for the mixed or iron silicate, respectively.

2.2. Characterization techniques

X-ray diffraction (XRD) measurements were performed using a Bruker D5005 diffractometer with the CuKα radiation, a graphite monochromator and a scintillation detector. The patterns were collected with a step size of 0.02° and counting time of 6 s per step in the angular range 15–65°/2θ.

Scanning Electron Microscopy (SEM) measurements were performed with a Zeiss EVO®-MA10-HR microscope.

The film thickness was measured by means of a stylus profilometer (KLA Tencor P6 Profiler), by applying a force of 20 μN. The active mass of the silicate thin films (about 30 μg i.e. 60 μg/cm^2) was measured by using an ultra sensitive microbalance (HIDEN ISOCHEMA IGA-001).

X-ray Photoelectron Spectroscopy (XPS) spectra were acquired on a sample deposited in the same way as FeMn on Ni substrate, in order to avoid the signal of Fe coming from stainless steel. XPS spectra were acquired *ex situ* by inserting the sample in a modified VG ESCALAB MkII system, with a base pressure of 10^{-10} mbar, equipped with a non-monochromatic Al Kα X-ray source. The photoelectrons were collected with an hemispherical energy analyzer working at pass energy 10 eV with an energy resolution of 0.9 eV. Sample surface was not treated in any way before the measurements. Si2p has been taken as energy reference in its silicate form (102 eV) [33], after this the binding energy of all the other peaks has been checked and was considered consistent.

The electrochemical tests were performed using a three-electrodes T-cell with lithium metal as the negative and the counter electrodes and a glass-wool (Whatman GF/A) disc as the separator. The electrolyte was 1 M $LiPF_6$ in ethylene carbonate/diethyl carbonate (EC/DEC) 1:1 (Merck). All the cells were assembled in a dry-box under Argon atmosphere. Cyclic voltammetry (CV) was performed by using an Autolab PGSTAT30 (Eco Chemie) at a scan rate of 0.2 mV s^{-1} in the potential range 2.5–4.0 V. The galvanostatic cycling tests were carried out at ambient temperature in the range 2.5–4.5 V using an Arbin battery cycler (model BT-2000).

3. Results and discussion

3.1. Film microstructure and composition

The target materials were thoroughly characterized before to proceed to thin films deposition. The crystalline nature of the