LiNiVO$_4$–promising thin films for use as anode material in microbatteries

M.V. Reddy, C. Wannek, B. Pecquenard[*], P. Vinatier, A. Levasseur

Ecole Nationale Supérieure de Chimie et de Physique de Bordeaux, Institut de Chimie de la Matière Condensée de Bordeaux, CNRS UPR 9048 16, Avenue Pey Berland, Pessac Cedex 33607, France

Abstract

Thin films of lithium nickel vanadates ($Li_xNiV_yO_z$) have been prepared by radio frequency magnetron sputtering from a LiNiVO$_4$ target. The discharge gas was either pure argon or a mixture of argon and oxygen. The deposition rates as well as the composition and morphology of the films strongly depend on the sputtering parameters. For a total pressure of 1 Pa, the V/Ni atomic ratio varies between 0.75 for films developed in a pure argon plasma and 1.65 when the partial pressure of oxygen is 100 mPa. The thin film containing the two types of transition metals in an equiatomic ratio ($Li_{1.1}NiVO_4$) has given the best electrochemical properties as an anode displaying a specific capacity that became stable at 1000 mAh/g after three cycles, which is at least as high as for bulk material.
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1. Introduction

Thin film solid state lithium and lithium-ion batteries are very attractive for many applications such as on-chip power sources for integrated circuit devices [1]. In order to suit the production facilities of the microelectronics industry, such microbatteries have to be prepared using physical vapour technology. After 15 years of intensive research efforts these systems are about to be launched on the market [2].

Recently, vanadates with various compositions and structures have been studied in bulk form [3–5]. Among them, we are especially interested in LiNiVO$_4$. This compound has the particularity to be usable either as a cathode [6,7] or as an anode [8,9]. Well crystallized, it is a high potential positive electrode material. When amorphous (or after amorphization upon charge/discharge), this material shows very promising electrochemical behaviour as an anode. It has a very high capacity between 3 and 0.02 V ($\sim$1100 mAh/g at the second cycle) [9], which is more than twice as high as that of the frequently used graphite electrodes. Although LiNiVO$_4$ reacts reversibly with about seven lithium ions per formula unit during the first cycles (two to three additional Li are trapped during the first reduction), its interest as bulk material is limited by a significant capacity fading [9].

Indeed, a good negative electrode material is defined by a high reversible capacity, a low capacity loss during the first cycles and a good cyclability. A first report about the synthesis of lithium nickel vanadates by radio frequency magnetron sputtering in a 1/1 gas mixture of Ar and O$_2$, including studies about the influence of the target composition on the electrochemical properties of the deposits, has been published only recently [10].

The present work is devoted to the preparation of lithium nickel vanadate thin films by sputtering from ceramic LiNiVO$_4$ in a mixed (Ar + O$_2$) atmosphere with a partial pressure of oxygen not exceeding 10% as well as their structural characterization and a preliminary lithium insertion study. In order to better understand the relation between the sputtering conditions and the composition, the structure and the electrochemical behaviour of the materials, we have studied the influence of some experimental parameters such as the total pressure and the partial pressure of oxygen in the plasma, the sputtering power and the distance between the target and the substrate.

2. Experimental

Thin films of lithium nickel vanadates have been prepared by radio frequency magnetron sputtering using a LiNiVO$_4$ target. This was prepared by solid state reaction from a stoichiometric mixture of Li$_2$CO$_3$, NiO and V$_2$O$_5$ at 730 °C

* Corresponding author. Tel.: +33-5-56-84-33-03;
fax: +33-5-56-84-66-98.
E-mail address: pecquen@icmcb.u-bordeaux.fr (B. Pecquenard).

for 12 h in air [11]. NiO was prepared by thermal decomposition of $Ni(NO_3)_2 \cdot 6\,H_2O$. All the starting chemicals were purchased from Aldrich. The obtained product was single phase $LiNiVO_4$, adopting the inverse spinel structure [12] with the cubic cell parameter, $a = 8.2197(2)$ Å. The targets ($\varnothing = 5$ cm) were prepared from $LiNiVO_4$ powder, cold pressed at 260 MPa followed by sintering at 600 °C for 8 h in air.

Before beginning the sputtering deposition, a vacuum of 4×10^{-5} Pa was obtained in the chamber. The discharge gas was either pure argon (99.995%) or a mixture of argon and oxygen (99.5%) with the partial pressure of oxygen not exceeding 10%. The total pressure was chosen between 1 and 4 Pa. By presputtering for 2 h under the same atmosphere used for the thin film deposition, the target was cleaned prior to use. To avoid contamination of the thin films prepared, we have used a sputtering unit connected to a glove box with an argon atmosphere and all characterization experiments were carried out in airtight conditions.

The films were deposited onto various substrates: disks of stainless steel ($\varnothing = 1.3$ cm), blocks of vitreous carbon and aluminium foil. The first two materials were polished with silicon carbide paper (granulometry up to 4000), all of them were cleaned with water and acetone in an ultrasonic bath before being used. Neither the target nor the substrate was heated during the sputtering process.

Auger spectroscopy (VG microlab 310-F) was used to examine the homogeneity of the samples and to estimate their relative contents of nickel, vanadium and oxygen. A combination of Rutherford backscattering spectroscopy (RBS) and $^7Li(p, \alpha)^4He$ nuclear reaction analysis (NRA) [13] has been used to determine quantitatively the respective amounts of all cationic species within thin samples deposited on vitreous carbon (Table 1; thickness of the films: 200–400 Å). The V and Ni contents were established by RBS performed at a backscattering angle of 165° using an incident beam of $^4He^+$ ions with an energy of 2 MeV. The spectra have been analyzed with the RUMP software [14]. The Li content was determined by NRA experiments using a

1 MeV proton beam and a LiF calibration standard. The experimental error commonly attributed to RBS and NRA results amounts to ±10%; the divergence between the results obtained for samples produced under the same nominal conditions was smaller than 5%.

The morphological studies were performed by scanning electron microscopy (JEOL, JSM-5200). Powder X-ray diffraction (Philips PW1050, Cu Kα radiation), was applied to check for crystallinity within the films. The electrochemical measurements were carried out using lithium nickel vanadate thin films (0.3 μm thick) as the positive electrode and metallic lithium as the negative one, separated by paper soaked in the electrolyte (1 M $LiPF_6$ in a EC–DMC 1:1 mixture). The batteries were galvanostatically cycled at room temperature between 3 and 0.02 V using the VMP system (Bio-Logic) with a current density of 10 μA/cm².

3. Results and discussion

3.1. Characterization of the thin films

3.1.1. Deposition rate

We have studied the influence of four different sputtering parameters on the deposition rate (Fig. 1). The deposition rate increased linearly with the applied radio frequency power between 30 and 50 W due to higher plasma density and momentum transfer to the target (Fig. 1a). The amount of particles deposited on the substrate, per unit area and time, increased drastically when the sputtering distance was reduced. When the target–substrate distance was changed from 10 to 8 cm, the deposition rate almost doubled (Fig. 1b). This phenomenon is due to the reduced probability of the sputtered particles to be scattered before arriving on the substrate, as well as to geometrical reasons. In fact, as the sputtering is effected approximately conically from the target surface, at lower distances a bigger part of the sputtered particle cone is intercepted by a given substrate. A considerable decrease of the deposition rate was observed when the sputtering gas total pressure was raised. Fig. 1c shows the relationship observed for the case of a pure argon plasma. Within the pressure range investigated, this correlation is approximately linear and can be mainly attributed to a smaller mean free path length of a sputtered particle. The sputtered atoms are more likely to be scattered and not reach the substrate. The presence of even very small amounts of oxygen in the plasma had a drastic effect on the deposition rate (Fig. 1d). It can be seen that the deposition rate decreases rapidly with the initial addition of oxygen to the discharge gas. Such a sudden decrease in the growth rate has been previously observed during the sputtering of $LiCoO_2$ under Ar/O_2 plasma [15]. This phenomenon could be related to the fact that considerable changes in the colour and composition of the surface of the target are observed when the partial pressure of oxygen in the plasma is varied. More systematic studies to understand this feature are under way.

Table 1
Chemical compositions of $Li_xNiV_yO_z$ thin films as a function of the partial pressure of oxygen in the plasma (for a total pressure of 1 Pa)

Partial pressure of oxygen (mPa)	Thin film composition[a]		
	Auger	RBS (ratio V/Ni)	NRA (Li) + RBS (Ni, V)[b]
0	$Li_xNiV_{0.8}O_{3.5}$	0.75	$Li_{1.01}NiV_{0.75}O_{3.38}$
1	–	0.75	–
4	–	0.85	–
10	$Li_xNiV_{1.0}O_{4.0}$	1.02	$Li_{1.12}NiV_{1.02}O_{4.11}$[c]
20	–	1.21	–
100	$Li_xNiV_{1.6}O_{5.8}$	1.65	–

[a] Uncertainties are ±10% for the RBS and NRA analyses (see text).
[b] The oxygen content of the films have been calculated by supposing formal oxidation states of (+I), (+II) and (+V) for Li, Ni and V, respectively.
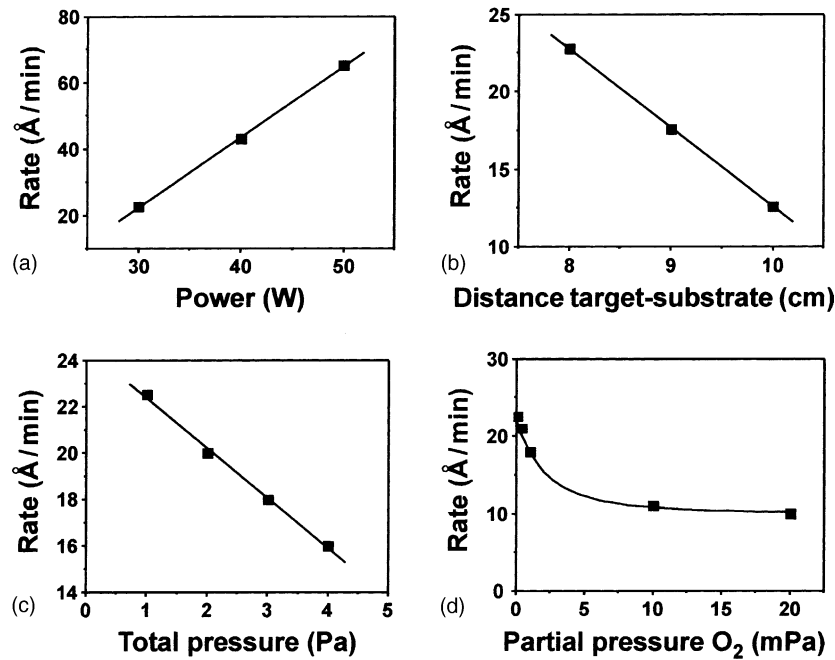[c] Referred to as $Li_{1.1}NiVO_4$ throughout the text.

Fig. 1. Deposition rates of lithium nickel vanadate thin films according to the sputtering power (a); the distance between target and substrate (b); the total pressure (c); and the partial pressure of oxygen during the process (d). Unless varied within one series of experiments, the parameters were fixed at the following values: $P = 30$ W, $d = 8$ cm, $p_{total} = 1$ Pa and $p(O_2) = 0$ mPa.

3.1.2. Structure and morphology of the deposit

No indication of crystallinity within the deposits prepared in a reactive plasma could be detected by X-ray diffractometry in θ–2θ geometry (film thickness up to 2 μm). The films produced in an absence of oxygen are partially crystallized: a single broad peak at $2\theta = 42.9\,^{\circ}$ is observed which we attribute to the (2 0 0) reflection of cubic NiO [16]. These observations are completely independent of the nature of the substrate used. The morphology of the lithium nickel vanadate thin films strongly depends on the total pressure and the partial pressure of oxygen within the plasma during the sputtering process. The deposits prepared at low total pressure and in a pure argon plasma are highly dense and not structured with a smooth surface. These conditions correspond to the highest deposition rate (Fig. 2a). Films deposited either under a high total pressure or in the presence of oxygen in the plasma show a columnar structure with a rough surface (Fig. 2b and c, respectively). At low deposition rate (high total pressure and in Ar + O$_2$ plasma; Fig. 2d) the thin film also has a columnar structure, which in addition is highly porous.

3.1.3. Chemical composition of the thin films

Auger spectroscopy has revealed that all deposited thin films were homogeneous in depth, no reaction with the substrate having been observed. Among all experimental parameters investigated, the partial pressure of oxygen in the plasma has the most considerable influence on the thin film composition. The compositions of deposits made at a total pressure of 1 Pa ($P = 30$ W, $d = 8$ cm) are listed in Table 1.

As the partial pressure of oxygen rises, the V/Ni ratio and the oxygen content increase. The values obtained by RBS and Auger correlate. The lithium content of the films is slightly higher than in the target material; a similar observation has been made for the material deposited in an oxygen-rich atmosphere [10]. Table 1 also shows that an equiatomic V/Ni ratio is achieved in $Li_{1.1}NiVO_4$ using a partial pressure of 10 mPa (1%). X-ray diffraction studies (not shown) performed on this material after annealing at 600 °C, clearly show the diffraction pattern of inverse spinel $LiNiVO_4$.
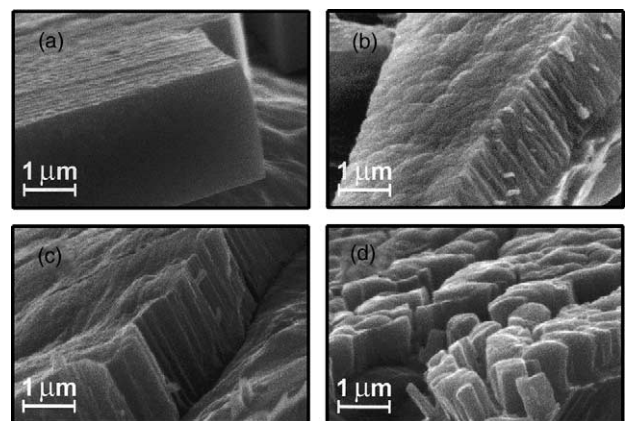

Fig. 2. SEM cross-sections of lithium nickel vanadate thin films deposited at two different total pressures (1 Pa, left; 4 Pa, right) and in absence (top) or presence (bottom) of oxygen within the plasma: (a) $p_{total} = 1$ Pa, $p(O_2) = 0$ mPa; (b) $p_{total} = 4$ Pa, $p(O_2) = 0$ mPa; (c) $p_{total} = 1$ Pa, $p(O_2) = 10$ mPa; (d) $p_{total} = 4$ Pa, $p(O_2) = 10$ mPa.
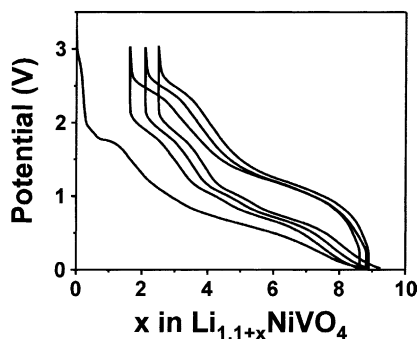
Fig. 3. Voltage vs. composition curve of an amorphous $Li_{1.1}NiVO_4$ thin film/Li cell. A current density of 10 µA/cm^2 was applied over the 3–0.02 V voltage range.

3.2. Electrochemical properties

Lithium intercalation and de-intercalation in amorphous as-deposited thin films have been studied in cells with lithium as the negative electrode and liquid electrolyte (1 M $LiPF_6$ in a EC–DMC 1:1 mixture). All of these thin films have been prepared with a total pressure of 1 Pa, a target–substrate distance equal to 8 cm and 30 W sputtering power. The first three cycling curves for $Li_{1.1}NiVO_4$ are represented in Fig. 3 and the capacity retention for 15 cycles is shown in Fig. 4. The lithium nickel vanadates reveal the typical behaviour of an amorphous material. During the first reduction, the $Li_{1.1}NiVO_4$ thin film is able to insert almost nine lithium per formula unit. However, the first cycle is not completely reversible and only 7.2 Li can be removed. This correlates with the results obtained with bulk $LiNiVO_4$ that can reversibly react either with seven lithium, if crystallized, or 7.5 Li when amorphous [9]. Whatever the composition, the capacity loss becomes negligible after the third cycle, as shown in Fig. 4, and then the capacity stabilizes at quite a high value as also seen in [3,17]. The electrochemical results strongly depend on the composition. The best results are obtained for thin film $Li_{1.1}NiVO_4$ containing equal amounts of vanadium and nickel. This particular composition displays a high capacity of 1000 mAh/g at the fifth cycle,
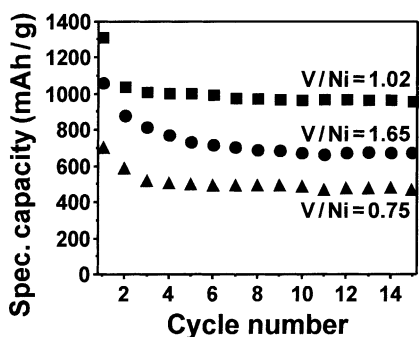
which is 2.5 times the capacity of a graphite electrode and somewhat higher than that obtained for the corresponding crystallized bulk material (920 mAh/g) [9]. It must be emphasized that we do not observe the large capacity fading highlighted for bulk materials and attributed to an increase of the polarization upon cycling. Assuming thin film $Li_{1.1}NiVO_4$ to have nearly bulk density, the results correspond to a specific capacity of $\sim$400 mAh/cm^2 µm, slightly inferior to the value obtained for $Li_{1.3}Ni_{0.8}VO_{3.0}$, sputtered from a $LiNiVO_4$ target in an 1/1 gas mixture of Ar and O_2 [10].

4. Summary

Homogeneous amorphous thin films of $Li_xNiV_yO_z$ are reproducibly prepared by radio frequency magnetron sputtering. Their composition and morphology are controlled by the choice of appropriate experimental conditions. The V/Ni atomic ratio in the deposits changes dramatically with the partial pressure of oxygen in the plasma. The electrochemical properties of these lithium nickel vanadates strongly depend on their composition: $Li_{1.1}NiVO_4$ exhibits the best performance. The capacity of thin film $Li_{1.1}NiVO_4$ compares well with that of $LiNiVO_4$, however the stability during cycling is even better.

Fig. 4. Discharge capacities of different $Li_xNiV_yO_z$ thin films (cycled between 3 and 0.02 V) vs. the cycle number.

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