Synthetic Pathways to New Hydrated Sodium and Lithium Vanadium Bronzes

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Synthesis of new hydrated sodium vanadium and lithium vanadium bronzes has been investigated by reaction of $VOSO_4 \cdot 5H_2O$, $VO(C_5H_7O_2)_2$, or V_2O_3 with compounds containing C−O bonds (such as acetates) and NaOH or LiOH solutions under refluxing conditions in aqueous media. These layered compounds are characterized by X-ray powder diffraction, IR, and TGA. Thermal treatment for temperatures higher than 310 and 450°C for sodium vanadium bronzes and lithium vanadium bronzes, respectively, leads to well-known anhydrous bronzes $Na_{0.33}V_2O_5$ and $Li_{0.22}V_2O_5$. © 2000 Academic Press

INTRODUCTION

In a previous paper (1) we presented a new layered hydrated sodium vanadium bronze $Na_{0.33}V_2O_5 \cdot 1.3H_2O$ obtained with an original synthesis method. In this compound, the electrochemical Li insertion was investigated by cyclic voltammetry and chronopotentiometry and showed that its behavior differs from that known for the sol–gel sodium-exchanged V_2O_5 xerogel and for the anhydrous monclinic bronze. The hydrated phases studied before concerned vanadium pentaoxide gels and xerogels $V_2O_5 \cdot nH_2O$, which adopt layered structure and sodium-layered vanadium oxide. Two main synthesis routes were known: sol–gel synthesis (2–7) and the synthesis by the hydrothermal treatment of equimolar aqueous solutions of vanadyl sulfate and alkali ions (8–11). In the third method that we have developed recently, an hydrated sodium vanadium bronze was obtained after heating (90°C) a solution of phosphonic acid (carboxymethyl phosphonic or carboxyethyl phosphonic acids), neutralizing it to pH 7 with a sodium hydroxide solution and adding $VOSO_4 \cdot 3H_2O$, obtaining a molar ratio of the reacting species equal to unity.

Some attempts undertaken to obtain the sodium vanadium bronze with phosphonic acids without the carboxylic function had failed. Thus, we concluded that the active part in phosphonic acid was not the phosphonic component but the carboxylic acid function.

Consequently, we have studied the possibility of obtaining hydrated sodium vanadium bronze by substituting phosphonic acid with some compounds which are less expensive and contain a carboxylic acid function.

This paper presents several synthetic methods to obtain some hydrated sodium and lithium vanadium bronzes. The compounds are characterized by powder X-ray diffraction (XRD), Fourier-transformed infrared spectroscopy (FTIR), differential thermal analysis, thermogravimetric analysis, and chemical analysis.

EXPERIMENTAL

All reagents were from commercial sources and used without further purification.

Synthesis

Hydrated Sodium Vanadium Bronzes

Two synthetic methods were developed.

First synthesis method. To 100 ml of solution of 0.001 M sodium acetate was added 0.01 mole of vanadyl sulfate $VOSO_4 \cdot 3H_2O$. A small amount of NaOH (1 M) was then added to adjust the pH value to 7. Distilled water was added to adjust the total volume to 150 ml and the resulting solution was refluxed for three days. A dark green precipitate, almost black, was formed. It was filtered *under vacuum*, washed with water and acetone, and finally dried in air at room temperature. Hereafter, we used the notation BronzeNa-I for the compound obtained using this process.

Second synthesis method. Five hundred milligrams of vanadyl acetylacetonate $(VO(C_5H_7O_2)_2)$ were dissolved in 20 ml distilled water, the pH of the obtained solution was approximately 7. This value was adjusted to 10 by adding

small amounts of a 1-M NaOH solution. The solution was then filled up to 150 ml with distilled water and refluxed for 3 days. The final product was recovered following the same protocol as described above. For the compound obtained using this procedure, we use hereafter the notation BronzeNa-II.

Hydrated Lithium Vanadium Bronzes

First synthesis method. We tried to obtain an hydrated lithium vanadium bronze using the same method as described in a previous paper (1) with carboxymethylphosophonic and carboxyethylphosphonic acid after substituting NaOH by LiOH. The obtained product is hereafter noted Bronze Li-I.

Second synthesis method. An equimolar mixture of Li_2CO_3 and V_2O_3 was dissolved in 100 ml distilled water and the pH value of the obtained solution was adjusted to 10 with a 1-M LiOH solution. The resulting solution was completed to 150 ml with distilled water and refluxed under stirring for 15 days. The obtained product was recovered in the same manner as that described for the sodium vanadium bronze and is hereafter noted BronzeLi-II.

BronzeLi-II compound was also obtained using the process described to synthesize BronzeNa-II but LiOH was used in place of NaOH.

Characterization

As shown in Fig. 1, the XRD patterns of the two sodium vanadium bronzes are quite similar to the diffractogram of the compound obtained with phosphonic acid: $Na_{0.33}V_2O_5 \cdot 1.3H_2O$. These compounds exhibit a high preference for the 001 orientation corresponding to the stacking of layers along a common direction (the *c* direction) perpendicular to the support. The corresponding interlamellar distance calculated with the four peaks (001), (003), (004), and (005), is 10.90 Å. We can note that a distance of 10.80 Å was obtained for the compounds $Na_{0.27}V_2O_5 \cdot 1.17H_2O$ and $Na_{0.37}V_2O_5 \cdot 1.03H_2O$ synthesized with the hydrothermal method (12).

The XRD patterns for the lithium vanadium bronzes are presented in Fig. 2. They show the same orientation phenomenon as that obtained for the sodium vanadium bronzes. The calculated interlamellar distances are 9.50 and 10.94 Å for the BronzeLi-I and BronzeLi-II, respectively.

Figures 3 and 4 show the IR spectra of the sodium–vanadium bronzes and the lithium vanadium bronzes, respectively. Water molecule presence is clearly demonstrated by broad band around 3500 cm^{-1} characteristic for the valence vibration νOH and by the deformation band δ(H–O–H) at 1616 cm^{-1}. The frequency domain between 1000 and 400 cm^{-1} displays a series of identical bands
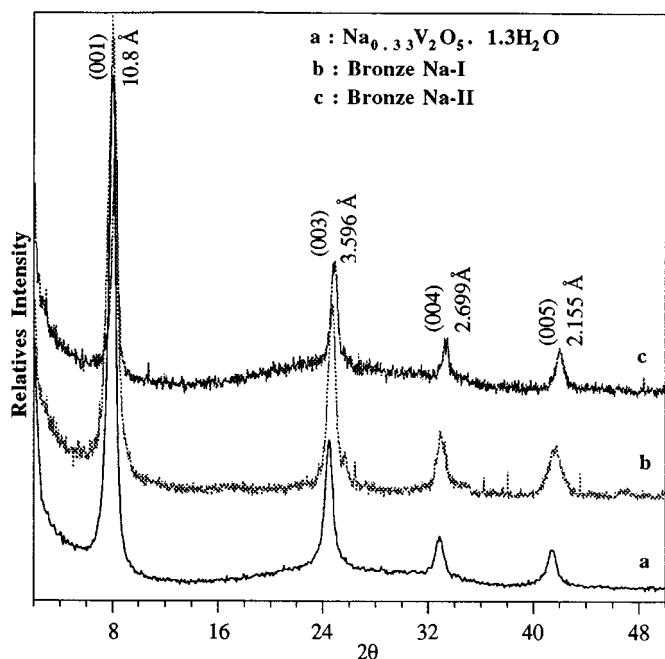

FIG. 1. XRD patterns of (a) $Na_{0.33}V_2O_5 \cdot 1.3H_2O$, (b) BronzeNa-I, (c) BronzeNa-II.

containing the lattice vibrations ν(V=O) and δ(V–O–V) (Table 1).

Thermic Behavior

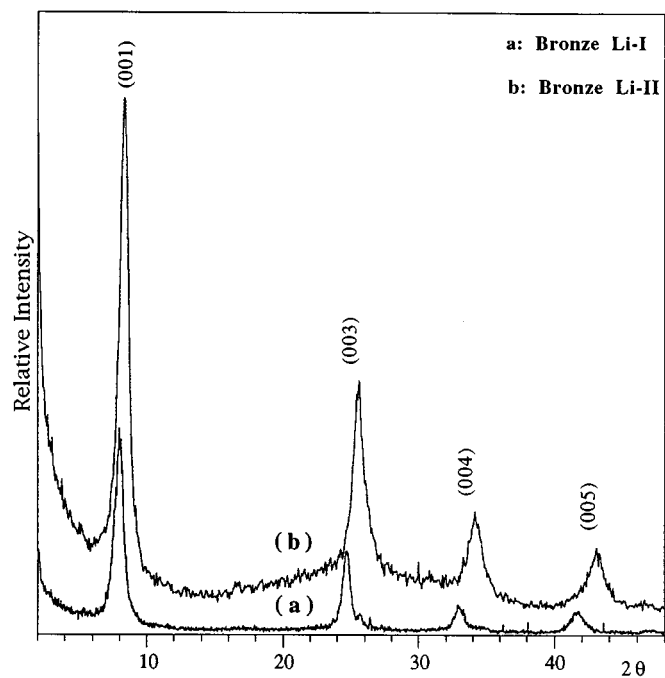TGA and DTA curves (of the compounds) are reported in Fig. 5 for the sodium–vanadium bronzes and Figs. 6 and 7

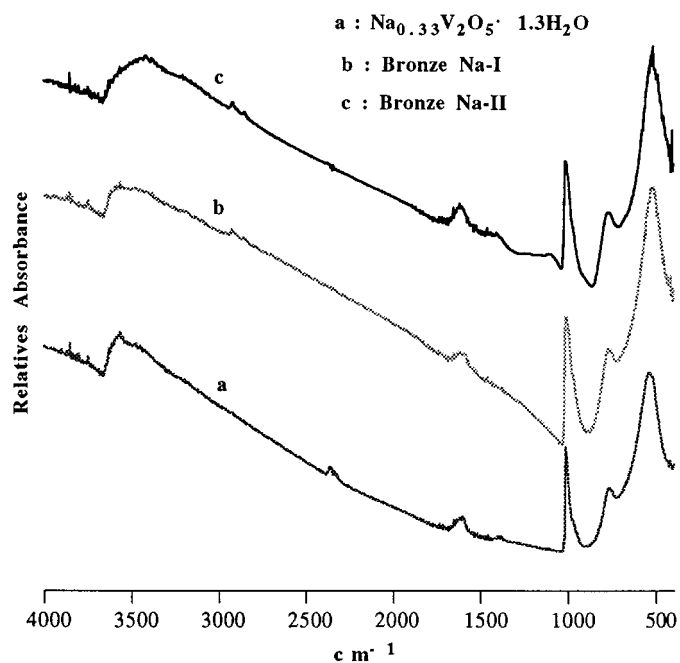**FIG. 2.** XRD patterns of (a) BronzeLi-I and (b) BronzeLi-II.

FIG. 3. FTIR spectra of (a) $Na_{0.33}V_2O_5 \cdot 1.3H_2O$, (b) BronzeNa-I, (c) BronzeNa-II.
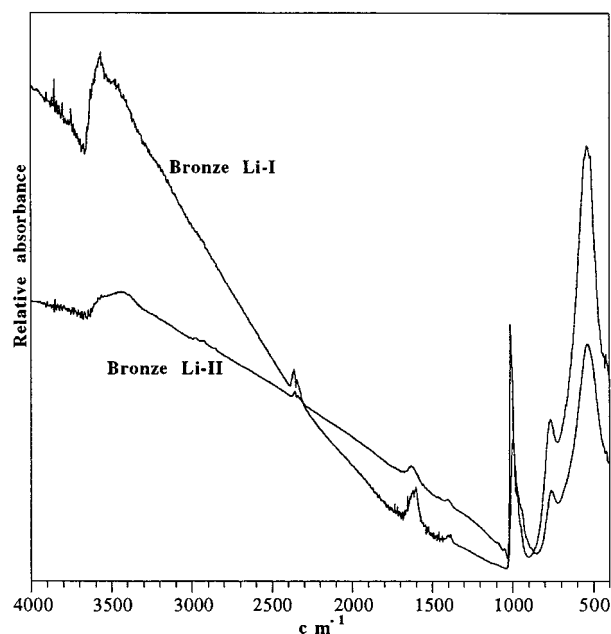

FIG. 4. FTIR spectra of (a) BronzeLi-I and (b) BronzeLi-II.

for the lithium–vanadium bronzes. The thermograms were performed between room temperature and 500°C at a heating rate of 5°C/min under air atmosphere. We noted different thermic behaviors for sodium vanadium bronzes compared to lithium vanadium bronzes.

For sodium vanadium bronzes, a significant and continuous weight loss occurs from around 25 to 166°C, which corresponds to the departure of water molecules weakly bound to the lamellar structure (1.22 H_2O/V_2O_5 for BronzeNa-I and 1.4 H_2O/V_2O_5 for BronzeNa-II). This water loss corresponds to an endothermic effect on the DTA curve. A small amount of residual water is lost between 166 and 330°C (0.08 H_2O/V_2O_5 for BronzeNa-I and 0.1 H_2O/V_2O_5 for BronzeNa-II). The complete transformation to the anhydrous bronze NaV_6O_{15} appears on the DTA curve as an exothermic peak at 334°C. This phenomenon was already reported by the BAFFIER *et al.* for the compound obtained by the sol–gel process (2).

Evolution of the X-Ray Diffraction Diagram versus Temperature

Samples of BronzeNa-I were heated under air atmosphere for 12 h. Afterward, they were quenched to room temperature and studied by X-ray diffraction. The diffractograms obtained are reported in Fig. 8. No modifications were observed on the X-ray patterns for heating temperatures below 300°C. At this temperature two phases exist: a residual part of lamellar bronze and the anhydrous sodium vanadium bronze NaV_6O_{15}. The transformation occurs between 280 and 305°C. The diffractograms obtained for 310°C and higher temperatures are similar to those given by the ASTM data no. 24-1155. It was surprising to notice from the TGA results that most of the water was released at 166°C, whereas the diffractograms exhibited no change up to 280°C, indicating that the water molecules have no effect on the interlamellar distance.

TABLE 1

	$Na_{0.33}V_2O_5 \cdot 1.3H_2O$ (cm^{-1})	BronzeNa-I (cm^{-1})	BronzeNa-II (cm^{-1})	BronzeLi-I (cm^{-1})	BronzeLi-II (cm^{-1})
ν(O–H)	3450–3571	3450–3571	3450–3571	3440–3600	3350–3570
δ(H–O–H)	1616	1616	1616	1623	1623
νV=O	1003	1003	1003	1007	1007
δ(O–V–O)	769	760	760	773	773
ν(V–O–V)	536	526	526	530	530
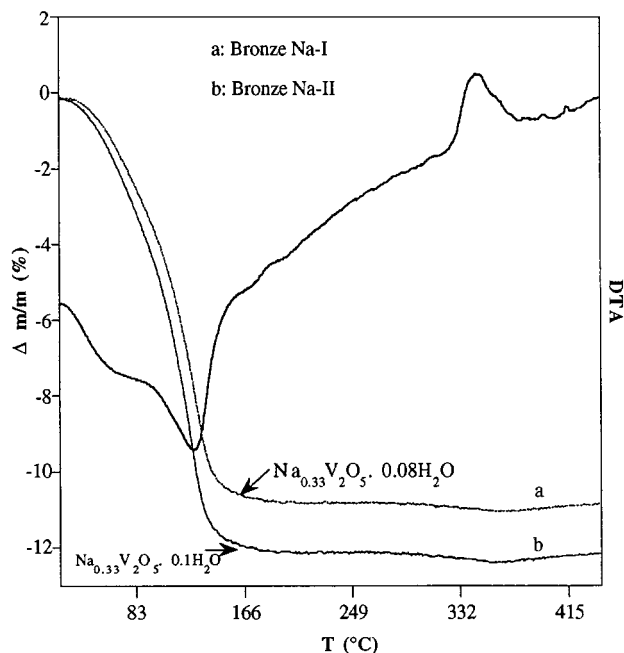
FIG. 5. TGA and DTA curves of BronzeNa-I and BronzeNa-II.

FIG. 7. TGA and DTA curves of BronzeLi-II.

This behavior, similar to that of $Na_{0.33}V_2O_5 \cdot 1.3H_2O$, contrasts with the thermic behavior reported for the sodium-exchanged xerogel, as well as xerogels prepared via the sol–gel method (2).

Chemical and thermogravimetric analysis permitted us to propose a chemical formula for these compounds (Table 2):
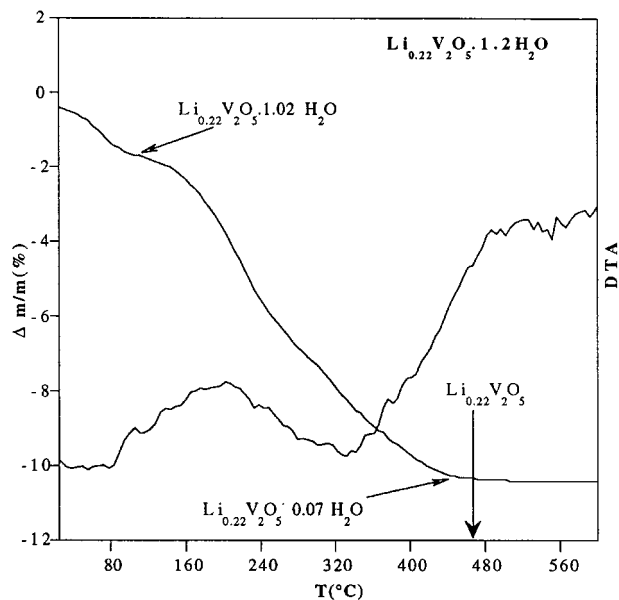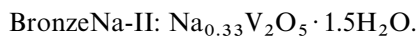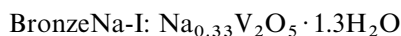
BronzeNa-I: $Na_{0.33}V_2O_5 \cdot 1.3H_2O$
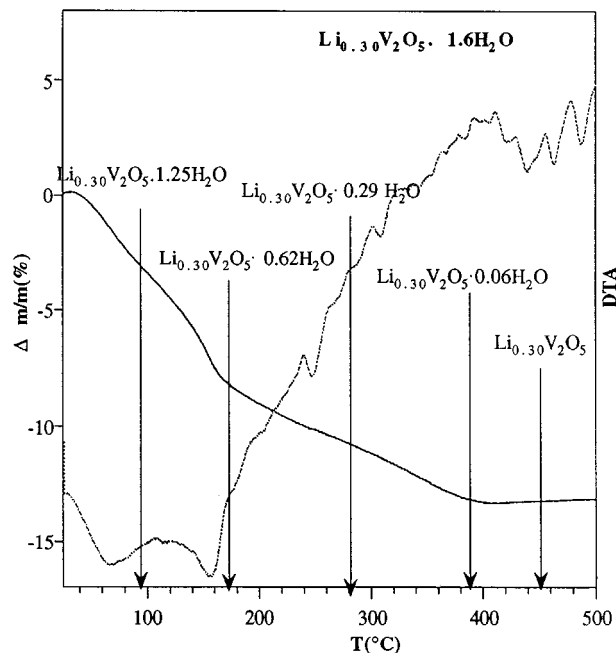
BronzeNa-II: $Na_{0.33}V_2O_5 \cdot 1.5H_2O$.

FIG. 6. TGA and DTA curves of BronzeLi-I.

The TGA curves of the two lithium compounds show (Figs. 6 and 7) remarkable differences, not only in the amount of water but also in the different steps of thermic decomposition. The experimental results show clearly that the water molecule layout in the interlamellar domain is notably different in the lithium vanadium bronzes compared to the sodium vanadium bronzes.

The final products obtained after heating correspond to the compositions $Li_{0.22}V_2O_5$ and $Li_{0.30}V_2O_5$ for BronzeLi-I and BronzeLi-II, respectively. The X-ray powder patterns for these compounds are shown in Figs. 9 and 10. Table 3 summarizes the TGA and chemical analysis results for these compounds. The proposed formulas are

BronzeLi-I: $Li_{0.22}V_2O_5 \cdot 1.2H_2O$

BronzeLi-II: $Li_{0.30}V_2O_5 \cdot 1.6H_2O$.
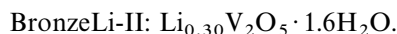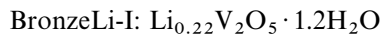
DISCUSSION

If we consider the tension–pH diagrams for the system vanadium–water it appears that a great variety of dissolved species can exist in an aqueous solution. However, vanadyl ions VO^{2+} or other species with tetravalent or trivalent vanadium atoms are not stable at all for pH values higher than 4–5. In our process to synthesize vanadium bronzes, the pH values are either 7 or 10, which are values favorable for pentavalent vanadium species. Then, the question was is it possible to obtain vanadium bronzes $M_xV_2O_5 \cdot nH_2O$

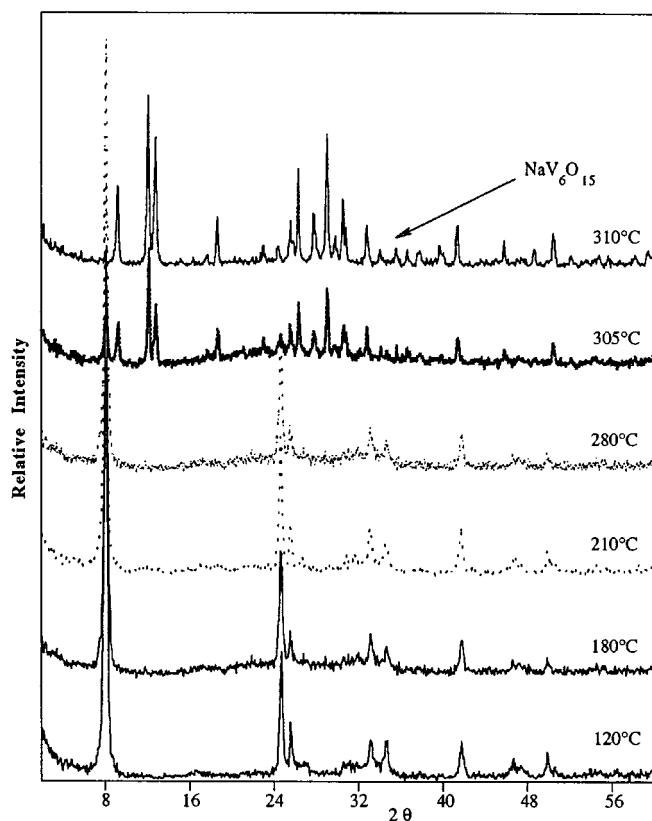**FIG. 8.** Evolution of the X-ray diffraction diagrams versus temperature for $Na_{0.33}V_2O_5 \cdot 1.3H_2O$.

FIG. 9. XRD patterns of BronzeLi-I after heating.

by neutralization of a vanadyl solution with an hydroxide solution of MOH?

We tried to prepare samples with different concentrations of $VOSO_4 \cdot 3H_2O$ solutions and 1-M NaOH solutions but we never obtained a precipitate. Consequently, it seems that the formation of hydrated vanadium bronzes from vanadyl or V_2O_3 materials is limited to the presence of some species containing C–O bonds such as acetate, carbonate, or acetylacetonate ions.

We know, for example, that it is possible to reduce a carboxylic function with strong reductors. Thus, we can imagine that in a basic medium, the vanadium species with low oxidation states are strong enough to reduce carboxylic groups, then we can obtain vanadium with an oxidation state equal to 5.

TABLE 2
Chemical Analysis Results for Sodium Vanadium Bronzes

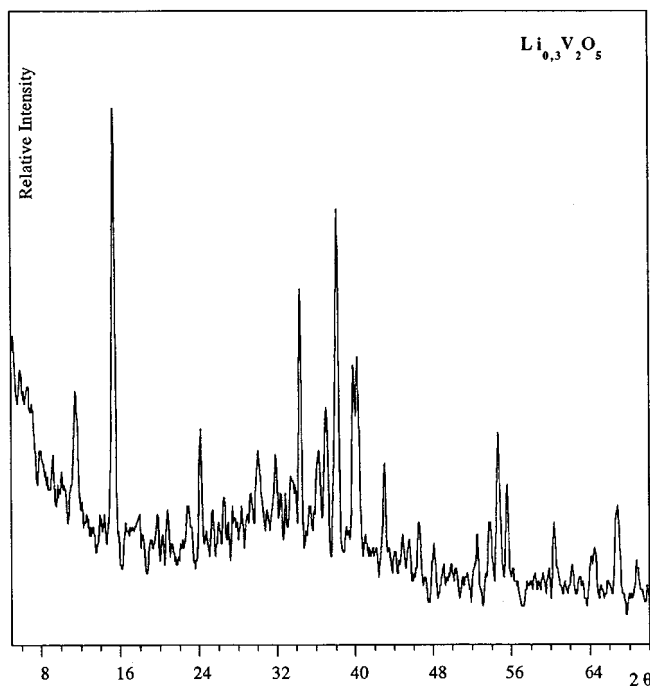|		Hydrogen	Sodium	Vanadium
Bronze-Na-I	% exp	0.96	4.21	50.1
	% calc	1.2	3.7	48.0
Bronze-Na-II	% exp	1.34	3.62	47.31
	% calc	1.38	3.50	47.00

FIG. 10. XRD patterns of BronzeLi-II after heating.

TABLE 3
Chemical Analysis Results for Lithium Vanadium Bronzes

		Hydrogen	Lithium	Vanadium	% H_2O
Bronze-Li-I	% exp	1.31	0.72	49.60	% exp 10.8
	% calc	1.16	0.75	49.72	% calc 10.5
Bronze-Li-II	% exp	0.90	1.02	48.00	% exp 13.3
	% calc	1.3	0.99	47.90	% calc 13.5

CONCLUSION

The present work shows that it is possible to obtain new hydrated vanadium bronzes with original synthesis methods. The experimental processes are easy enough and do not need expensive initial products. Different hydrated compounds were obtained and one of them has been studied by chronopotentiometric and cyclic voltammetric experiments (1). It showed a behavior that differs from that known for the sol–gel sodium-exchanged V_2O_5 xerogel and for the anhydrous monoclinic bronze. In another way, preliminary experiments were carried out on $Na_{0.33}V_2O_5 \cdot H_2O$ which show that exchange properties exist for the Na^+ cation when a suspension of the layered bronze is kept for several days under stirring at room temperature in a concentrated solution of another cation such as K^+ or VO^{2+}. The next step is now to test the electrochemical properties of all these materials in order to understand the specific role of water molecules in the electrochemical process.

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