Table IV. Identification of Sites in Some Polytypes of SiC[a]

polytype		sequence	OK	GP	HRSW
2H	Si	hhhhh	123	IV	D
3C	Si	ccccc	000	I	A
6H	Si(1)	cchcc	000	III	B
	Si(2)	chcch	112	II	C
	Si(3)	hcchc	013	I	A
15R	Si(1)	hchcc	002	III	B
	Si(2)	chcch	112	II	C
	Si(3)	hcchc	013	I	A
	Si(4)	cchch	000	III	B
	Si(5)	chchc	123	II	C

[a] The numbering of silicon atoms is that used by Guth and Petusky (GP).[1] OK refers to the present work, and HRSW refers to Hartman et al.[2]. "Sequence" shows the two layers above and below the layer in question (bold).

merals for GP and letters for HRSW) in the "hc" notation is according to the symbol of the layer (boldface) and that preceding it. They are as follows:

cc I A hc II C ch III B hh IV D

This classification neatly explains the observation of three equal peaks in 6H and three peaks at approximately the same positions but in an intensity ratio 1:2:2 in 15R.

It is not planned to enter a discussion of the factors entering into NMR shifts at this point. However, it is pointed out that sites of types I and III (A and B) have exactly the same number of geometrical and topological neighbors as each other, as do sites of types II and IV (C and D). In Table IV the sites in the polytypes under discussion (and 2H) are identified, and the different classifications given. If the distribution of carbon neighbors should prove to be an important factor in NMR shifts, then a division into three groups, (000 and 011), (002 and 013), and (112 and 123), is proposed from examination of the data in Table III. This classification would equally explain the data, but the identification of correspondences between different polytypes is different. To resolve such questions, NMR data on more polytypes will be required. As can be seen from Table IV, data for 2H would be particularly interesting.

Discussion

The analysis presented here is readily extended to further neighbors if required for very complex polytypes should that prove necessary at some time in the future.

Changing a layer from h to c or vice versa does not, as has been seen, change the numbers of neighbors of an atom in that layer; it merely rotates those "above" the plane by 180° with respect to those "below". Should such an effect prove important, as proposed[2,3] for NMR, the sites identified in the present paper will all split into two twin-related sets, but the present analysis will still stand. One simply has to replace, e.g., 123 by 123h and 123c according to whether the layer in question is h or c. On the other hand, effects such as subtle changes of interlayer spacings with "hexagonality"[12] have not been considered and may well be important in some instances.

Acknowledgment. This work was supported by a grant (DMR 8813524) from the National Science Foundation. I am grateful to W. T. Petusky and P. Schields for useful discussions.

Registry No. SiC, 409-21-2.

(12) Guth, J.; Petusky, W. T. *J. Phys. Chem. Solids* **1987**, *48*, 541.

Sol-Gel Route to Niobium Pentoxide

P. Griesmar, G. Papin, C. Sanchez,* and J. Livage

Laboratoire de Chimie de la Matière Condensée, URA 302, Université Pierre et Marie Curie, 4, Place Jussieu, 75252 Paris cedex 05, France

Received October 12, 1990. Revised Manuscript Received January 2, 1991

Niobium pentoxide powders were synthesized via the sol-gel route. Monolithic gels can be reproducibly obtained when the hydrolysis of niobium alkoxides $Nb(OR)_5$ is performed in the presence of acetic acid. This carboxylic acid reacts with the alkoxide and leads to the formation of new $Nb(OR)_{5-x}(OAc)_x$ ($0 < x < 1$) precursors. Therefore the whole hydrolysis-condensation process is modified. The different steps of the synthesis, from the molecular precursor $Nb(OPent^n)_5$ ($Pent^n$ is a normal pentyl group) to the crystalline oxide were characterized by ^1H NMR, ^{13}C CP MAS NMR, and infrared spectroscopies, thermal analysis, and X-ray diffraction. Xerogels are obtained after drying the gel at 80 °C. They are made of an oxo-polymer network in which some alkoxy groups and acetate ligands remain bonded to niobium. These organic groups are removed upon heating in air leading to the crystallization of T-Nb_2O_5 at around 550 °C.

Introduction

Sol-gel processing is a very promising approach for the synthesis of glasses or ceramics.[1,2] One of the main reasons for this interest arises from the rheological properties of sols and gels that allow the easy fabrication of fibers[3] or coatings[4] by such techniques as spin drawing or dip coating. Sol-gel chemistry is based on inorganic polymerization reactions.[5] Molecular precursors, mainly metal alkoxides, are generally used as starting materials. A macromolecular network is then obtained via hydrolysis and condensation. Transition-metal alkoxides with a d^0 electronic configuration (Ti(IV), Zr(IV), Ta(V), Nb(V), etc.)

(1) Brinker, C. J.; Clark, D. E.; Ulrich, D. R., Eds. *Better Ceramics Through Chemistry*; Elsevier: New York, 1984.
(2) Brinker, C. J.; Clark, D. E.; Ulrich, D. R., Eds. *Better Ceramics Through Chemistry*; Elsevier: New York, 1986.
(3) Sakka, S.; Kamiya, K. *J. Non-Cryst. Solids* **1982**, *48*, 31.
(4) Dislich, H.; Hinz, P. *J. Non-Cryst. Solids* **1982**, *48*, 11.
(5) Livage, J.; Henry, M.; Sanchez, C. *Prog. Solid State Chem.* **1988**, *18*, 259.

0897-4756/91/2803-0335$02.50/0 © 1991 American Chemical Society

are very reactive toward hydrolysis. Adding water to such alkoxides readily leads to precipitates that are not suitable for making fibers or coating. Sols and gels must be stabilized in order to prevent precipitation. This can be done by using nucleophilic chemical additives such as alcohols, polyols, carboxylic acids, β-diketones, or other chelating reagents.[6] These additives react with alkoxides giving new molecular precursors with different structure, reactivity, and functionality.[7] Such a chemical modification promotes decoupling between hydrolysis and condensation reactions, allowing the formation of sols and gels.[7,8] Nowadays, most sol–gel studies are devoted to silica,[9] alumina,[10] titania,[11,12] or zirconia[12-14] based materials. Niobium oxides also lead to interesting applications in the field of reversible cathodes,[15] display devices,[16] or ferroelectric ceramics.[17] However very few papers dealing with niobium pentoxide gels have been published.[18-20]

This work reports on the synthesis of niobium pentoxide sols and gels via the chemical modification of $Nb(OPent^n)_5$ by acetic acid. These sols are suitable candidates for making films. They crystallize into tetragonal Nb_2O_5 when heated above 500 °C. A characterization of the chemical species involved in the various steps of the process, from the molecular precursor $Nb(OPent^n)_5$ to the xerogel and the crystalline niobium oxide is presented. It is based on infrared, liquid-state NMR (^{13}C and ^1H), and CP MAS solid-state NMR (^{13}C) spectroscopies, thermal analysis, and X-ray diffraction.

Experimental Section

The different chemical species involved in this synthesis were characterized with the following techniques:

Infrared absorption experiments were carried out with a 580 Perkin-Elmer spectrometer working in the 4000–200-cm^{-1} frequency range. Solutions were studied by putting a droplet between two KRS5 windows, while powders were dispersed into KBr pellets.

^{13}C and ^1H liquid-state NMR spectra were recorded on a Brucker 250 spectrometer equipped with a nitrogen-cooled cryostat. Samples were diluted in $CDCl_3$/TMS mixtures. ^{13}C cross-polarization magic-angle-spinning (CP MAS) solid-state NMR experiments were performed on a Brucker MSL 400 spectrometer operating at 400.17 MHz for ^1H and 100.53 MHz for ^{13}C. MAS spectra were recorded at a spinning frequency of 4 kHz. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) experiments were carried out under argon, on a Setaram CS92 thermal analyzer. Thermal analysis was performed up to 900 °C at heating rates of 10 °C /min. X-ray diffraction was performed on a Philips diffractometer working at Cu $K\alpha_1$ = 1.54 Å equipped with a variable-temperature platinum setup working between 300 and 815 °C (heating rate = 5 °C/min).

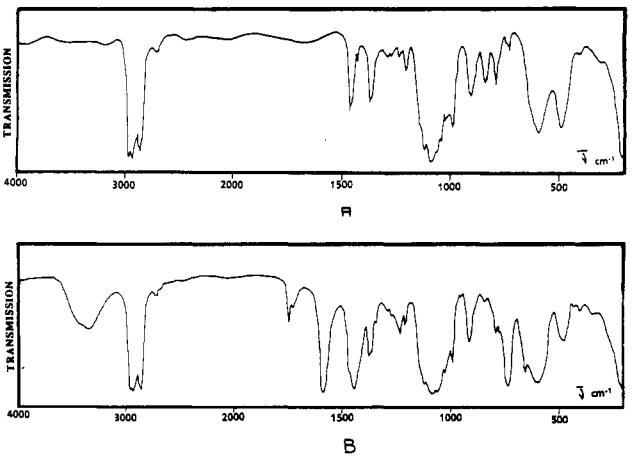

Figure 1. (A) Infrared spectrum of $Nb(OC_5H_{11}^n)_5$. (B) Infrared spectrum of $Nb(OC_5H_{11}^n)_5$ modified by acetic acid (AcOH/Nb = 1).

Table I. ^1H and ^{13}C NMR Chemical Shifts of $Nb(OC_5H_{11}^n)_5$

^1H NMR spectrum		^{13}C NMR spectrum	
δ	attribution	δ	attribution
4.4	Nb–O–CH_2 terminal groups	73.2	Nb–O–CH_2 terminal groups
4.1	Nb–O–CH_2 bridging groups	72.6	Nb–O–CH_2 bridging groups
1.9–0.8	Nb–O–CH_2–C_4H_9	33.1 to 13.9	Nb–O–CH_2–C_4H_9

Results and Discussion

Synthesis of $Nb(OPent^n)_5$. Niobium ethoxide $Nb(OEt)_5$ (Et=C_2H_5) was purchased from Alfa. It is very sensitive toward moisture and therefore quite difficult to handle for a long period of time. It is well-known that the reactivity of metal alkoxides decreases when the length of the alkyl chain increases. Therefore the less reactive alkoxide $Nb(OPent^n)_5$ (Pent = C_5H_{11}) was synthesized via alcohol interchange. $Nb(OEt)_5$ (25 g) is dissolved into a solution containing 38 g of dry *n*-pentanol and 41.2 g of dry cyclohexane. Alcoholysis occurs as follows:

$$Nb(OEt)_5 + x\,HOPent^n \rightarrow Nb(OEt)_{5-x}(OPent^n)_x + x\,EtOH \qquad (x = 1\text{–}5)$$

Ethanol is removed via azeotropic distillation so that the reaction leads to the formation of the completely substituted $Nb(OPent^n)_5$ alkoxide.

The infrared spectrum of $Nb(OPent^n)_5$ is shown in Figure 1a. High-energy bands located at 2860–2960 cm^{-1} correspond to ν(C–H) stretching vibrations of the alkyl groups of pentoxy ligands. Two sets of bands can be seen in the middle of the spectrum. Sharp bands at 1375 and 1515 cm^{-1} can be respectively assigned to $\delta(CH_2)$ and $\delta(CH_3)$ deformation vibrations of the alkyl groups. The broad band around 1150 cm^{-1} should correspond to the $\nu(C\text{–}O\text{–}C_5H_{11})$ stretching vibrations of different pentoxy ligands bound to niobium atoms. A more accurate assignment of these vibrations in terms of terminal or bridging pentoxy groups would not be straightforward.[21] The low-energy frequency range is mainly dominated by two large bands around 500 and 600 cm^{-1} due to ν(Nb–O)

(6) Mehrotra, R. C.; Kapoor, P. N. *J. Less Common Met.* **1964**, *7*, 176.
(7) Yoldas, B. E. *J. Mater. Sci.* **1986**, *21*, 1087.
(8) Sanchez, C.; Livage, J.; Henry, M.; Babonneau, F. *J. Non-Cryst. Solids* **1988**, *100*, 65.
(9) Chen, K. C.; Tsuchiya, T.; Mackenzie, J. D. *J. Non-Cryst. Solids* **1986**, *81*, 227.
(10) Debsikdar, J. C. *J. Mater. Sci.* **1985**, *20*, 44.
(11) Sanchez, C.; Babonneau, F.; Doeuff, S.; Leaustic, A. *Ultrastructure processing of ceramics, glasses and composites*; San Diego, 1987.
(12) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. In *Metal Alkoxides*; Academic Press: New York, 1978.
(13) Emili, M.; Incoccia, L.; Mobillio, S.; Faghezazzi, G.; Gugliemi, M. *J. Non-Cryst. Solids* **1985**, *74*, 11.
(14) Debsikdar, J. C. *J. Non-Cryst. Solids* **1986**, *86*, 231.
(15) Reichman, B.; Bard, A. J. *J. Electrochem. Soc.* **1981**, *128*, 344.
(16) Reichman, B.; Bard, A. J. *J. Electrochem. Soc.* **1980**, *127*, 241.
(17) Eichorst, D. J.; Howard, K. E.; Payne, D. A.; Wilson, S. R. *Inorg. Chem.* **1990**, *29*, 8.
(18) Alquier, C.; Vandenborre, M. T.; Henry, M. *J. Non-Cryst. Solids* **1986**, *79*, 383.
(19) Vandenborre, M. T.; Poumellec, B.; Alquier, C.; Livage, J. *J. Non-Cryst. Solids* **1989**, *108*, 333.
(20) Ko, E. I.; Mauer, S. M. *J. Chem. Soc., Chem. Commun.* **1990**, *15*, 1062.
(21) Bradley, D. C.; Westlake, A. H. *Proc. Symp. Coord. Chem., Tihany, Hung.* **1965**, 309.

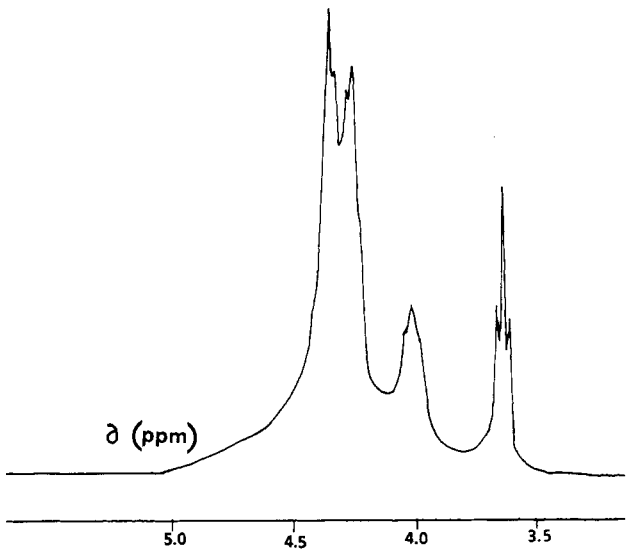

Figure 2. ^1H NMR spectrum of $Nb(OC_5H_{11}^n)_5$ at 203 K.

stretching vibrations. The presence of several large ν(Nb–O) bands is typical of oligomeric alkoxides.

^1H and ^{13}C NMR chemical shifts measured at room temperature are reported together with their assignment in Table I. All signals correspond to pentoxy groups bound to the Nb atom.

Except for methyl groups, all ^{13}C NMR peaks exhibit two components in a 1/4 ratio, suggesting the presence of two kinds of pentoxy ligands, i.e., terminal and bridging.

^1H NMR resonances located upfield are poorly resolved. This is typical of a multiplet broadening arising from chemical exchange between different alkoxy groups. Such a dynamic behavior of the ^1H NMR spectrum was already reported for $Nb(OMe)_5$ by Hubert-Pfalzgraf.[22] However Nb–OCH_2 protons give rise to two distinct broad resonances located at 4.1 and 4.4 ppm in a 1/4 ratio. They can be assigned respectively to bridging and terminal pentoxy groups. The ^1H NMR spectrum, recorded at 203 K, clearly shows (Figure 2) the presence of three different –OCH_2 peaks located at 4.0, 4.3, and 4.4 ppm in a 1/2/2 ratio. These signals can be respectively assigned to bridging, terminal (axial), and terminal (equatorial) pentoxy groups.

Molecular weight measurements of $Nb(OPent^n)_5$ performed by cryoscopy in benzene are consistent with a dimeric structure[23] in agreement with ^1H NMR data performed at 200 K. However at room temperature, equilibrium between oligomeric species cannot be neglegted. Recent ^{93}Nb NMR experiments carried out at room temperature on niobium alkoxides diluted in different dry solvents (alcohol or benzene) show two broad resonances about 1160 ppm apart.[24] Such behavior suggests the presence at room temperature of two species, probably dimers and solvated monomers. This assignment agrees with Bradley's results showing that upon hydrolysis primary niobium alkoxides follow a polymerization process based on dimers and solvated monomers.[25] $Nb(OPent^n)_5$ precursors could then be described as dimers $Nb_2(\mu_2\text{-}OPent^n)_2(OPent^n)_8$ (main species), in which the niobium atoms would be 6-fold coordinated in equilibrium with a small amount of monomeric species.

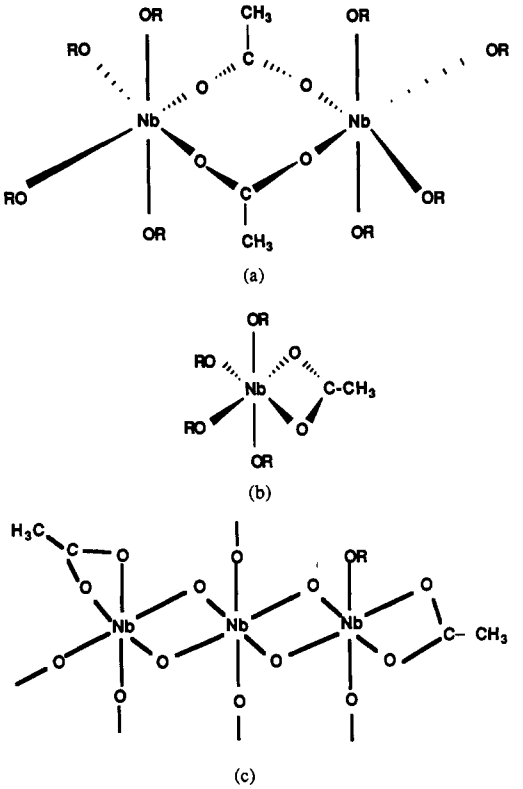

Figure 3. (A) Structure of dimeric species of $Nb(OC_5H_{11}^n)_5$ modified by acetic acid (AcOH/Nb = 1). (B) Structure of monomeric species of $Nb(OC_5H_{11}^n)_5$ modified by acetic acid (AcOH/Nb = 1). (C) Structural model of the oxopolymer network of the niobium pentoxide xerogel.

Chemical Modification with Acetic Acid. The chemical reactivity of $Nb(OPent^n)_5$ remains too high. Hydrolysis still leads to precipitation rather than gelation. Therefore further stabilization was obtained by adding acetic acid following a procedure already described for the synthesis of TiO_2 gels.[11] Glacial acetic acid is added to pure $Nb(OPent^n)_5$ in a 1/1 molar ratio. A weakly exothermic reaction takes place, and a clear solution is obtained. Chemical modification of the alkoxide is presumed to occur as follows:[8,26]

$$Nb(OPent^n)_5 + xHOAc \rightarrow Nb(OPent^n)_{5-x}(OAc)_x + xHOPent^n$$

New ^1H and ^{13}C NMR peaks can be observed when pure acetic acid is added to $Nb(OPent^n)_5$. They are located at $\delta(CH_3)$ 23.7, $\delta(CO)$ 179.3, and $\delta(CH_3)$ 2.1. They can be assigned to acetate groups bonded to a transition metal. Morever the ^1H peak assigned to the –OCH_2 groups of bridging pentoxy ligands ($\delta(OCH_2)$ 4.1) strongly decreases in intensity, indicating that such groups are no longer present in the species formed. This suggest that bridging pentoxy groups are preferentially removed by acetate ligands. The complexation of niobium pentoxide by the acetate group can be explained as a nucleophilic reaction (entrance of an acetate group and elimination of pentanol). The limiting step should be the proton transfer between the entering molecule (CH_3COOH) and the oxygen of the leaving group ($HOPent^n$).[5] In agreement with the mechanism proposed for the formation of some oxoalkoxides,[27,28]

(22) Hubert-Pfalzgraf, L. G.; Riess, J. G. *Bull. Soc. Chim. Fr.* **1968**, *11*, 4348.
(23) Bradley, D. C.; Hursthouse, H. B.; Rodessier, P. F. *Chemical Commun.* **1968**, 1112.
(24) Griesmar, P.; Maquet, J.; Sanchez, C.; Livage, J. *Chem. Commun.*, in preparation.
(25) Bradley, D. C. *Coord. Chem. Rev.* **1967**, *2*, 299.
(26) Livage, J.; Sanchez, C.; Henry, M.; Doeuff, S. *Solid State Ionics* **1989**, *32/33*, 633.
(27) Tolédano, P.; Ribot, F.; Sanchez, C. *C. R. Acad. Sci., Paris* **1990**, *311*, 1315.
(28) Tolédano, P.; In, M.; Sanchez, C. *C. R. Acad. Sci. Paris* **1990**, *311*, 1161.

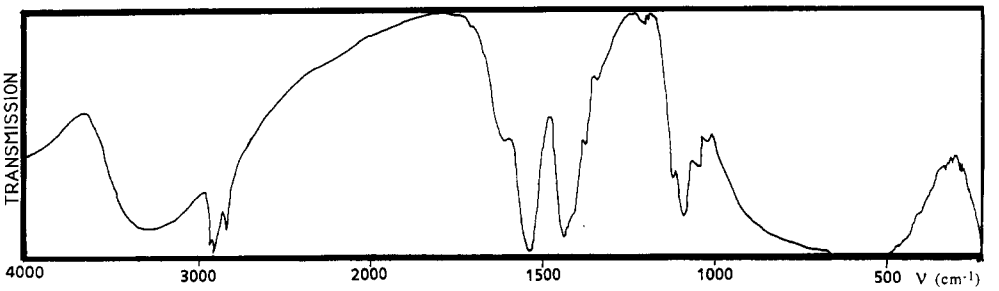

Figure 4. Infrared spectrum of niobium pentoxide xerogels (AcOH/Nb = 1, H_2O/Nb = 1.8).

alkoxy bridging groups appear to be the most easily protonated groups probably because of their higher negative charge.

The infrared spectrum of $Nb(OPent^n)_5$ after addition of acetic acid is shown in Figure 1B. The broad absorption band at 1140 cm^{-1} assigned to the stretching vibration ν(C–O) of pentoxy groups is still present. However some new bands can be seen around ν(O–H) = 3500 cm^{-1} and ν(C–O) = 1755 cm^{-1}. They correspond to free pentanol formed via the nucleophilic substitution of pentoxy groups by acetates. A new set of bands appear around 1500 cm^{-1}. The strongest ones can be assigned to the symmetric and antisymmetric stretching vibrations of carboxylate groups: ν_{as}(COO) = 1585 (strong) and 1570 cm^{-1} (shoulder), ν_s(COO) = 1445 (strong) and 1465 cm^{-1} (shoulder). Their position and their frequency splitting $\Delta\nu = \nu_{as} - \nu_s$ ($\Delta\nu$ = 140 and 95 cm^{-1}) are typical of bridging and chelating bidentate acetate groups.[29] However bridging acetates seem to be somewhat more abundant. It is interesting to point out the presence of two small bands located at 1747 and 1237 cm^{-1}, characteristic of ν(C=O) vibrations of pentyl acetate ester. This shows that even for a stoichiometric ratio (AcOH/Nb = 1) the nucleophilic subtitution of pentoxy groups by acetates does not go to completion as was observed for titanium alkoxides.[11]

IR and ^1H NMR results suggest that acetic acid leads to a mixture of monomeric and dimeric modified niobium alkoxides. Recent ^{93}Nb NMR studies show the presence of only two species.[24] Assuming a 6-fold coordination for niobium atoms (higher coordination is anticipated for the higher complexation ratio), the most likely molecular structures of the modified niobium alkoxide species are shown in Figure 3. However dimers (Figure 3a) where 6-fold coordinated niobium atoms are bonded together via carboxylate bridges should be dominant.

Hydrolysis of the Modified Precursors. Stable sols and gels were obtained by substoichiometric hydrolysis of the modified precursors. Precipitation occurs readily when the hydrolysis ratio $h = H_2O/Nb$ is larger than 2, whereas monolithic gels were obtained for h = 1.9. Hydrolysis is performed by adding water diluted in n-pentanol (10 wt % of water) under vigorous stirring. A transluscent sol is obtained within a few minutes. It transforms spontaneously into a white monolithic gel after ageing for 1 month in a closed vessel. The stability of these colloidal solutions increases when h decreases slightly ($1.6 < h < 1.8$) or when the complexation ratio increases (AcO/Nb = 1.5). The gels are then dried in air at 80 °C for 24 h. White powders were obtained. These xerogels are amorphous as shown by X-ray diffraction.

The infrared spectrum of the xerogel is shown in Figure 4. The broad absorption band at low frequency corresponds to ν(Nb–O–Nb) vibrations. It shows that a niobium oxide network is formed. Moreover the characteristic features of chelating carboxylate ligands (ν_s(COO) = 1450 cm^{-1}, ν_{as}(COO) = 1550 cm^{-1}, and $\Delta\nu$ = 100 cm^{-1}) as well as those of pentoxy groups (ν(C–OPent^n) = 1100–1150 cm^{-1}) are still visible.

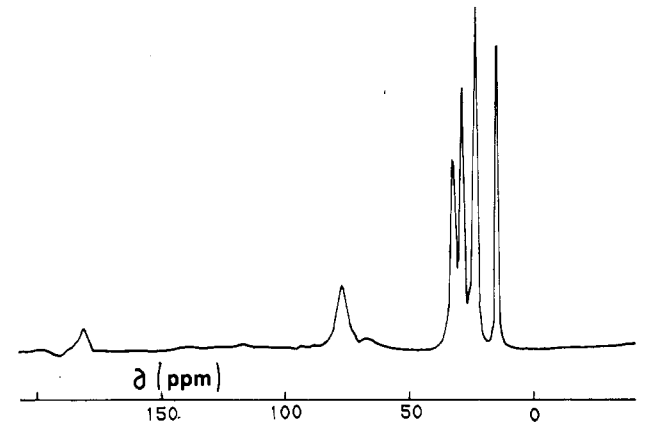

Figure 5. ^{13}C CP MAS NMR of niobium pentoxide xerogels (AcOH/Nb = 1, H_2O/Nb = 1.8).

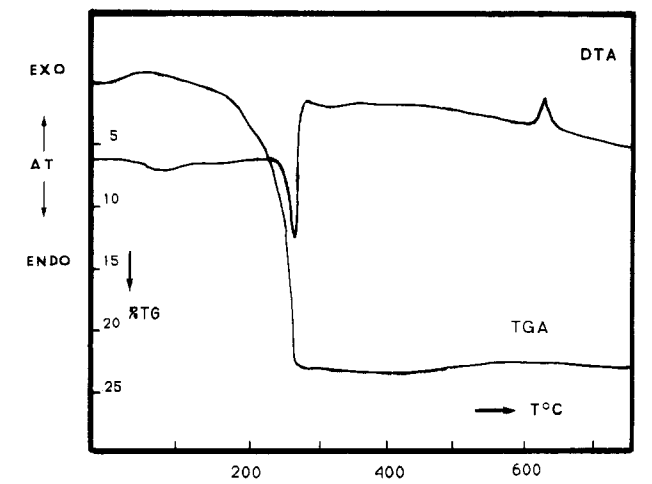

Figure 6. DTA and TGA curves of niobium pentoxide xerogels (AcOH/Nb = 1, H_2O/Nb = 1.8).

This is confirmed by the ^{13}C CP MAS NMR spectrum of the xerogel (Figure 5), which shows the ^{13}C chemical shifts typical of carboxylate ligands (δ(CO) 181.5, $\delta(CH_3)$ 23.2) and pentoxy groups ($\delta(CH_3)$ 14.5, $\delta(CH_2)$ 23.2, $\delta(CH_2)$ 28.7, $\delta(CH_2)$ 32.3, $\delta(CH_2O)$ 76.1). Integrated intensities suggest that the pentoxy/acetate ratio should be close to 1.1.

Thermal analysis curves are shown in Figure 6. No significant weight variation is observed below 200 °C, whereas a sharp weight loss (20%) can be seen in the TGA curve between 200 and 270 °C. The corresponding differential thermal analysis signal exhibits both endothermic and exothermic features, suggesting that organic species

(29) Nakamoto, K. *Infrared and Raman Spectra of Inorganic Compounds*, 3rd ed.; Wiley: New York, 1978.

are removed and burnt. The rather high temperature at which these phenomena occur shows that these organic groups are chemically bonded to the oxide network and not adsorbed only as solvent molecules. All organic ligands have not been removed by the substoichiometric hydrolysis (h = 1.9). The xerogel should then be described as an oxopolymer $Nb_2O_{5-x}(OR)_{2x}$ where OR correspond to both OAc and OPent^n groups (Figure 3c). TGA shows that x is around 0.8, and NMR experiments suggest that the OAc/OPent ratio is close to 1/1. The powder remains amorphous up to 620 °C, where the exothermic peak corresponds to the crystallization of T-Nb_2O_5.[23] Actually X-ray diffraction experiments performed in a heating chamber show that crystallization occurs at lower temperatures, near 550 °C.

Conclusions

The synthesis of monolithic gels requires a careful control of the chemistry. Uncontrolled precipitation must be avoided. The synthesis of polymeric gels must be promoted.[30] Monolithic niobium pentoxide based gels can be reproducibly obtained when substoichiometric hydrolysis of niobium alkoxide precursors $Nb(OR)_5$ (OR = OPent) is performed in the presence of acetic acid. This carboxylic acid changes the alkoxide precursor at a molecular level and leads to new precursors $Nb(OPent)_{5-x}(OAc)_x$ (x = 0.1). They are mainly dimers and monomers with acetate ligands in both bridging and chelating positions. ^{93}Nb NMR experiments are in progress in order to provide a better identification of the different molecular precursors in the solution. The chemical control of hydrolysis and condensation reactions seems to be related to the role of acetate ligands, which are difficult to remove.[30,31] More precisely, as shown from IR measurements, chelating acetates are still present in the xerogel, suggesting that bridging carboxylates are preferentially removed over chelating ones. Monolithic transition-metal oxide gels are preferentially obtained with polymeric networks. Their formation is promoted by decreasing the functionality of the precursor. Condensation rates also have to be slowed down with respect to the hydrolysis rate.[30,31] As a consequence niobium oxide based gels synthesized in the presence of acetic acid probably have a polymeric nature. SAXS experiments should provide more information on the shape and morphology of such gels. The xerogel obtained after drying the gel at 80 °C is an oxopolymer containing organic groups chemically bonded to the oxide backbone. Upon heating in air at 500 °C pure tetragonal Nb_2O_5 powders have been obtained.

Registry No. $Nb(OEt)_5$, 3236-82-6; $Nb(OPent)_5$, 105091-67-6; $Nb(O)_5$, 1313-96-8; acetic acid, 64-19-7.

(30) Sanchez, C.; Livage, J. *New J. Chem.* **1990**, *14*, 513.

(31) Doeuff, S.; Henry, M.; Sanchez, C.; Livage, J. *J. Non-Cryst. Solids* **1987**, *89*, 206.

Dimensionally Stable MEEP-Based Polymer Electrolytes and Solid-State Lithium Batteries

K. M. Abraham* and M. Alamgir

EIC Laboratories, Inc., 111 Downey Street, Norwood, Massachusetts 02062

Received November 9, 1990. Revised Manuscript Received January 21, 1991

Several methods have been developed to dimensionally stabilize polymer electrolytes based on poly[bis((methoxyethoxy)ethoxy)phosphazene] (MEEP). In contrast to the poor dimensional stability exhibited by complexes of MEEP with most Li salts, those prepared with $LiAlCl_4$ have been isolated as the first example of free-standing MEEP-$(LiX)_n$ films. The mechanical properties of dimensionally unstable MEEP-$(LiX)_n$ complexes can be significantly improved by forming composites with polymers such as poly(ethylene oxide), poly(propylene oxide), poly(ethylene glycol diacrylate) and poly(vinylpyrrolidinone). The conductivity of 6.7×10^{-5} Ω^{-1} cm^{-1} at 25 °C exhibited by 55 wt% MEEP/45 wt% PEO-$[LiN(CF_3SO_2)_2]_{0.13}$ is among the highest values reported to date for a dimensionally stable electrolyte. The preparation and conductivity, calorimetric, and electrochemical studies of these electrolytes are described. Cyclic voltammetric data indicated that they are anodically stable at least up to 4.5 V versus Li^+/Li. They have shown excellent compatibility with Li metal, making them suitable for use as Li^+ conductive solid electrolytes in solid-state Li batteries. Li/TiS_2 solid-state cells utilizing some of these electrolytes have exceeded 200 cycles.

Introduction

Li^+-conductive polymer electrolytes derived from Li salt complexes of poly[bis((methoxyethoxy)ethoxy)phosphazene] (MEEP), due to their high ambient temperature conductivity, are of considerable importance for the fabrication of solid-state Li batteries.[1-3] They have exhibited 3-4 orders of magnitude higher conductivity at room temperature than electrolytes based on their poly(ethylene oxide) (PEO) counterparts. However, the poor mechanical properties of MEEP-based electrolytes has presented practical problems when attempts were made to fabricate all-solid-state Li batteries incorporating them.[2,4] At room temperature and above, these complexes are glutinous materials with a tendency to flow under pressure. Several

* To whom correspondence should be addressed.

(1) Blonsky, P. M; Shriver, D. F.; Austin, P.; Allcock, H. R. *J. Am. Chem. Soc.* **1984**, *106*, 6854.

(2) Abraham, K. M.; Alamgir, M.; Perrotti, S. J. *J. Electrochem. Soc.* **1988**, *135*, 535.

(3) Semkow, K. W.; Sammels, A. F. *J. Electrochem. Soc.* **1987**, *134*, 766.

(4) Alamgir, M.; Reynolds, R. K.; Abraham, K. M. In *Proceedings of the Symposium on Materials and Processes for Li Batteries*; Abraham, K. M., Owens, B. B., Eds.; The Electrochemical Society: Pennington, NJ, 1989; PV89-4, p 321.

0897-4756/91/2803-0339$02.50/0 © 1991 American Chemical Society