Synthesis and Characterization of a H^+ Exchanged Zirconate

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Abstract. A new protonated oxide has been synthesized by ion exchange of lithium by proton in lithium metazirconate, Li_2ZrO_3. Easy and complete ion exchange has been achieved in acidic medium. Characterization of the protonated solid by means of X−ray powder diffraction and thermogravimetric analysis allow to propose the nominal formulation “H_2ZrO_3“. However vibrational spectroscopy suggests that a more appropriate formulation would be as an oxyhydroxide $ZrO(OH)_2$.

Keywords: Lithium zirconate; Ion exchange; Proton exchange; Zirconium dioxide

Introduction

In the search of low-temperature proton conductors as solid electrolytes for fuel cell applications we have recently reported the preparation of a proton exchanged tetragonal tungsten bronze using nitric acid as exchanging agent to form $H_xNa_{1-x}NbWO_6$ [1]. In this compound, high conductivity has been detected to be dependant on proton exchange. However, oxidation state of both transition metals, Nb^V and W^{VI} are not likely to be stable under the reductive conditions present in the anode side of a real fuel cell system. In fact the bronze reacts readily with pure hydrogen inducing electronic conductivity [2]. Regarding our search for stable metal valencies, we report in this work the preparation and characterization of a protonated zirconium oxide obtained through a proton exchange reaction starting from lithium metazirconate, Li_2ZrO_3 [3].

Proton conductivity is not new in zirconium oxides. In fact chemisorption and physisorption of water on Yttrium stabilised zirconia can be analysed by means of conductivity measurements. In these cases conduction mechanism takes place in the absorbed water layer as is probably carried by protons. In the 150 °C−450 °C range, proton conduction is facilitated by chemisorbed water. At lower temperatures ($T<100$ °C), a physisorbed water layer facilitates the proton conduction [4]. In our work we are trying to obtain a zirconium oxide where proton may enter into the framework structure of the oxide and gives rise to proton conductivity at low temperature. For this reason a compound as Li_2ZrO_3 where the Li ions are located in the tunnels of a Zr-O framework (see Fig.1) has been chosen as a host to proton exchange reactions.

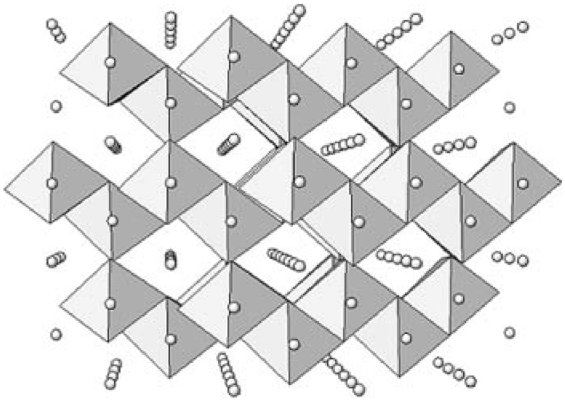

Fig. 1 Schematic representation of Li_2ZrO_3 crystal structure. Small spheres in tunnels represent lithium atoms. Octahedra represent coordination of Zr in the structure.

Experimental

Lithium metazirconate was synthesized by solid state reaction of Li_2CO_3 (Aldrich, purity 99+%) and ZrO_2 (Alfa Aesar, purity 99.5 %) [3]. Stoichiometric quantities of reagents were ground and heated at 700 °C for 12 h. The product was pelletised and treated in air at 1050 °C for 21 h.

Ion exchange of lithium by proton was performed by refluxing the powdered solid in a 5M aqueous solution of HNO_3 at 80 °C for 24 h. The solid product was washed with distilled water until no trace of $LiNO_3$ was found by IR analysis. The sample was then dried under vacuum for 7 days.

Powder X−ray diffraction data were collected by means of a Bruker D8 high-resolution X−ray powder diffractometer, using monochromatic $CuK_{\alpha1}$ radiation ($\lambda=1.5406$ Å) obtained with a germanium primary monochromator, and equipped with a position sensitive detector (PSD) MBraun PSD−50M. Structure was analyzed with the Rietveld method using the Fullprof program [5].

Lithium analysis was carried out using a VARIAN SpectrAA 220 atomic absorption spectrophotometer. $LiNO_3$ (Merck CertiPUR) was used a standard solution.

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Thermogravimetric experiments were carried out in a SEIKO TG/DTA 6200 thermobalance under nitrogen flow. Temperature range of measurements was 25 to 800 °C. Heating rate was set to 10 °C/min.

Infrared spectra were recorded in KBr pellets using a Perkin Elmer 2000 spectrometer, in wavenumber 4500−370 cm^{-1} range.

Results and Discussion

The X-ray powder diffraction pattern (Figure 2a) was indexed in the monoclinic space group Cc, corroborating the formation of single phase monoclinic Li_2ZrO_3. Unit cell parameters were a = 5.4243(3) Å; b = 9.0277(5) Å; c = 5.4217(3) Å; β= 112.700(2)° in good agreement with those reported in the literature [6].

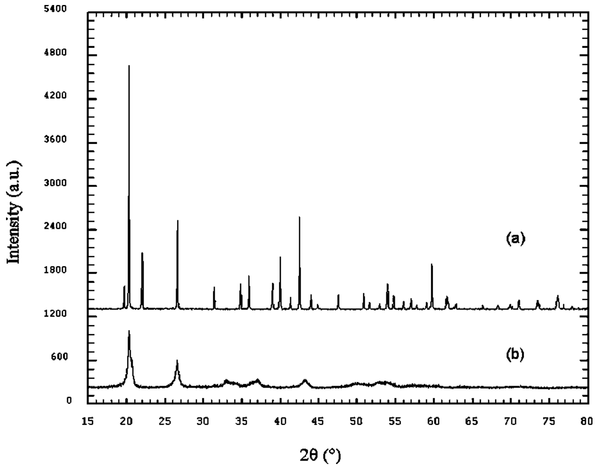

Fig. 2 X−Ray diffraction patterns of nominal (a) Li_2ZrO_3, (b) $ZrO(OH)_2{\cdot}0.14H_2O$

Ion exchange of lithium by proton was performed by using 5 M aqueous solution of HNO_3 at 80 °C for 24 h, according to the general exchange reaction:

$$Li_2ZrO_{3(s)} + x\ HNO_{3(aq)} \rightarrow H_xLi_{2-x}ZrO_{3(s)} + x\ LiNO_{3(aq)}$$

Lithium analysis of the filtrate confirmed that complete ion exchange took place (x=2).

Exchanged product, $ZrO(OH)_2$ hereafter, showed a X−ray diffraction pattern with broad reflections (Fig. 2b) which are indicative of either low crystallinity or small particle size in the exchanged material. Nevertheless, the structure seems to be kept in some way after acidic treatment, since both diagrams exhibit the same main diffraction maxima.

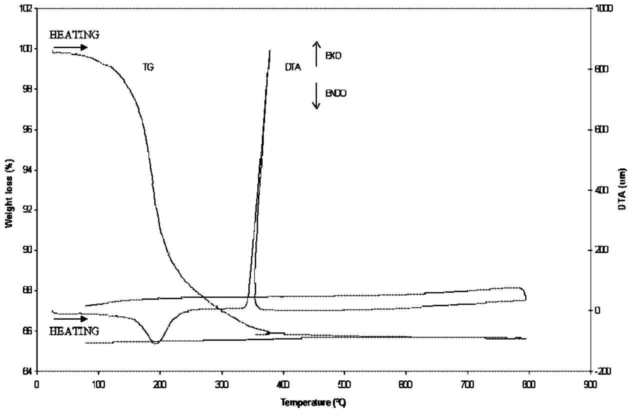

Fig. 3 TG / DTA plot of $ZrO(OH)_2{\cdot}0.14H_2O$

Thermogravimetric analysis of the exchanged product is shown in Fig. 3. Weight loss covers a rather wide temperature range, from 150 to 350 °C. The total weight loss (14.2 %) is slightly higher than expected weight loss for a quantitative exchange reaction of 2 Li^+ by 2 H^+ (12.8 %) as determined by AAS. An explanation for this higher weight loss is that the exchanged product is obtained as hydrated form $ZrO(OH)_2 \cdot y\ H_2O$ with $y \approx 0.14$ (note that exchange reaction was performed using an aqueous solution). However, from our thermogravimetric data it is not possible to distinguish processes corresponding to hydration water loss and proton loss (also as water and forming ZrO_2). On the other hand only a quite broad minimum can be registered in DTA.Then thermal decomposition reaction can be formulated as

$$ZrO(OH)_2{\cdot}0.14H_2O \rightarrow ZrO_2 + 1.14\ H_2O$$

Protonated samples treated from ca. 190 °C to 300 °C are amorphous. The process corresponding to the sharp exothermic peak at 350 °C without further weight loss is due to the crystallization of amorphous zirconia as it has been previously reported for related cases [7]. This transformation has been monitored by high temperature in situ X−ray powder diffraction (HT-PXRD). It can be depicted from Fig. 4 that heating above the transition temperature induces the formation of tetragonal ZrO_2 which gradually changes to the more stable monoclinic form. At the maximum temperature (1000 °C), only monoclinic ZrO_2 was present. It has been reported that low temperature tetragonal zirconia can be obtained by thermal treatment of various zirconium compounds [7−14], but the mechanism of its stabilization is still a matter of controversy. However, the formation of this metastable tetragonal phase at relatively low temperature can be explained by the presence of OH groups [13] or by small particle size [14]. Therefore, the method reported in the present work is a new route to obtain tetragonal zirconia where likely the presence of OH groups and small particle size is playing a role and confirm previous reports.

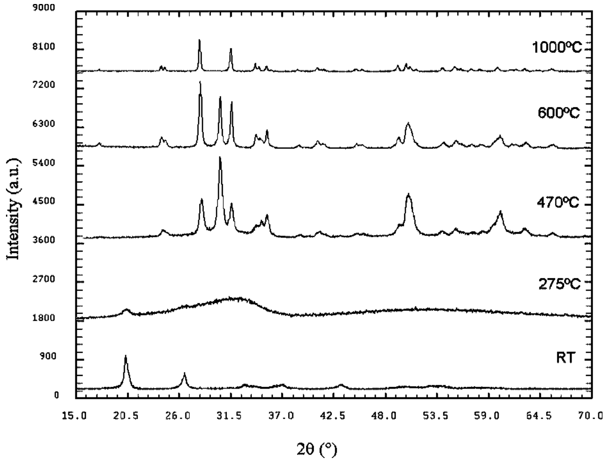

Fig. 4 XRD evolution with temperature of $ZrO(OH)_2 \cdot 0.14H_2O$

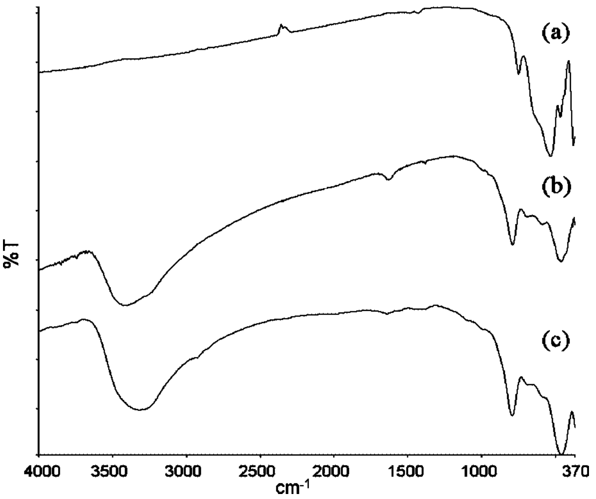

Fig. 5 IR spectra of nominal (a) Li_2ZrO_3 (b) $ZrO(OH)_2 \cdot 0.14H_2O$ (c) dried $ZrO(OH)_2$

IR spectra have been recorded in order to find out the nature of proton in $ZrO(OH)_2 \cdot 0.14H_2O$. The IR spectrum of $ZrO(OH)_2 \cdot 0.14H_2O$ (Fig. 5) revealed a broad absorption around 3400 cm^{-1} and a sharp absorption around 1600 cm^{-1} corresponding to the stretching and bending modes of water molecule [15]. $ZrO(OH)_2 \cdot 0.14H_2O$ dried at 50 °C in vacuum showed only the 3400 cm^{-1} absorption, indicating that protons are forming OH groups in the structure.

Conclusions

Li_2ZrO_3 has been used as a parent compound to perform proton exchange reactions. An easy and quantitative ion exchange took place by using aqueous nitric acid at moderate temperature. The as-obtained $ZrO(OH)_2 \cdot 0.14H_2O$ decomposes (with water loss) to give amorphous ZrO_2, which crystallizes at 350 °C via ZrO_2 (t) to ZrO_2 (m). Electrical measurements are presently in progress.

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References

[1] A. Kuhn, F. García-Alvarado, H. Bashir, A. L. Dos Santos, J. L. Acosta, *Mat. Res. Soc. Symp. Proc.* **2002**, 755; A. Kuhn, F. García-Alvarado, H. Bashir, A. Dos Santos y J. J. Acosta, *Solid State Chem.* **2004**, *177*, 2366−2372.
[2] A. Kuhn, F. García-Alvarado (unpublished results)
[3] L. J. Enriquez, P. Quintana, A. R. West, *Trans. Brit. Ceram. Soc.* **1982**, *81*, 17.
[4] S. Raz, K. Sasaki, J. Maier, I. Riess, *Solid State Ionics* **2001**, *143*, 181−204.
[5] J. Rodriguez-Carvajal, *Phys. B* **1993**, *19*, 55; see also a report in CPD of IUCr, Newsletter **2001**, *26*, 12.
[6] G. Dittrich, R. Hoppe, *Z. Anorg. Allg. Chem.* **1969**, *371*, 306.
[7] J. Livage, K. Doi, C. Maziéres, *J. Am. Ceram. Soc.* **1967**, *51*, 349−353.
[8] T. Sato, *J. Therm. Anal. and Calorimetry* **2002**, *69*, 255−265.
[9] S. Xie, E. Iglesia, A. T. Bell, *Chem. Mater.* **2000**, *12*, 2442−2447.
[10] S. A. Selim, M. El-Akkad, *J. Appl. Chem. Biotechnol.* **1977**, *27*, 58−66.
[11] G. Y. Guo, Y. L. Chen, W. J. Ying, *Mat. Chem. Phys.* **2004**, *84*, 308−314.
[12] G. Stefanic, S. Music, B. Grzeta, S. Popovic, A. Sekulic, *J. Phys. Chem. Solids* **1998**, *59*, 879−885.
[13] R. Cyprès, R. Wollast, J. Raucq, *Ber. Dtsch. Keram. Ges.* **1963**, *40*, 527−32.
[14] R. C. Garvie, *J. Phys. Chem* **1965**, *69*, 1238−43.
[15] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds* 4th ed., John Wiley & Sons, USA, 1986, p. 115.