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NH_4Y AND HY ZEOLITES AS ELECTROLYTES IN HYDROGEN SENSORS

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Partly exchanged NH_4Y and HY zeolites and H_3O^+ β/β″-alumina have been studied as solid electrolyte in a Nernst-type hydrogen sensor. The zeolites were examined on structure using X-ray diffraction and TGA. The electrical properties were studied using impedance spectroscopy. As solid electrode material $H_{0.34}MoO_3$ was investigated. NH_4Y is a promising material. Response times of a test probe with NH_4Y as solid electrolyte were less than 8 min. The sensor exhibits excellent Nernst response.

1. Introduction

Non-destructive hydrogen sensors are of practical interest because of the importance to detect hydrogen enclosed in construction metals, and in atmospheres in several chemical processes. Nernst-type chemical sensors are attractive because of their selectivity, fast response, and ease of use. Moreover, the probe can be elegantly adapted to the measurement of H_2 in atmospheres (indirect hydrogen activity sensor: IHAS) and hydrogen dissolved in a metal or alloy (direct hydrogen activity sensor: DHAS). In the latter case a direct contact is made between the sample metal and the solid electrolyte.

Several investigations have been reported on materials for use in these probes [1]. As reference electrode PdH_x [1–4], WO_3 [3,5], PbO_2 [6] and H_xMoO_3 [4] were tested. As solid electrolyte a variety of materials has been examined, like hydrogen uranyl phosphate (HUP) [1,2,7,8], $(Zr(HPO_4)_2 \cdot nH_2O)$ [9], and Nafion, a perfluorosulphonic acid resin [3]. Of these, HUP has been studied widely. However, HUP can be used only within a limited temperature range (25–60°C), because dehydration causing the protonic conduction to vanish, occurs at elevated temperatures.

In general, proton conduction is assumed to occur according to two mechanisms, the first being the migration of polyatomic ions like H_3O^+ or NH_4^+, and the second one involving proton hopping along "receivers", accompanied by reorientation of these molecules [10]. Usually the second mechanism is dominating because of its lower activation enthalpy.

This type of conduction is also found in zeolites like HY and NH_4Y, which can be prepared from NaY by cation exchange up to about 45% HY or NH_4Y [10]. These compounds exhibit better thermal stability than HUP. In addition, the loss and uptake of H_2O is at least partially reversible.

The ceramic proton conductor H_3O^+ β/β″-alumina can be made by cation exchange of Na^+ β/β″-alumina [11,12]. This material also exhibits good thermal stability.

The present paper deals with the synthesis and characterization of these material using IR spectroscopy, X-ray diffraction, thermo gravimetric analysis (TGA) and atomic emission spectrometry (AES). Conductivity properties are studied using small signal ac response studies in a wide frequency range. The impedance data are fitted to an electrical circuit model description.

The compound $H_{0.34}MoO_3$ was also prepared and structurally characterized for use as solid reference electrode.

Finally a test probe comprising of $H_{0.34}MoO_3$, NH_4Y and Pd as the sensing electrode, is examined on its Nernst behaviour and response time in H_2/N_2 mixtures.

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2. Experimental

A mixture of about 45% NH_4Y and 55% NaY was obtained by exchanging NaY (Union Carbide) in 0.1 M NH_4Cl solution for 24 h at room temperature. The partly exchanged NaY was washed with water and dried at 50°C.

HY was obtained by calcining NH_4Y at 450°C for 4.5 h. A heating rate of 1°C/min was used to prevent any possible deformation.

H_3O^+ β/β″-alumina was prepared by ion exchange in concentrated H_2SO_4 at 300°C for six days.

$H_{0.34}MoO_3$ was prepared using the procedure of ref. [13]. Zn was added to a solution of MoO_3 in 1.64 M HCl. After 24 h the precipitate was washed, and dried over P_2O_5.

IR spectra of NH_4Y and HY in KBr were recorded. X-ray diffraction (Cu Kα) was carried out with all compounds, using a Guinier–de Wolff camera. The TGA measurements were performed on a home-made thermobalance with a commercial temperature controller (Eurotherm). The TGA measurements on the zeolites were made both in water saturated and dry air. Inductively Coupled Plasma AES was carried out on the zeolites with a Perkin Elmer Plasma II.

The electrical properties were studied using impedance spectroscopy in the frequency range 0.1 to 65000 Hz. Here too, a comparison was made as concerning the zeolites between the response in two different ambients, i.e. dry air and water saturated N_2. The equipment consisted of a stainless steel conductivity cell provided with resistive heating and two Pt contacts (fig. 1), a Solartron 1250 frequency response analyser and a Solartron 1286 electrochemical interface, coupled to an Olivetti M24 PC. 2-point measurements were performed on pressed pellets of 1 cm in diameter, and about 2 mm thickness, of the solid electrolytes and solid reference electrode. A pressure of 630 MPa was used. Sputtered Pt on both sides served as electrode (Edwards 150B sputter coater).

A software package was developed, involving coordinated data storage, graphical presentation, and a Marquardt non-linear least squares parameter estimation for complex data. With this program the experimental dispersions can be fitted to equivalent circuit descriptions.

NH_4Y is measured from room temperature up to 190°C, HY from room temperature up to 350°C, and H_3O^+ β/β″-alumina from room temperature to 250°C. $H_{0.34}MoO_3$ is measured from room temperature up to 100°C.

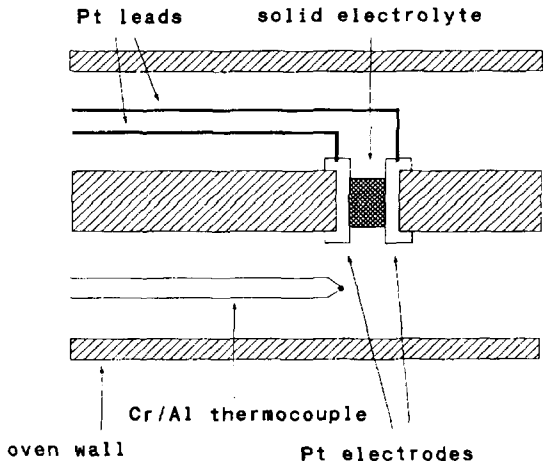

Fig. 1. Measuring cell for impedance spectroscopy.

A sensor was made by pressing together the solid electrolyte NH_4Y or HY and the reference electrode material. Two mixtures of both compounds in different proportions were required to obtain a mechanically stable interface. Pd was finally sputtered onto the solid electrolyte as a sensing electrode. The probe was tested in H_2/N_2 mixtures as shown in fig. 2. The gases were lead over Pd and Cu catalysts, respectively. The NH_4Y sensor was tested on Nernst behaviour at $T=28$°C and $T=63$°C.

3. Results and discussion

The zeolites NH_4Y and HY revealed X-ray diffraction patterns which were in good agreement with ASTM reference cards, indicating that the zeolite Y-structure was well conserved during the synthesis. The presence of NH_4^+ cations in NH_4Y was detected by infrared spectroscopy. An absorption peak at 1400 cm^{-1} could be assigned to the presence of NH_3 groups. In HY this absorption was absent. The formula of the zeolites is written as

$$Na_x^+ M_y^+ Al_{55}Si_{137}O_{384} \quad (1)$$

with M denoting NH_4^+, respectively, H^+. The AES measurements yielded a Si/Al proportion of 2.4 for

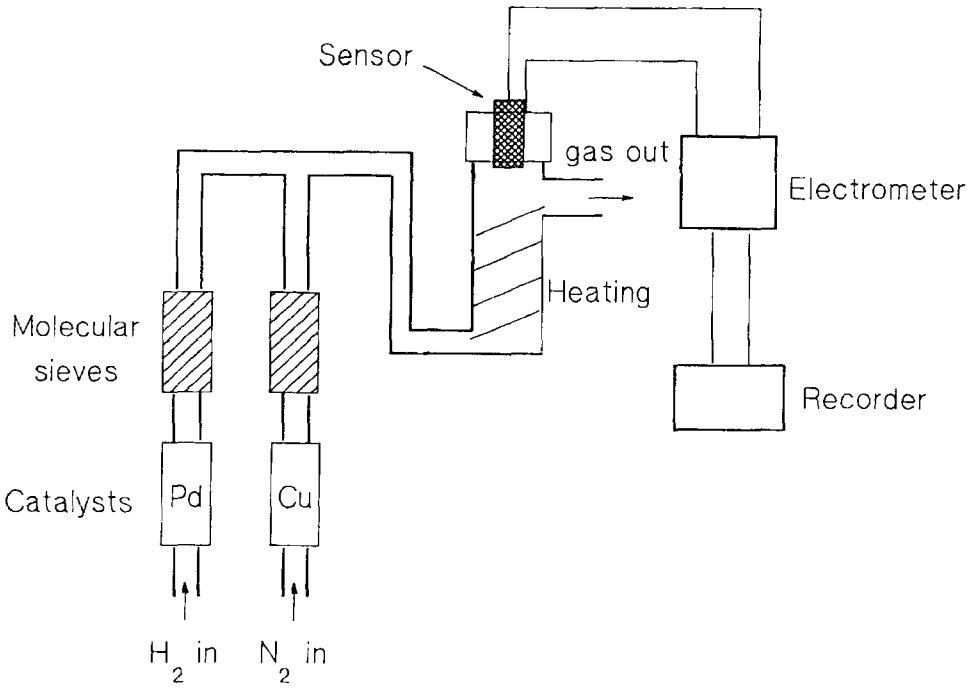

Fig. 2. Schematic of setup for testing a hydrogen sensor.

both compounds, which is in reasonable agreement with these formulae.

Thermogravimetric analyses yielded results shown in fig. 3. Both zeolites appear to loose weight gradually. For HY the weight loss occurs in the temperature range 50–200°C (water-saturated air), respectively, 50–300°C (dry air), while for NH_4Y the range of 50–350°C is found to be valid for both ambients. To explain the difference between the two compounds the loss of NH_3 in NH_4Y beyond 200°C is of importance [14]. Dehydration may be completed at lower temperatures than 350°C, followed by NH_3 loss. NH_3 constitutes only 3.5 wt% of the dry solid electrolyte, and the weight loss above 200°C is accordingly small. Another indication for the loss of NH_3 could be the presence of small but sharp weight decreases above this temperature to be seen in a differential TGA plot (dTGA, fig. 3b), at temperature near 280°C. These peaks are lacking in the graphs for HY (fig. 3d).

The difference in temperature ranges for weight losses of HY in dry and water-saturated air indicates an incomplete dehydration of the zeolites in wet atmospheres up to > 300°C. It is well known that complete dehydration of the zeolites leads to an irreversible reorganisation of the structure of the compound. As a consequence conductivity pathways disappear, and hence application as solid electrolyte should be restricted to these temperature limits.

Analyses of the impedance spectra provided bulk conductivities, presented as an Arrhenius plot in fig. 4. NH_4Y turned out to be the better ionic conductor. Bulk conductivities could be determined with our equipment from room temperature onwards. As an upper limit 200°C was chosen, in concordance with the results of the TGA experiments which indicate the compound to disintegrate above this temperature. The ionic conductivity is increasing up to 65°C with an activation enthalpy of 0.4 eV in dry air and slightly less in water-saturated nitrogen. The conductivity exceeds that of HUP [2,7]. At low temperatures the conductivity in water saturated N_2 is much higher than in dry air. The conduction is thus very sensitive to the water content in the environment. Above 65°C, the influence of the water content of the environment is small, which is in agree-

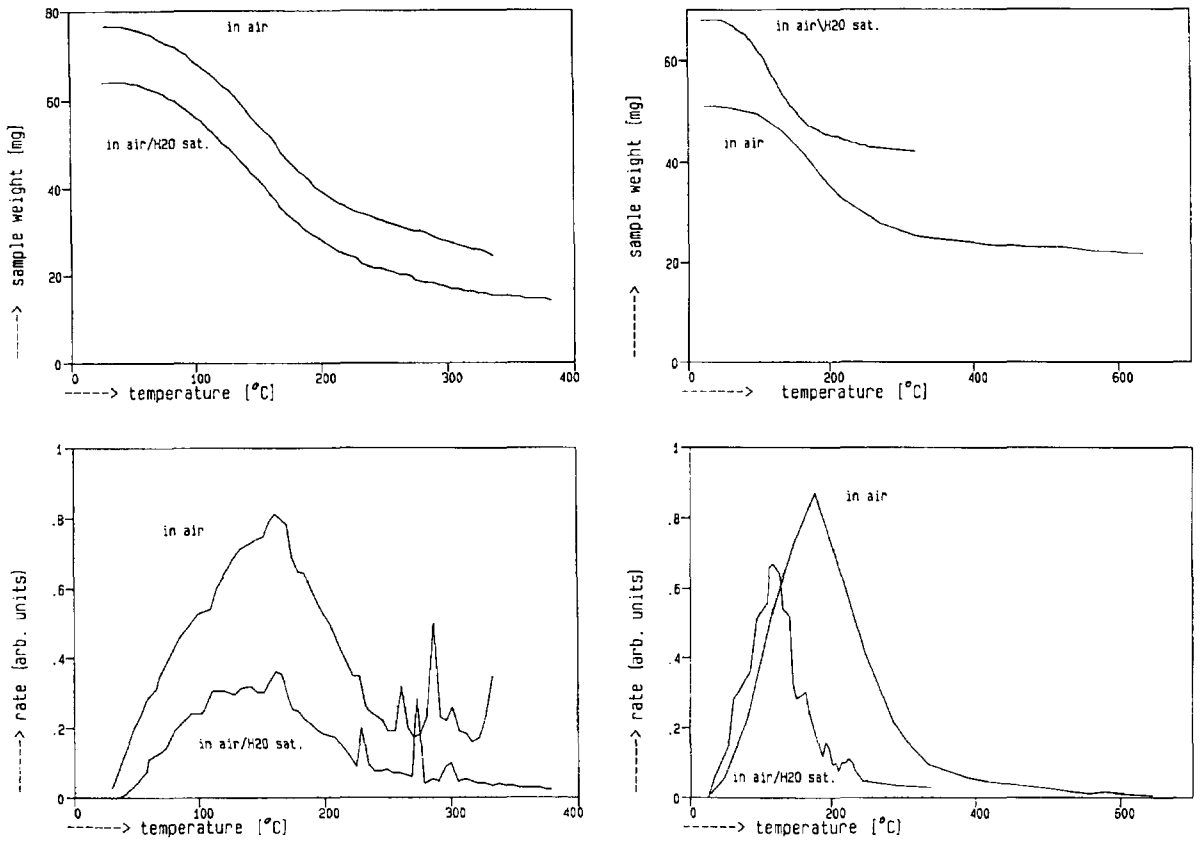

Fig. 3. (a) TGA of NH_4Y in dry and water saturated air respectively; (b) dTGA of NH_4Y in dry water saturated air respectively; (c) TGA and HY in dry and water saturated air respectively; (d) dTGA of HY in dry and water saturated air respectively.

ment with the TGA spectra. From 65°C onwards dehydration is occurring, and a gradually decreasing conductivity is observed. It is expected however, that the ionic conductivity will increase once more beyond about 250°C, when the structure will become essentially that of HY. This however is not relevant for application, because these processes, both complete dehydration and loss of NH_3, appeared to be irreversible in our measurements, in agreement with the literature [14]. So NH_4Y may well be applicable up to 200°C.

For HY the hypothesis of a smaller loss of water in H_2O-saturated ambients as indicated by the TGA results is supported by the observation that the conductivity increases more rapidly with temperature in a wet ambient than in a dry ambient. Hence a slightly higher conductivity is observed above 250°C. The activation enthalpy above 200°C was in both cases about 0.7 eV. Below 200°C the dehydration area is characterized by rather unstable bulk conductivities. Only the measurements in air in this range are represented here. The conductivity was much lower than in NH_4Y, and at room temperature the conductance was too low to be detected reliably with the present equipment.

The dispersions of the zeolites were fitted to an equivalent circuit given in fig. 5. An example of a fit for NH_4Y at 127°C is shown in fig. 6. The temperature dependence of the parameters R_{gb}, Q_{dl} and Q_g for NH_4Y are presented in fig. 7. In the model R_b denotes the bulk resistance. The constant phase element Q_g may be associated with geometrical capacitance. The α value is quite high, indicating the predominant capacitive effects. Below 60°C this element was replaced by a capacitance. Q_{dl} and R_{gb} represent interface effects (blocking and diffusion limited con-

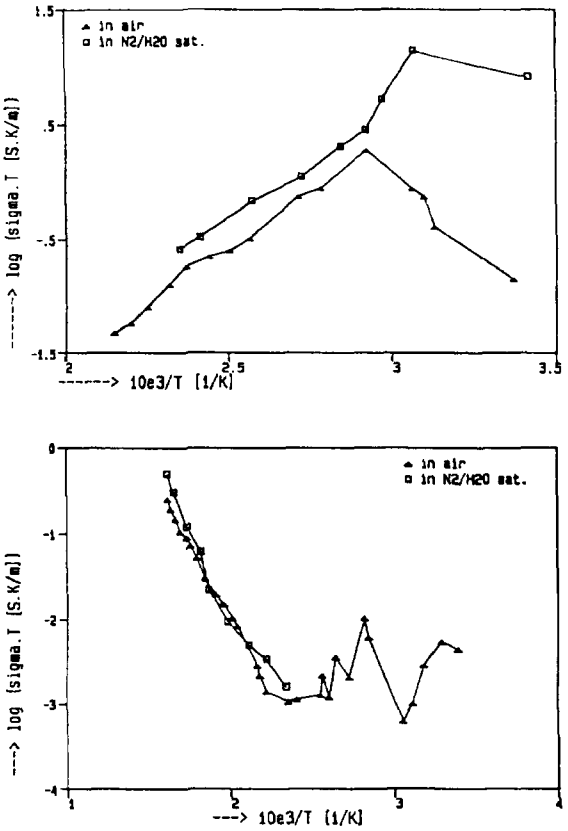

Fig. 4. (a) Arrhenius plot of the bulk conductivity of NH_4Y in dry air and water saturated N_2 respectively; (b) Arrhenius plot of the bulk conductivity of HY in dry air and water saturated N_2 respectively.

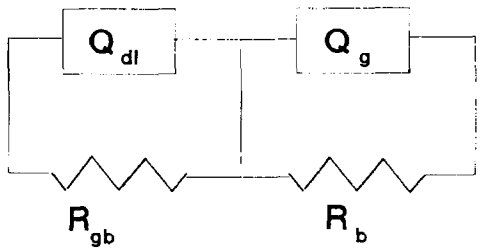

Fig. 5. Equivalent circuit used to fit the dispersions of NH_4Y.

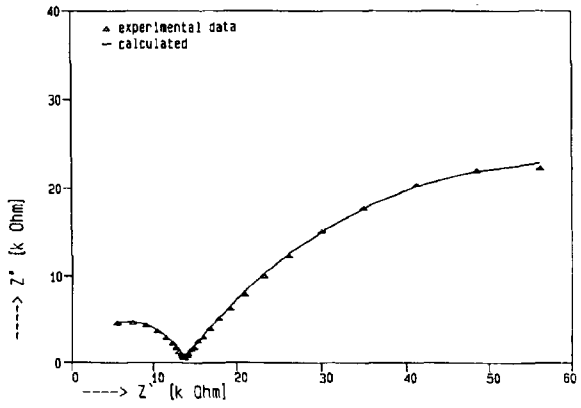

Fig. 6. Example of a non linear least squares fit: NH_4Y in dry air at 127°C.

ductance) and grain boundary resistance, respectively. R_{gb} is decreasing with temperature. Hence it is improbable that this quantity can be assigned to a surface conductance which might be present at low temperatures, but merely with grain boundary effects within the structure. The interface effects are not strongly dependent on temperature. Most of the fits show less than 12% relative error, and from the smooth temperature dependence of the parameters involved one may conclude that one conductance mechanism dominates in the whole temperature range. The highest temperatures could indicate a change, but these points are too few in number to base any conclusion on.

Concerning H_3O^+ β/β″-alumina no references X-ray data seem to exist. The pattern recorded here revealed strong reflections at 5.75, 3.46, 2.88, 2.64 and 2.58 Å spacing, and moderate intensity lines at 4.19, 3.51, 2.18, 2.02, 1.73, 1.64 and 1.415 Å spacing.

Differential TGA revealed two peaks at about 110°C and 260°C, respectively (fig. 8). The high temperature peak can be ascribed to dehydration as has been reported in the literature [11]. The low temperature peak is ascribed to H_2O loss in the surface areas of the grains.

The conductivity of our materials appeared to be in the order of 10^{-5} S/m. Hence it was not tested in a sensor.

The X-ray pattern of $H_{0.34}MoO_3$ revealed the material to be amorphous. This need not be a problem for the use as an electrode as long as a well-fixed hydrogen activity can be established at the interface electrode/electrolyte. TGA measurements showed one peak at about 100°C. Impedance spectra revealed a rather complex behaviour (fig. 9). As in the case of H_3O^+β/β″-alumina, the impedance spectra were not fitted to an equivalent circuit.

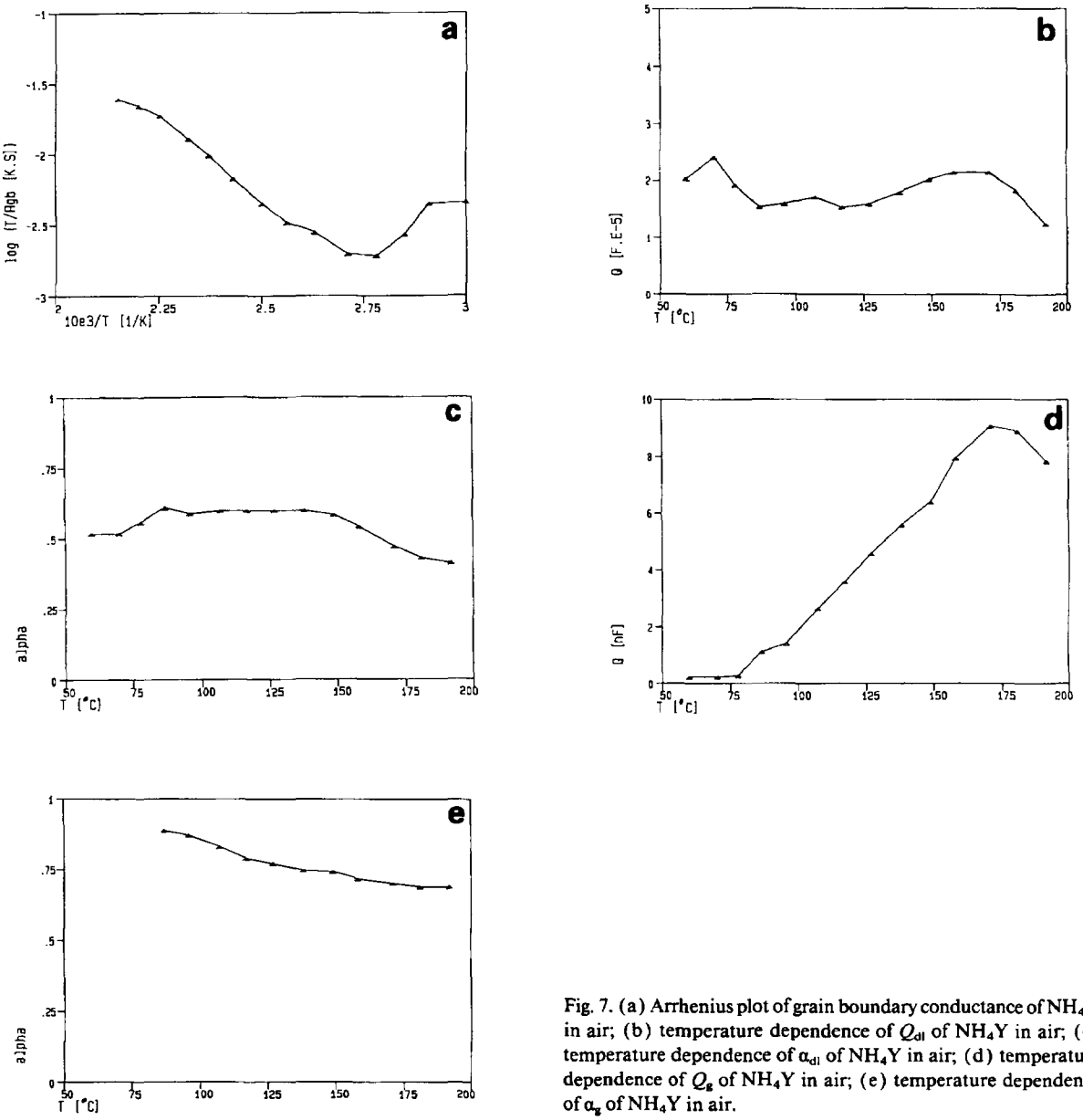

Fig. 7. (a) Arrhenius plot of grain boundary conductance of NH_4Y in air; (b) temperature dependence of Q_{dl} of NH_4Y in air; (c) temperature dependence of α_{dl} of NH_4Y in air; (d) temperature dependence of Q_g of NH_4Y in air; (e) temperature dependence of α_g of NH_4Y in air.

The sensor prototype has been tested on Nernst behaviour in the range from 0 to 100 mole% H_2 in N_2 and response time. Assuming the hydrogen activity at the reference electrode to be constant, the Nernst formula for the cell is

$$E = \Delta E_0' + 2.303 \frac{RT}{nF} \log a_H , \qquad (2)$$

giving a slope of 0.030 V at $T = 28\,^\circ C$ and 0.033 V at $T = 63\,^\circ C$. The response showed excellent agreement with theory at both temperatures (fig. 10). The experimental slopes were 0.031 at 28 °C, and 0.030 at 64 °C. Measurements at higher temperatures will be done in the future.

Response times were all found between two and eight minutes. Some preliminary experiments with

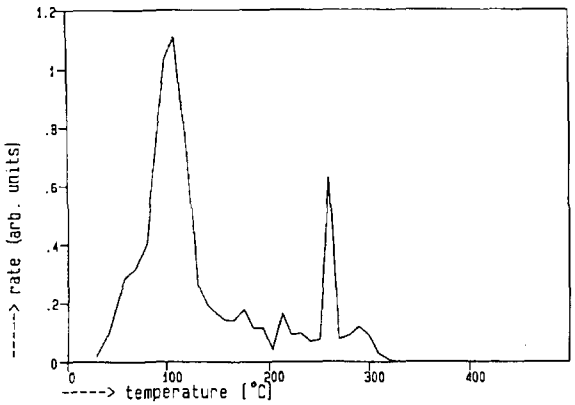

Fig. 8. dTGA of H_3O^+ β/β″-alumina in air.

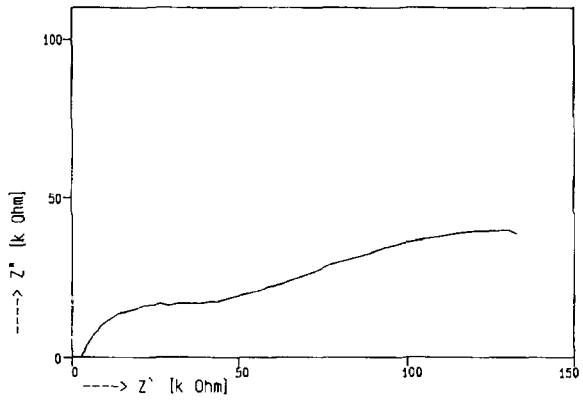

Fig. 9. Example of a dispersion of $H_{0.34}MoO_3$: in air at 60°C.

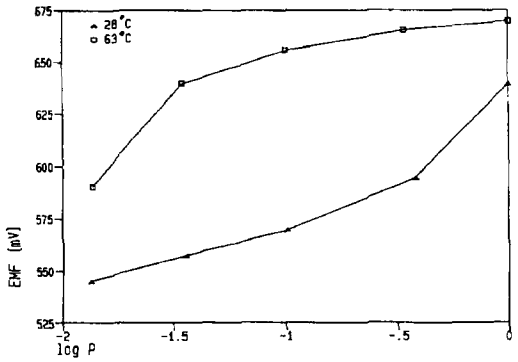

Fig. 10. Dependence of the EMF on P_{H_2} of a probe consisting of $H_{0.34}MoO_3$, NH_4Y and hydrated Pd, at 28 and 63°C respectively.

a sensor using HY as an electrolyte yielded faster response times, even at low temperatures. An example is given in fig. 11.

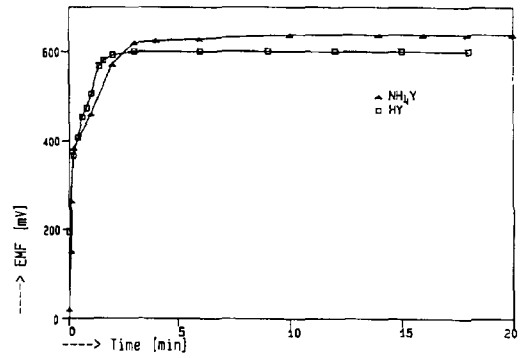

Fig. 11. Response times at 28°C with solid electrolyte NH_4Y and HY respectively.

4. Conclusions

NH_4Y zeolite is a promising candidate for use as a solid electrolyte in hydrogen sensors. Its protonic conductivity is higher than HUP, and the applicable temperature range is wider (20–200°C). In addition, the zeolite HY could be useful between 150 and 250°C, its conductivity being high enough in this temperature region. In the ranges of application the zeolites to not undergo any discontinuity concerning structure and conductance mechanism. In combination with amorphous $H_{0.34}MoO_3$ as solid reference electrode and PdH_x as sensing electrode, a Nernst response can be achieved at least up to 65°C. The response time of the sensor prototype is relatively short.

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