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ORIGINAL PAPER

# The zirconium/hydrogen system as the solid-state reference of a high-temperature proton conductor-based hydrogen sensor

**M. P. Hills · C. Schwandt · R. V. Kumar**

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**Abstract** A new solid-state hydrogen reference electrode has been developed that is based on the two-component two-phase mixture of *β*-zirconium and *δ*-zirconium hydride, and is suitable for use in conjunction with the high-temperature proton-conducting $CaZr_{0.9}In_{0.1}O_{3-\delta}$ solid electrolyte. Coulometric titration studies have confirmed the presence of a true two-phase plateau, existing over a wide composition range, which may be exploited as a precision thermodynamic buffer for reference hydrogen partial pressure. Cell voltage measurements have demonstrated that potentiometric hydrogen sensors incorporating this reference electrode exhibit Nernstian response over a broad range of temperature and hydrogen partial pressure, as well as excellent thermal cycling and long-term stability. The new solid-state hydrogen reference electrode is of considerable technological relevance and has already found application in a commercialised sensor unit.

**Keywords** Calcium zirconate · Proton conductor · Solid electrolyte · Hydrogen · Zirconium · Reference electrode · Sensor

## 1 Introduction

Partially substituted perovskites based on cerates and zirconates like $SrCeO_3$, $BaCeO_3$ and $CaZrO_3$ are the most important class of high-temperature proton-conducting solid electrolytes. In these materials, substitution of the tetravalent cerium or zirconium with trivalent metals introduces negatively charged point defects on the B-sites, and these are charge-compensated by positively charged vacancies on the oxygen sites. Upon exposure to moist atmospheres at elevated temperatures, a quantity of water is dissolved and dissociated in these oxides and proton conduction established. Owing to the wide range of conditions under which proton conduction prevails, these materials have been receiving considerable attention with regard to possible applications in sensors, fuel cells and electrolysers [1–3].

The most straightforward mode of operating a potentiometric solid-state electrochemical gas sensor is by comparing the unknown partial pressure of the relevant gas species at the measuring electrode against the known partial pressure of the same species at the reference electrode. For hydrogen as the analyte, such a sensor can be represented as a hydrogen gas concentration cell

$$H_2', \text{Pt}\,|\text{proton conductor}|\,\text{Pt}, H_2'' \tag{1}$$

where $H_2''$ and $H_2'$ denote hydrogen gas at the measuring and the reference electrode, respectively. The cell voltage obeys the Nernst equation, provided the transference number for protons is close to unity.

$$U = -\frac{RT}{2F}\ln\frac{p''_{H_2}}{p'_{H_2}} \tag{2}$$

where $U$ is the cell voltage, $R$ is the universal gas constant, $T$ is the absolute temperature, $F$ is the Faraday's constant, and $p$ is the partial pressure of the species indicated.

The presence of a known partial pressure of hydrogen at the reference electrode is a fundamental requirement for a potentiometric hydrogen sensor. The most basic solution is to deliver a mixture of hydrogen gas diluted in an inert gas directly to the reference electrode. This has the advantage that the reference hydrogen partial pressure is defined

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expressly and independently of temperature. The disadvantage, however, is that the gas must be supplied from a pressurised bottle, which complicates sensor design as it necessitates a high-temperature hermetic seal between gas supply system and solid electrolyte, and makes sensor usage inflexible. A more preferable solution is to generate a fixed partial pressure of hydrogen at the reference electrode in situ by means of a solid-state reference. This renders the sensor completely self-contained and facilitates its miniaturisation, and also provides for substantially improved thermal shock and thermal cycling resistance.

Early attempts to incorporate solid-state reference electrodes into high-temperature proton conductor-based potentiometric hydrogen sensors involved the application of hydrates, even though these materials actually control the water partial pressure rather than the hydrogen partial pressure at the reference electrode. Iwahara et al. [4–6] used compounds like $Ce_2(SO_4)_3 \cdot 8H_2O$ or the mixture of $AlPO_4 \cdot 0.34H_2O$ and $La_{0.4}Sr_{0.6}CoO_3$ as the reference materials in combination with proton conductors based on $SrCeO_3$ or $CaZrO_3$. Sensor measurements were performed in molten aluminium and a clear response to hydrogen was observed. However, a number of fundamental problems were encountered in that the sensors did not follow the Nernst equation over the entire hydrogen pressure range or exhibited insufficient reproducibility and long-term stability.

Subsequent efforts of integrating solid-state reference electrodes into potentiometric hydrogen sensors involved metal/hydrogen systems, as these are able to generate a thermodynamically fixed hydrogen partial pressure provided a two-phase mixture is present. Zheng et al. [7–9] used a mixture of calcium metal and calcium hydride as the reference material in conjunction with a $SrCeO_3$-based solid electrolyte. Sensor measurements gave a stable voltage for several hours but ultimately showed some drift. This was attributed to the thermodynamic instability of the interface between the electrolyte and the reference electrode, causing the oxide-based electrolyte to be partially reduced by the reactive metal-based reference material.

Recently, it has been demonstrated that a mixture of the solid solutions of hydrogen in $\alpha$-titanium and $\beta$-titanium may be applied as the reference electrode in a potentiometric hydrogen sensor employing the $CaZr_{0.9}In_{0.1}O_{3-\delta}$ solid electrolyte [10]. The sensor obeyed the Nernst equation at temperatures of 773–1,073 K over the hydrogen partial pressure range 10–$10^5$ Pa. Notably, the sensor remained functional over long periods and showed little, albeit non-negligible, drift. A distinct feature of this sensor is that the oxide electrolyte and the metal/hydrogen reference are in a chemically stable contact. The oxygen content of the titanium metal precursor was identified as the critical parameter to achieve this. After empirical optimisation, a combination of materials was arrived at, in which the oxygen content of the metal-based reference material was sufficiently high to preclude reduction of the oxide-based electrolyte but still sufficiently low to not compromise the two-component two-phase approach. Experimentally, the two-phase mixture of hydrogen-containing $\alpha$-titanium and $\beta$-titanium has to be established through coulometric titration of hydrogen, which is due to the narrow composition range over which these two phases co-exist. Owing to the considerable experimental efforts involved, such an approach is inconvenient for the manufacture of a large quantity of sensors. Furthermore, the coulometric titration studies revealed the absence of a true plateau in the hydrogen partial pressure in the small two-phase composition range, and instead displayed a more s-shaped curve which was attributed to impurities in the titanium metal used. Whilst this does not affect the general functioning of the sensor, it may adversely affect long-term performance of the sensor in case small compositional changes in the reference material occur, and has a bearing on reproducibility between different sensors.

The zirconium/hydrogen system potentially offers an advantage over the titanium/hydrogen system regarding its application as the solid-state reference electrode in a potentiometric hydrogen sensor. Figure 1 presents the zirconium/hydrogen phase diagram, and this shows a wide composition range over which the $\beta$-phase and the $\delta$-phase co-exist at the relevant temperatures and at pressures below atmospheric. The $\beta$-phase is a high-temperature phase of zirconium which contains dissolved hydrogen, and the $\delta$-phase is hydrogen-deficient zirconium hydride $ZrH_{2-\delta}$. The subject of this study has been the incorporation of this two-component two-phase mixture into a proton conductor-based potentiometric hydrogen sensor. $CaZr_{0.9}In_{0.1}O_{3-\delta}$ has been selected as the solid electrolyte because of its good mechanical, thermal and chemical stability, as well as its high proton transference number over a wide range of conditions [11–13].

## 2 Experimental

### 2.1 Preparation of solid electrolyte

The solid electrolyte of nominal composition $CaZr_{0.9}In_{0.1}O_{3-\delta}$ was prepared via the conventional solid-state chemical route. Powder precursors of calcium carbonate, $CaCO_3$, zirconium dioxide, $ZrO_2$, and indium sesquioxide, $In_2O_3$, were dried at 373 K for 48 h, before being weighed in the required proportions. The powder mixture was ball-milled in propanol-2 for 24 h, dried, sieved, and calcined at 1,573 K in air for 8 h. The calcined material was milled in propanol-2 for 48 h with additions of 1 mass% of organic

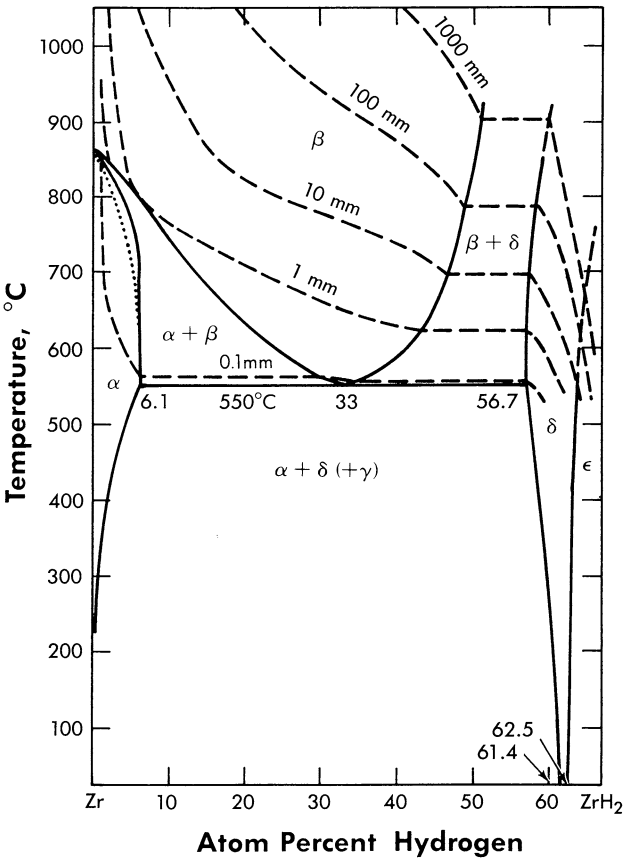

**Fig. 1** Phase diagram of the zirconium/hydrogen system; the *dashed lines* are the equilibrium hydrogen pressures in mm Hg (reproduced from [14] with permission from Elsevier)

binder (80% PVB/20% PVA) and 0.5 mass% of a low molecular weight plasticiser (PEG, $M = 200$ g mol$^{-1}$), and then dried and sieved. The impregnated powder was compacted into thimbles by isostatic pressing at 135 MPa, and the thimbles were sintered at 1,923 K in air for 8 h. The final electrolyte composition was checked by X-ray diffraction analysis and confirmed to be identical with that used previously [10].

### 2.2 Preparation of sealing glass

Sealing glasses were manufactured that are based on the oxides of calcium, aluminium, barium and boron. Compositions presented earlier [15] were adjusted so as to achieve two glasses, denoted CA860 and CA940, with melting points of approximately 1,133 and 1,213 K, respectively. It has been demonstrated that glasses in this system are suitable for usage in hydrogen because of their high redox stability [10]. The glasses were synthesised from oxide or carbonate powder precursors. These were dried, weighed and mixed, and then calcined and melted by heating to 1,473 K for 30 min. The glass melts were allowed to cool, and the solidified melts were ground into glass frits.

### 2.3 Assembly and manufacture of sensor

The full sensor assembly is shown in Fig. 2. A layer of platinum paste was deposited on the inner and outer portions of the sintered solid electrolyte thimble at its closed end, and a coiled platinum wire was fitted to its inner cavity. Firing to 1,273 K in air resulted in the formation of a porous layer of platinum on either side of the electrolyte and an inner electrical connection via the platinum wire. Short lengths of zirconium wire were placed inside the thimble for use as the precursor of the solid-state reference material. The zirconium wire was analysed for oxygen (ONH-2000, Eltra) and found to contain approximately 1,500 ppm by mass of oxygen. Suitably shaped alumina pieces and yttrium oxide powder were used to occupy the remaining dead volume. Glass frit of type CA860 or CA940 was mixed into a slurry with acetone and deposited over the top of the sensor assembly with a paintbrush.

The reference electrode of the sensor was formed by first hydriding the zirconium metal and then hermetically sealing the inner cavity with the sealing glass. To this end, the sensor assembly was placed in the alumina tube of an electric furnace and heated in an atmosphere of pure dry hydrogen gas. On heating, the furnace was first held at 523 K for 3 h in order to allow uptake of a quantity of hydrogen into the zirconium metal. The temperature was then increased at a rate of 5 K min$^{-1}$ to 1,133 or 1,213 K and held for 10 min, so as to melt the CA860 or CA940 glass and form a hermetical seal over the just created reference electrode. On cooling, a rate of 5 K min$^{-1}$ was

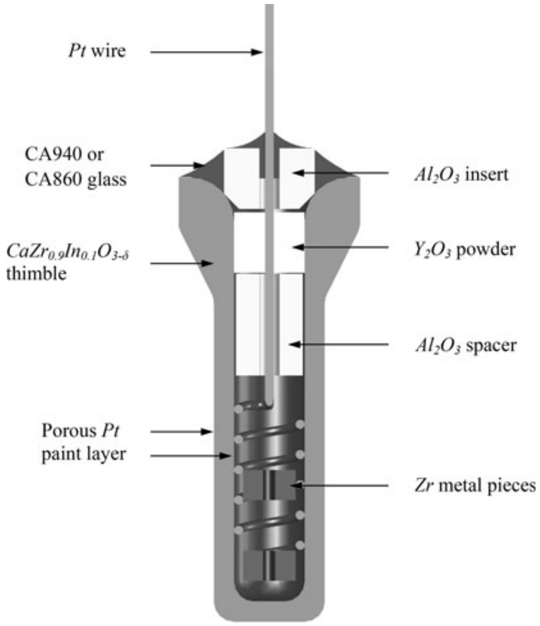

**Fig. 2** Schematic of sensor assembly, showing individual components and materials

applied, except for the range 973–773 K where a rate of 0.5 K $\mathrm{min}^{-1}$ was used to ensure stress relief in the glass during its passage through the glass transition temperature.

### 2.4 Electrochemical measurements

Two types of electrochemical studies, coulometric titrations and cell voltage measurements, were performed. For these, sensors prepared as detailed above were mounted in a purpose-built alumina holder. An electrical furnace was used to control temperature, and a gas mixing device was used to establish different hydrogen partial pressures with argon as the balance. All gas mixtures were humidified by bubbling through distilled water at room temperature and applied at a flow rate of 200 mL $\mathrm{min}^{-1}$. Platinum leads were used to make electrical connections to the sensor electrodes. The tip of an unsheathed R-type thermocouple was positioned next to the closed end of the sensor to determine its precise operating temperature.

Coulometric titrations were performed on sensors that had been sealed at 1,133 K with the CA860 glass. Titrations were made at 973 and 1,023 K in pure hydrogen using a constant current source (manufactured in-house). The current was 30 μA at 973 K and 100 μA at 1,023 K, and selected such that the applied voltage was less than 300 mV and thus well below the decomposition potential of the solid electrolyte. The current was interrupted periodically, and the sensor voltage recorded with a high-impedance electrometer (manufactured in-house) after waiting 30 min for readings to stabilise.

Cell voltage measurements were performed with various sensors that had been sealed at 1,213 K with the CA940 glass. Voltage measurements were made at temperatures 773–1,073 K in the hydrogen partial pressure range 10–$10^5$ Pa using a high-impedance electrometer (manufactured in-house). Reproducibility of the cell voltage was examined by thermal cycling between 973 K and room temperature, and long-term stability was assessed by soak testing at 973 K for 100 h.

## 3 Results and discussion

### 3.1 Coulometric titrations

Figures 3 and 4 present the results from two coulometric titration experiments performed at 973 and 1,023 K, respectively, in pure hydrogen. The origin of the abscissa corresponds to the as-sealed sensor assembly, and the amount of charge passed refers to hydrogen removed from the sealed inner compartment of the sensor during titration. The left-hand ordinate gives the cell voltage before and after the various titration intervals. By combining Eq. 1 with the measured cell voltage and the known hydrogen partial pressure in the surrounding gas, it is possible to calculate the partial pressure of hydrogen in the inner compartment. This pressure is given by the right-hand ordinate.

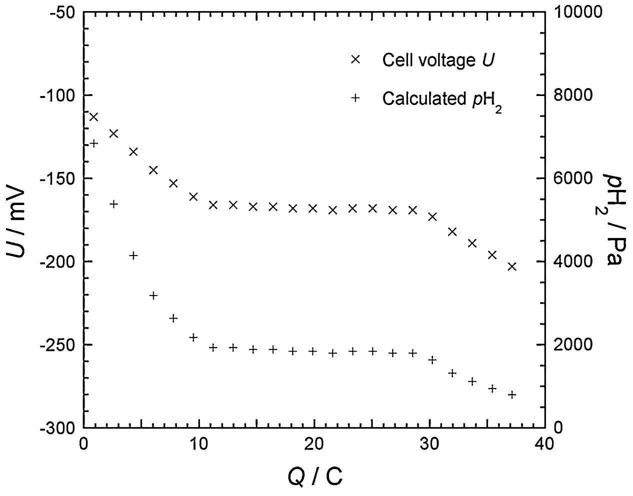

**Fig. 3** Results from a coulometric titration experiment carried out at the temperature of 973 K in an atmosphere of pure hydrogen gas. The amount of zirconium wire used was 28.9 mg, and sealing was performed at 1,133 K in pure hydrogen

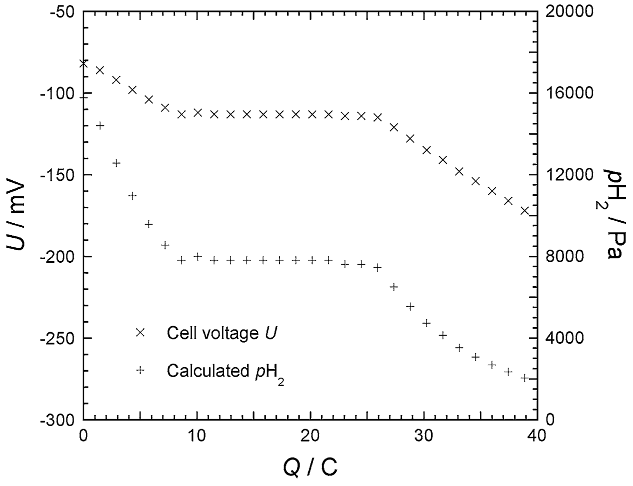

**Fig. 4** Results from a coulometric titration experiment carried out at the temperature of 1,023 K in an atmosphere of pure hydrogen gas. The amount of zirconium wire used was 32.0 mg, and sealing was performed at 1,133 K in pure hydrogen

In both coulometric titration experiments shown in Figs. 3 and 4, the hydrogen partial pressure in the sealed inner compartment of the sensor assembly initially falls, then reaches a plateau, and finally falls again. This behaviour can be readily understood by considering the phase fields of the zirconium/hydrogen system. Figure 5 displays an extensive collection of literature data concerning pressure isotherms in the zirconium/hydrogen system for different temperatures. During manufacture, the sensor assembly was heated to 1,133 K in pure hydrogen. This state corresponds to point A on the figure and is inside the $\delta$-zirconium phase field. As a hermetic seal is formed at point A, the H-to-Zr atom ratio in the inner compartment is established. The state of the system at lower temperatures is defined by the dotted line extending downward from point A. Thus, at the start of a titration experiment at 973 or 1,023 K, single-phase $\delta$-zirconium hydride is the equilibrium phase. As hydrogen is electrochemically removed from the inner compartment, the H-to-Zr atom ratio is gradually lowered, and there is a corresponding reduction in the partial pressure of hydrogen in equilibrium with the $\delta$-zirconium hydride. As the removal of hydrogen progresses, the system leaves the single-phase region and enters a two-phase region where $\beta$-zirconium and $\delta$-zirconium hydride are in equilibrium. In this region the partial pressure of hydrogen is thermodynamically fixed according to Gibbs' phase rule. It is apparent from Fig. 5 that there is a wide composition range over which the $\beta$-phase and $\delta$-phase co-exist, and this is reflected in the extended flat plateaux visible in Figs. 3 and 4 where the partial pressure of hydrogen remains constant whilst the H-to-Zr atom ratio is continuously lowered. As more hydrogen is removed, the system eventually leaves the two-phase region and enters a single-phase region where $\beta$-zirconium is the equilibrium phase. In this region the equilibrium partial pressure of hydrogen is no longer fixed, and gradually declines as hydrogen continues to be removed. Overall, the results from the coulometric titration experiments are consistent with the information on the zirconium/hydrogen phase diagram.

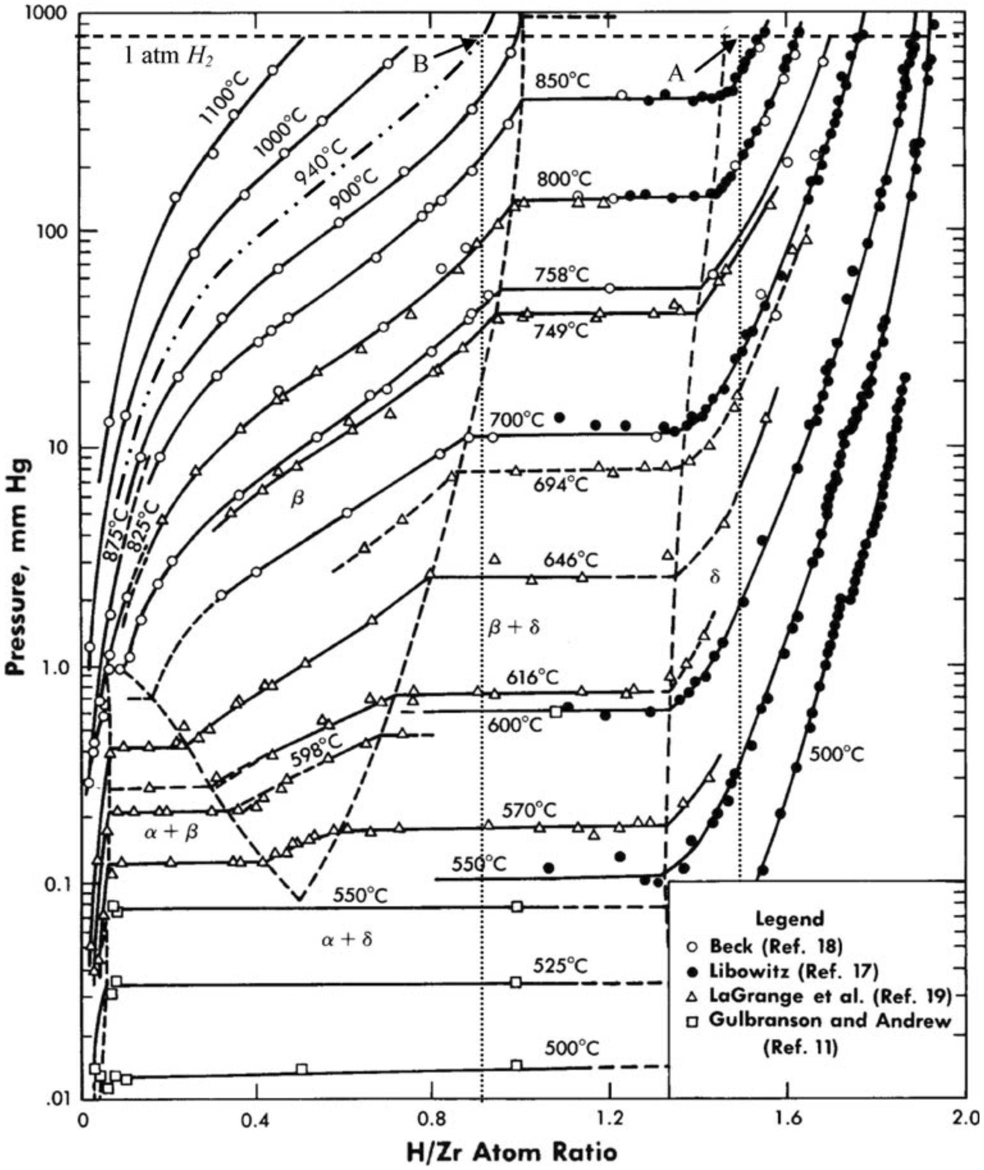

**Fig. 5** Pressure isotherms for the zirconium/hydrogen system for different temperatures. The isotherm for 940 °C is an extrapolation derived on the basis of the original data in the figure (reproduced and adapted from [14] with permission from Elsevier)

The existence of a flat plateau in hydrogen partial pressure over a wide composition range is highly desirable for a reference electrode of a potentiometric hydrogen sensor. In practical applications there will always be a tendency for composition at the reference electrode to change when there is a difference in partial pressure of hydrogen across the sensor. Compositional changes may occur as a result of physical transport of hydrogen through porosity in the solid electrolyte body and/or imperfections in the glass seal; and even if these are negligible, a small quantity of hydrogen will be transferred electrochemically across the electrolyte due to diffusion of minority charge carriers. The existence of a two-phase mixture of $\beta$-zirconium and $\delta$-zirconium hydride hence provides an effective thermodynamic buffer that ensures that the reference hydrogen partial pressure remains constant even if the hydrogen content is subject to some variation. This renders the hydrogen reference electrode based on the broad $\beta + \delta$ phase field of the zirconium/hydrogen system superior to that based on the narrow $\alpha + \beta$ phase field of the titanium/hydrogen system described in an earlier study [10].

### 3.2 Cell voltage measurements

It is possible to achieve the desired two-phase mixture of $\beta$-zirconium and $\delta$-zirconium hydride by way of coulometric titration of hydrogen from essentially any starting composition in the zirconium/hydrogen system. However, this method of establishing a reference electrode is inconvenient when preparing a large number of sensors. By examining Fig. 5, it is apparent that the two-phase $\beta + \delta$ mixture may be attained in an alternative way. This consists in forming the hermetic glass seal of the sensor assembly at 1,213 K in pure hydrogen. This state corresponds to point B on the figure and is inside the $\beta$-zirconium phase field. On cooling, the system follows the dotted line extending from point B and moves into the two-phase $\beta + \delta$ field. Thus, at a typical sensor operating temperature of around 973 K, the reference electrode consists of a two-phase mixture and the reference hydrogen partial pressure becomes thermodynamically fixed. It is evident that this single-step manufacturing process is advantageous over the two-step process involving coulometric titration.

Figure 6 compiles the cell voltages of a sensor, whose reference electrode compartment had been sealed at 1,213 K in pure hydrogen, when measured over a temperature range 773–1,073 K and a hydrogen partial pressure range in the external gas of 10–$10^5$ Pa. The results prove that sensor response is fully Nernstian under the conditions investigated. Response times to changes of gas composition were on the order of minutes.

Figure 7 presents the cell voltages of numerous sensors, whose reference electrode compartments had been sealed at 1,213 K in pure hydrogen, when operated at the temperatures of 873, 973 and 1023 K under an external hydrogen partial pressure of 1,000 Pa. It is seen from the figure that there is good reproducibility between the various sensors.

As discussed, the partial pressure of hydrogen inside the sealed sensor reference compartment may be calculated by

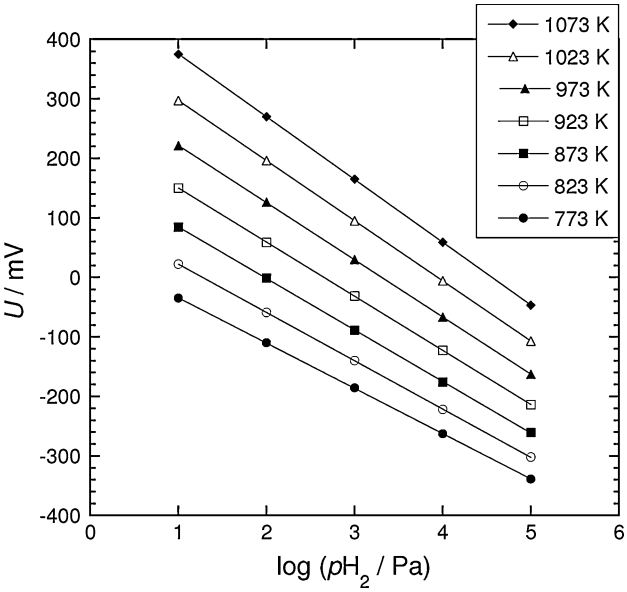

**Fig. 6** Cell voltage measurements at temperatures ranging from 773 to 1,073 K and external hydrogen partial pressures ranging from 10 to $10^5$ Pa. The *lines* through the measured data have been calculated by linear regression; for each temperature the slope of the line agrees to better than 1% with the theoretical Nernstian slope of $-(2.303RT)/(2F)$ (note that the reference electrode is slightly outside the two-phase $\beta + \delta$ field at 1,073 K)

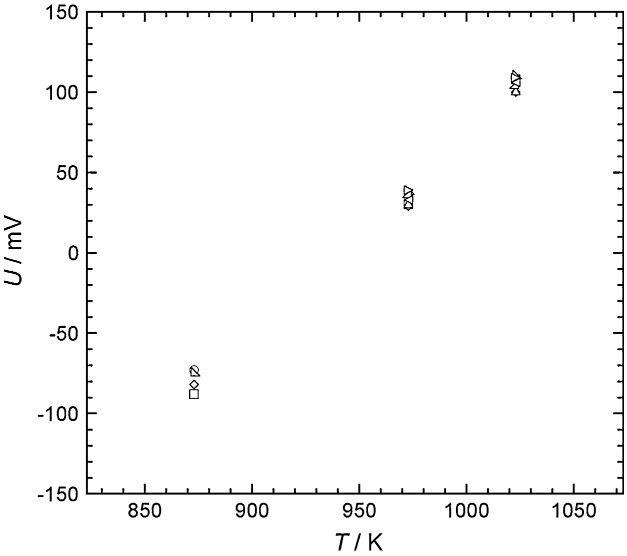

**Fig. 7** Cell voltage measurements on nine different sensors at the temperatures 873, 973 and 1023 K and at the external hydrogen partial pressure of 1,000 Pa

means of Eq. 1 from the measured cell voltage and the known hydrogen partial pressure in the surrounding gas. Figure 8 presents the hydrogen partial pressures in the reference compartment calculated from the data in Fig. 7 as well as the hydrogen pressures extracted from the pressure isotherms in Fig. 5. The type of presentation has been chosen because, for a constant enthalpy of solution, the dependence of logarithm of pressure on reciprocal temperature should be linear, as indicated by the trend line through the literature data. Overall, Fig. 8 shows that there is a fair agreement between the data obtained from the cell voltage measurements and the data derived from Fig. 5.

It is noted that the calculated hydrogen partial pressures inside the sensor reference compartment shown in Fig. 8, as well as the hydrogen partial pressure plateaux in Figs. 3 and 4, are marginally, but consistently, higher than would be expected from the literature data, and it is also seen from Fig. 8 that this tendency increases with increasing temperature. The reason for this deviation is suspected to lie in the transference properties of the $CaZr_{0.9}In_{0.1}O_{3-\delta}$ solid electrolyte. It is well established that oxide ion conductivity occurs in $CaZr_{0.9}In_{0.1}O_{3-\delta}$ at very small oxygen partial pressures, even if the hydrogen partial pressure is high, and rises with temperature [16, 17]. In a foregoing study on the application of the titanium/hydrogen system as the solid-state reference electrode in the given type of sensor, a systematic investigation of this issue was possible, as titanium metal specimens with different and well-defined oxygen contents are readily available commercially [10]. In that study it was concluded that the oxygen content in the titanium metal precursor has a critical impact on the functioning of the reference electrode, and that very low oxygen contents in the metal give rise to an extent of oxide ion conductivity in the solid electrolyte. For a non-zero transference number for oxide ions, the gradient in oxygen partial pressure across the sensor under typical measuring conditions then acts to make the sensor voltage more positive, which in turn indicates an apparently increased hydrogen partial pressure in the reference compartment. In the zirconium/hydrogen system a similar situation will apply, but a rigorous analysis is difficult because of the lack of suitable samples. However, the observation that the reference hydrogen partial pressures in this study appear to be slightly higher than expected on the basis of known data is again consistent with the proposition of a small but non-negligible degree of oxide ion transference across the electrolyte. Whilst of academic interest, this phenomenon does not adversely affect sensor performance. The only practical implication is that sensors intended for use in high-precision measurements require initial calibration at operating temperature.

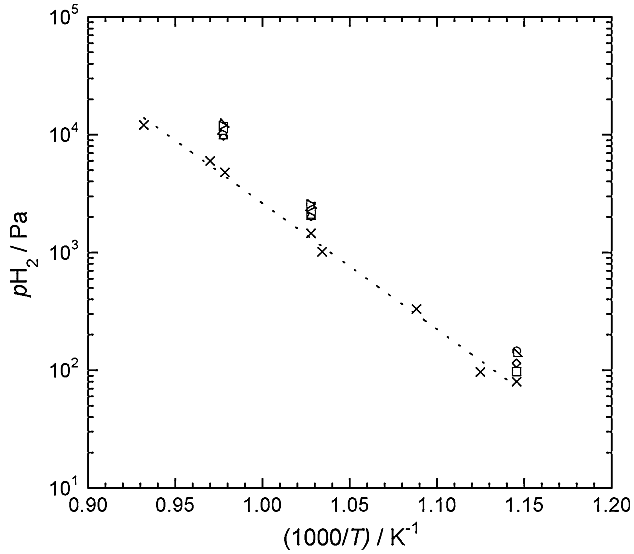

**Fig. 8** Hydrogen partial pressure inside the sensor reference compartment at the temperatures 873, 973 and 1023 K, as calculated from cell voltage measurements in Fig. 7; the hydrogen partial pressures denoted by *crosses* and connected by the *dotted trend line* are extracted from Fig. 5

Additional sensor experiments were performed in order to assess practically relevant aspects like reproducibility and long-term stability of the sensor signal. In Fig. 9, cell voltages were recorded during thermal cycling of a sensor between 973 K and room temperature, and the results show that the sensor signal reproducibly returns to the same value after repeated thermal cycling. In Fig. 10, cell voltages were monitored during soak testing at 973 K over 100 h, and it is seen that the sensor signal exhibits excellent long-term stability throughout the entire run. Overall, the results in Figs. 9 and 10 indicate reliable and robust sensor performance.

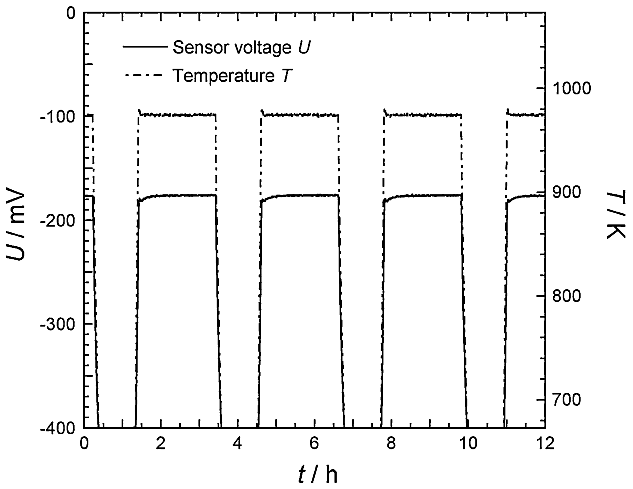

**Fig. 9** Cell voltage measurements during thermal cycling between 973 K and room temperature in pure hydrogen gas

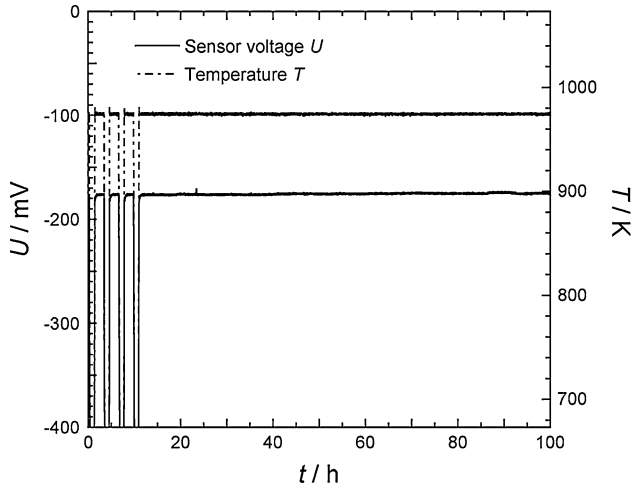

**Fig. 10** Cell voltage measurements during soak testing at 973 K in pure hydrogen gas

## 4 Conclusions

A new solid-state hydrogen reference electrode has been developed that is based on the zirconium/hydrogen system and may be applied in combination with the high-temperature proton-conducting $CaZr_{0.9}In_{0.1}O_{3-\delta}$ solid electrolyte. Coulometric titration studies have confirmed that a true plateau in hydrogen partial pressure exists over a wide composition range, corresponding to the two-phase equilibrium between $\beta$-zirconium and $\delta$-zirconium hydride. For practical purposes, this two-phase mixture may conveniently be achieved in a single manufacturing step, without the need for coulometric titration. Cell voltage measurements with hydrogen sensors relying on the new reference electrode have demonstrated Nernstian response over a broad temperature and hydrogen partial pressure range, as well as excellent thermal cycling and long-term stability.

There are many practical applications for potentiometric hydrogen sensors with this type of reference electrode, and it has already found use in the ALSPEK H sensor for measurement of dissolved hydrogen in molten aluminium [18–20]. Other foreseeable applications are in fuel cell gas analysis, gas purity measurement, and process control.

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