# Electrochemical moisture analysis by combining oxygen- and proton-conducting ceramic electrolytes

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## ARTICLE INFO

## ABSTRACT

The fabrication and characterization of a new intermediate-temperature electrochemical cell for analyzing moisture concentrations in gas mixtures are discussed in the present investigation. The as-fabricated electrochemical cell consists of a diffusion barrier and two ceramic materials based on a yttria-stabilized zirconia (YSZ) electrolyte with unipolar oxygen ion conductivity and a Sr-doped lanthanum yttrate ($La_{0.9}Sr_{0.1}YO_{3-\delta}$, LSY) electrolyte with proton transport properties. The possibility of measuring humidity in a nitrogen atmosphere is demonstrated and the operational capability of the cell is evaluated. The original design of the proposed electrochemical cell opens new opportunities in electrochemical analysis and in the application of proton-conducting electrolytes, including the simultaneous measurement of the concentration and the mutual diffusion coefficient of water in gases.

## 1. Introduction

High-temperature proton conductors (HTPCs) have found applications in a range of intermediate- and high-temperature devices, including solid oxide fuel cells (or protonic ceramic fuel cells) [1–3], electrolysis cells [4], hydrogen permeating membranes [5] and reformers/converters [6]. These systems can also be used for analytical purposes, for example, in electrochemical sensors for hydrogen or moisture detection [7–9]. The presence of proton transport in HTPCs along with an oxygen ion transport allows the functionality of such devices to be extended and thus the concentration/activity of hydrogen or hydrogen-containing compounds to be determined in gases [10,11], melts [12,13] and solids [14].

There are different types of electrochemical cells based on proton-conducting ceramic electrolytes, which operate in amperometric [15, 16], conductimetric [17,18] or potentiometric [12–14] sensor modes. Only sensors of the last two types have been proposed for the analytical measurement of humidity. For example, a galvanic cell based on $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ (SCY) was proposed by Iwahara et al. in 1983 [19] to determine the pressure of water vapor in air (from 0.008 to 0.135 atm). Their next work [20] had a similar aim, and another design of the SCY-based electrochemical cell was presented. It should be noted that the proposed cells showed a clear response to the variation in the partial pressure of the water vapor; however the experimental results were found to differ from the theoretically predicted values. This can be explained by the choice of material, because under working conditions the SCY electrolyte exhibits electron and oxygen-ion conductivity along with the proton one [21], which causes the observed disparities. From this viewpoint, proton-conducting materials based on $Ba(Ce,Zr)O_3$ [10,12,15], $CaZrO_3$ [11,13,17] or $LaYO_3$ [16] would seem to be more suitable electrolytes for sensors due to their negligible n-type electronic conductivity in reducing atmospheres, and lower p-type electronic conductivity in oxidizing atmospheres [6].

In the present investigation a new electrochemical cell and a method for the determination of moisture concentration at intermediate temperatures are presented. The novelty of the proposed electrochemical cell rests in the fact that moisture concentration is analyzed using an amperometric approach rather than a potentiometric one. In order to obtain the desired results, a proton-conducting electrolyte based on $LaYO_3$ was selected and used together with the traditional oxygen-conducting zirconia material.

## 2. Experimental

Fig. 1 depicts the operating principles of the as-fabricated electrochemical cell. It can be seen that the cell consists of two ceramic electrolytes, YSZ and LSY, and a capillary tube. Commercially available YSZ was chosen as a well-known electrolyte providing oxygen-ion transport over a wide temperature range, excellent mechanical properties (high mechanical strength and toughness, low thermal expansion coefficient value) and good thermodynamic stability [22]. The proton-conducting

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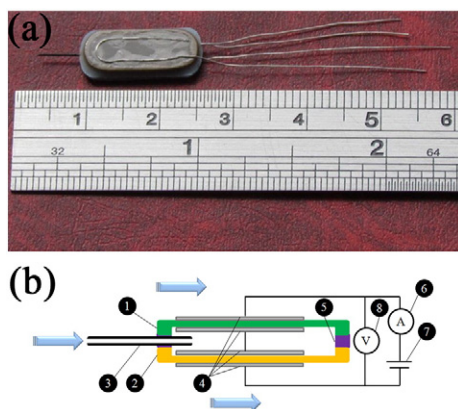
**Fig. 1.** (a) The general view and (b) the working scheme of the electrochemical cell based on combined oxygen- and proton-conducting electrolytes: 1 – YSZ electrolyte, 2 – LSY electrolyte, 3 – capillary, 4 – platinum electrodes, 5 – high-temperature glass sealant, 6 – amperometer, 7 – DC current source, 8 – voltmeter.
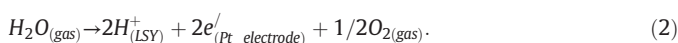
electrolyte ($La_{0.9}Sr_{0.1}YO_{3-\delta}$, LSY) was chosen on the basis of recently obtained results [23,24]. In particular, this material exhibits a very wide electrolytic domain boundary, a low contribution of hole conductivity in oxidizing atmospheres and a thermal expansion coefficient close to that of YSZ [23]. In reducing atmospheres, materials based on $LaYO_3$ exhibit almost protonic transport over a wide temperature range [24]. Porous platinum electrodes were formed on both sides of each individual ceramic material; this was followed by high-temperature annealing (1200 °C, 1 h) to achieve a good contact between the electrodes and the electrolyte. Platinum wires were then attached to the porous electrodes, painted with platinum paste and calcined at 900 °C for 1 h. Finally, the capillary tube and the electrolytes with the symmetrically formed electrodes were joined together with the aid of a high-temperature silicate glass sealant [10]. The capillary tube allows communication of the gas between internal and external spaces (Fig. 1b).

The distinctive feature of the as-fabricated electrochemical cell is the fact that the inner electrodes were shorted together, forming a common electrical circuit. The sensor was placed in the oven, which was heated up to the required temperature (most of the electrochemical investigations were performed at 650 °C). The external spaces of the cell were fed by $N_2 + H_2O$ gas mixtures with a water vapor partial pressure ($pH_2O$) ranging from 0.004 to 0.078 atm. $pH_2O$ values of 0.023–0.078 atm were obtained by $N_2$ saturation in a temperature-controlled bubbler (18–40 °C); the lowest $pH_2O$ value was achieved by mixing a dry $N_2$ atmosphere ($pH_2O = 1 \cdot 10^{-4}$ atm, nitrogen was passed through a zeolite column) with $N_2$ containing $pH_2O = 0.023$ atm, taking into account the flow rates. Prior to the measurements, the cell was kept at the specified conditions for a period of 1–2 h for equilibrium to be attained between the internal and external spaces of the cell on the one hand and between the ceramic electrolytes and the gas atmosphere on the other. A DC voltage (U) was then applied externally to the outer electrodes of the cell in such a manner that "plus" corresponded to the outer electrode of the oxygen-ion electrolyte and "minus" to that of the proton-conducting electrolyte. A GPD-723-03S device was used as a direct current source.
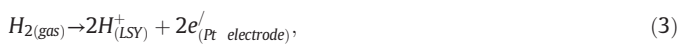
The decomposition of water mixed with $N_2$ is initiated by the direct current supply. As a result, the following electrochemical reactions take place on the inner electrode of YSZ:

$$H_2O_{(gas)} + 2e'_{(Pt\ electrode)} \rightarrow O^{2-}_{(YSZ)} + H_{2(gas)}, \tag{1}$$
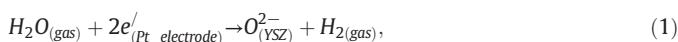
and on the inner electrode of LSY:

$$H_2O_{(gas)} \rightarrow 2H^+_{(LSY)} + 2e'_{(Pt\ electrode)} + 1/2O_{2(gas)}. \tag{2}$$

The as-formed molecular hydrogen and oxygen can also be pumped out as follows:

$$H_{2(gas)} \rightarrow 2H^+_{(LSY)} + 2e'_{(Pt\ electrode)}, \tag{3}$$

$$1/2O_{2(gas)} + 2e'_{(Pt\ electrode)} \rightarrow O^{2-}_{(YSZ)}. \tag{4}$$

In this way, the water flow electrochemically pumped out from the internal space of the cell is compensated for equilibrium reasons by the $H_2O + N_2$ flow permeating through the diffusion barrier from the external space to the internal one. According to Faraday's law, this flow corresponds to an electrical current, the amount of which (measured using a digital GDM 8246 multimeter) firstly increases and then stabilizes with the gradual increase of the applied voltage. The unchanged value of the current (limiting current) with varying applied voltage corresponds to the steady-state condition, when the concentration of water inside the electrochemical cell becomes negligible. The limiting current ($I_{lim}$) in the case of low partial pressure of the analyzed component (less than 0.1 atm) can theoretically be found using the following eq. [25]:

$$I_{lim} = \frac{2F \cdot D(H_2O) \cdot S \cdot P}{RTL} pH_2O, \tag{5}$$

where $S$ is the inner diameter of the capillary, $P$ is the absolute pressure of the analyzed gas, $L$ is the length of the capillary and $D(H_2O)$ is the diffusion coefficient of the water, which depends on temperature and pressure [26]. It can be seen from Eq. (5) that the limiting current level depends linearly on $pH_2O$. This makes it possible to obtain a calibration curve, which can then be used to analyse unknown moisture concentrations in gas mixtures.

## 3. Results and discussion

Fig. 2a shows the typical volt-ampere characteristics of the electrochemical cell operating in $N_2 + H_2O$ gas atmospheres. These data reveal that the current increases with increasing applied voltage until the limiting current is reached; its value depends on the water vapor pressure in the atmosphere being analyzed. For example, the current stabilizes at a voltage of 0.4 V at $pH_2O = 0.004$ atm and at a voltage of 0.9 V at $pH_2O = 0.078$ atm (650 °C). At the same time, as the $pH_2O$ level increases the voltage at which the limiting current is obtained shifts to higher $U$ values, showing that a higher potential difference must be applied to the cell in order to decompose the additional amounts of water vapor. As can clearly be seen in Fig. 2b, the limiting current depends linearly on $pH_2O$, corresponding qualitatively to Eq. (5). Since this equation includes known or easily calculated parameters, it is possible to demonstrate the quantitative agreement of the experimental data with the calculated ones. The value of $D(H_2O)$ can be calculated using the following equation:

$$D(H_2O) = D_o(H_2O) \left(\frac{T}{T_o}\right)^n \frac{P_o}{P}, \tag{6}$$

where $D_o(H_2O)$ is the diffusion coefficient at $T_o = 273.15$ K and $P_o = 1$ atm, $n$ is an empirical coefficient which is equal to 3/2 for an ideal gas and higher for real gases, sometimes reaching 2 [26]. By combining Eqs. (5) and (6), one can obtain:

$$I_{lim} = \frac{2F \cdot D_o(H_2O) \cdot S \cdot P_o}{R \cdot L \cdot (T_o)^n} \cdot pH_2O \cdot T^{n-1}. \tag{7}$$

Expression (7) is very useful, since the unknown parameters $D_o(H_2O)$ and $n$ can be estimated experimentally on the basis of the temperature dependence of the limiting current (Fig. 3a). Taking the logarithmic Eq. (7), these parameters can be graphically extracted by