Solid-state hydrogen sensors based on calixarene—12-phosphatotungstic acid composite electrolytes

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A R T I C L E   I N F O

A B S T R A C T

An electrochemical system sensitive to hydrogen was studied. A composite proton conductor based on calixarene sulfonic acid and 12-phosphotungstic acid was used as a solid electrolyte membrane. The system is tolerant to CO impurities (up to 200 ppm) in H_2. The catalytic properties of the composite electrolyte can be described using percolation theory. Variation in the composition of the solid composite electrolyte in the investigated system allowed to adjust its properties and improve the performance of potentiometric hydrogen sensors under ambient conditions.

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1. Introduction

The development hydrogen energetics have become essential for alternative energy sources and control of these important technological processes, such as biomass processing, by gasification, obtaining syngas and garbage incineration, which are carried out in the presence of CO [1–3]. However, for such use of hydrogen there are major challenges in its storage, transport and distribution, and as a colourless and odourless gas with a lower explosive limit (LEL) of 4% in air there are safety concerns too. Accordingly it is important to have access to robust, sensitive, reliable, compact, low cost and low power consumption hydrogen sensors operating under ambient conditions for early detection of any leakage (especially in the presence of CO impurities).

Potentiometric solid-state electrochemical sensors for the determination of the hydrogen concentration in air under ambient conditions have been developed and used for a long period of time. These sensors typically consist of a proton-conductive membrane and two electrodes (i.e., working (sensing) and reference) [4–7].

The reference electrode maintains a constant potential regardless of the environmental changes. Solid electrodes (typically PbO_2 and TiH_2 systems [5]) with high exchange currents with electrolyte are mainly used for such tasks.

The working electrode typically consists of highly dispersed platinum on different supporting materials (carbon or oxides). By adjusting the composition of the support, the sensor performance and sensitivity can be increased, and its tolerance to many impurities, such as CO, can be improved.

In general, proton-conductive membranes for ambient conditions hydrogen sensors consist of Nafion-like polymers [4] or various crystalline conductors with good conductive properties (i.e., uranyl phosphate [6] or heteropoly compounds (**HPC**) [8–10]). Several studies have demonstrated that HPC does not act as an inert conductor in processes involving hydrogen and oxygen. HPC catalyzes many electrochemical processes including the oxidation of carbon monoxide [11,12]. In addition, their electrocatalytic properties are affected by both the anion composition (i.e., type of heteropoly acid) and the cation type (if HPC is used as a salt) [13].

The main disadvantage of HPC is that it is easily dehydrated with a loss of conductivity at temperatures above 40 °C or at humidity. Heteropoly acids and their soluble salts exhibit a substantial loss of conductivity along with a temperature decrease due to a high activation energy (0.35–0.45 eV).

Recently, we have discovered a new class of highly effective proton conductors (i.e., calixarene sulfonic acids). These conductions

have several advantages compared to HPC or Nafion. Their highly conductive phase exists in a much wider temperature range, and the relationship between conductivity and ambient humidity is considerably weaker [14–16]. Calixarene sulfonic acids also possess high plasticity, which allows for the production of sensors without the introduction of non-conductive plasticizers, such as polyethylene, into the solid electrolytes. There is only one work deal with calixarene in sensors [17] used as stabilizer for carbon nanomaterials in liquid electrolyte.

The purpose of this study was to investigate the influence of the composition of the electrolyte based on calixarene sulfonic acids and their composites with 12-phosphotungstic acid on the sensitivity, performance and stability of an ambient conditions potentiometric hydrogen sensor and its tolerance to carbon monoxide.

2. Materials and methods

2.1. Materials and synthesis

The 5,11,17,23-tetra-sulpho-25,26,27,28-tetrahydroxy calix(4)arene (calixarene) was synthesized by sulfonation [18] of the starting 25,26,27,28-tetrahydroxy calix(4)arene, which was purchased from abcr GmbH, Germany. A commercial 12-phosphotungstic acid (PTA) (Acros organics, Belgium) was purified using ether extraction as described in Ref. [19].

The composite electrolytes were derived via the evaporation of aqueous solutions consisting of PTA and calixarene with different molar ratio at 60 °C followed by grinding. After mixing of colourless PTA and the calixarene water solutions, the resulting solution turned yellow-orange. The calixarene content in the composite varied from 0 vol.% (pure PTA) to 100 vol.% (pure calixarene). The calixarene content in volume percentages was determined directly from molar ratio of the mixture.

2.2. Thermal stability

The thermal stability of the samples was determined by simultaneous thermal analysis (**STA**) along with mass spectrometric analysis of the decomposition products using a Netzsch STA 409 PC Luxx® instrument and a QMS 403C Aëolos instrument. The thermogravimetric analysis (**TGA**) and differential scanning calorimetry (**DSC**) curves were recorded in a temperature range of 25–250 °C under an argon atmosphere at a heating rate of 5 °C/min.

2.3. IR spectroscopy

The prepared samples were analysed using IR absorption spectroscopy, IR ATR spectroscopy and Raman spectroscopy with a resolution of 4 cm^{-1} (vacuum FTIR spectrometer Bruker Vertex 70/70 V with diamond ATR and RAMII module (λ_B = 1064 nm), Bruker).

The number of water molecules per molecule of calixarene was calculated from the weight loss:

$$n = \frac{\Delta m \times M}{M_w(100 - \Delta m)}$$

where Δm—weight loss (in %), M_w and M—molar mass of water and composite, respectively.

$$M = M_{calix} \times x + M_{PTA} \times y$$

where x and y—the fraction of calixarene and PTA molecules in composite, respectively.

$$\Delta n = n - (n_{calix} \times x + n_{PTA} \times y)$$

Где n_{calix} и n_{PTA}—the number of water molecules per calixarene and PTA molecule, respectively.

2.4. X-ray powder diffraction (XRD)

XRD patterns were registered on an X-ray diffraction meter ADP-2-01 (Cu Kα-radiation, Ni filter) using X-ray software for automation of obtaining, processing and analysing the data obtained from X-ray diffraction from a DRON series.

To determine the phase composition, the exposure was conducted in an angle range of 2θ = 10–90°. The approach increment of the detector block was 0.050, and the exposure time as 2 s.

2.5. Electrochemical measurement

Two types of symmetric electrochemical cells were used for electrochemical measurements:

I—C/analysed electrolyte/C (C is a carbon foil),

II—TiO$_2$(Ru) + Pt + SWNTs/analysed electrolyte/TiO$_2$(Ru) + Pt + SWNTs.

Type I cells with the blocking electrodes were used to measure the proton conductivity only. Type II cells were used for the investigation of the electrode reaction rate dependence on the hydrogen concentration in air and the composition of the electrolyte. The electrodes in this cell were catalytically active to oxygen reduction and hydrogen oxidation in the hydrogen-air mixture, which leads to the formation of a compromise potential determined by the ratio of the reaction rates.

$$H_2 \rightarrow 2H^+ + 2e^- \tag{1}$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{2}$$
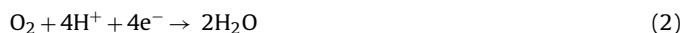
The cells contained the electrolyte samples with thickness of 0.5–1.8 mm and a diameter of 5 mm. Catalytic electrodes were used for measuring the parameters of the electrode reactions in the type II cell. Because the sensitive platinum electrode on the carbon carrier is not tolerant to carbon monoxide in the air-hydrogen mixture, we used a carrier based on titanium dioxide doped with ruthenium (TiO$_2$(Ru)) for the platinum catalyst (10% Pt) [20]. We added 5% of single-walled carbon nanotubes (**SWNTs**) to increase the conductivity.

The proton transfer parameters of the powder samples were determined by impedance spectroscopy in a temperature range of 20–50 °C at a relative humidity (**RH**) 32–75%. Equilibrium with the environment was monitored over the course of several days based on stabilization of the cell resistance. The frequency dependence of the sample impedance was obtained on Z-3000 and Z-500PX impedance meters (Elins LLC, Russia) in a frequency range 0.014 Hz–3 MHz with a measurement signal amplitude of 10–70 mV.

2.6. Sensors

An electrochemical cell with the following composition was studied as a sensor system (hereinafter referred to as the "sensor"):

WE/H$^+$SE/RE

where WE is the working electrode, which consist of TiO$_2$(Ru), 10% Pt and 5% SWNTs, H$^+$SE is the analysed electrolyte, and RE is the reference electrode, which consists of PbO$_2$. To increase the bulk ionic conductivity of RE and the reversibility of the interphase RE/SE, 20% conducting lead calixarene sulfonic acid salt (calix-Pb^{2+}) was added to PbO$_2$.

The sensor scheme is shown in Fig. 1. The sensor was formed by consecutive pressing of layers consisting of electrolyte, reference