



Short communication

Hydrogen production by water electrolysis using tetra-alkyl-ammonium-sulfonic acid ionic liquid electrolytes[☆]



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HIGHLIGHTS

- An improved performance of water electrolysis as measured by HER is observed with TEA–PS·BF₄.
- The novel electrolysis process operates with high efficiencies and high current densities.
- Hydrogen production increases with increasing temperature.
- This process decreases the activation energy for water electrolysis.

ARTICLE INFO

Article history:

Received 16 March 2013

Received in revised form

12 June 2013

Accepted 13 June 2013

Available online 22 June 2013

Keywords:

Ionic liquid

Hydrogen production

Water electrolysis

TEA–PS·BF₄

ABSTRACT

Triethylammonium–propanesulfonic acid tetrafluoroborate (TEA–PS·BF₄) is used as an electrolyte in the water electrolysis. The electrolysis of water with this ionic conductor produces high current densities with high efficiencies, even at room temperatures. A system using TEA–PS·BF₄ in an electrochemical cell with platinum electrodes has current densities (i) up to 1.77 A cm⁻² and efficiencies between 93 and 99% in temperatures ranging from 25 °C to 80 °C.

The activation energy observed with TEA–PS·BF₄ is ca. 9.3 kJ mol⁻¹, a low value that can be explained by the facilitation of proton transport in the organised aqueous ionic liquid media.

The unexpectedly high efficiency of this system is discussed by taking into account the high conductivities associated with the Brønsted and Lewis acidity characteristics associated with these ionic conductive materials.

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1. Introduction

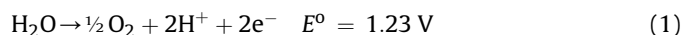
Global sustainability depends on the balance of multiple factors, including the sources of energy and the production of environmental pollution [1]. Hydrogen, an energy source with high potential for improved energy storage capacity, has generated increasing interest as an environmentally clean technology [2,3].

Hydrogen used in industrial applications is currently produced by catalytic reforming reactions [4–7]. Various other methods of hydrogen production have been developed, including the water electrolysis. Interest in these other processes is limited, mainly due to economic reasons [8]. The most important factors in an evaluation of novel hydrogen production technologies are the cost and the

availability of processing energy, a factor that is dependent on geopolitical conditions and varies in different countries around the world.

The half reactions occurring on the anode and cathode of electrolysis can be written in the following ways:

Anode (+):



Cathode (-):



The overall chemical reaction of the water electrolysis can be written as:

Overall reaction:



The availability of clean hydrogen produced from water electrolysis has an enormous impact on the choice of the fuel cell

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technology used to produce energy. The historical use of noble metals, such as palladium, for fuel cell electrodes is no longer necessary to resist the contaminants present in the hydrogen synthesised by reforming reactions. The expense of these types of metals can change the context in which this technology is important and viable.

With a combination of high conductivity and stability, ionic liquids (ILs) have been successfully used as electrolytes for water electrolysis and in other applications [9–13]. The availability of electrolytes that are able to perform water electrolysis with high efficiencies and high current densities has been thought of as the limiting factor in the economical industrial use of electrolysis, representing a non-negligible contribution in the development and implementation of a hydrogen economy [14,15].

Imidazolium based ILs have been used in the direct efficient electrolysis of water at room temperature using low concentrations of 1-butyl-3-methylimidazolium tetrafluoroborate (BMI·BF₄) IL [14,16].

Even with favourable reaction stability characteristics, a major limitation in the development of technology using IL is the expense and the extensive time required for their synthesis.

In this work, new types of ILs are described that demonstrate both Brønsted and Lewis acidity characteristics [17]. These ILs are easily prepared from inexpensive reagents using simple procedures with short reaction times. One characteristic compound, 3-triethylammonium–propanesulfonic acid tetrafluoroborate (TEA–PS·BF₄), demonstrates advantageous abilities as an electrolyte in water electrolysis.

2. Experimental

The 3-triethylammonium–propanesulfonic acid tetrafluoroborate (TEA–PS·BF₄) is prepared by a reaction of 3-triethylammonium–propanesulfonate (TEA–PS) with tetrafluoroborate acid (HBF₄).

2.1. Preparation of TEA–PS and TEA–PS·BF₄

The TEA–PS is prepared using procedures available in the literature [18]. In a typical reaction, 51.38 g of 1,3-propanesultone (Aldrich) and 42.46 g of triethylamine (Vetec) are mixed with 20 mL of ethyl acetate [19]. The reaction is stirred at 50 °C for 2 h and filtered, producing a white solid. The precipitate is washed with three aliquots of 10 mL of ethyl acetate and dried at 100 °C for 2 h, producing 3-triethylammonium–propanesulfonate (TEA–PS) as a white powder [18] in a 61% yield. [¹H NMR (300 MHz, DMSO, ppm): δ 1.18 (t, 3H), 1.89 (m, 2H), 3.21 (m, 2H), 3.42 (m, 2H)].

The TEA–PS·BF₄ is prepared by reacting 56.78 g of TEA–PS dissolved in 4.6 mL of water and 31.5 mL of tetrafluoroboric acid (Riedel-de-Haën) at room temperature. After 2 h at 90 °C, the water is removed under reduced pressure, producing 75.98 g of 3-triethylammonium–propanesulfonic acid tetrafluoroborate (TEA–PS·BF₄) as a white viscous liquid in a 96% yield. [¹H NMR (300 MHz, DMSO, ppm): δ 1.17 (t, 3H), 1.88 (m, 2H), 3.22 (m, 2H), 3.32 (m, 2H), 4.23 (s, 1H). ¹³C NMR (75 MHz, DMSO, ppm): δ 7.00, 17.78, 47.35, 51.97, 54.88].

2.2. Analytical procedures

Vibrational spectra (FTIR) were obtained using a Shimadzu FT-IR spectrometer Model RT-21 Prestige (KBr pellets). Nuclear Magnetic Resonance (NMR) spectra were obtained using a Varian VNMRs 300 using deuterated dimethyl sulfoxide (DMSO) as a solvent and tetramethylsilane (TMS) as the internal standard. The conductivity (σ) of the solutions was measured using a Hach

sension 7 conductivity meter. The pH values are determined using a pHmeter Digimed DM-22.

2.3. Electrolysis

The water electrolysis experiments are performed in a 100 mL Hoffmann cell [20] with platinum wires as the reference, working and counter electrodes. The working electrode area is 0.23 cm². The concentrations of the electrolyte used in the cell varied in the range from 0.1 to 0.7 M, and the temperature is controlled by a thermostatic bath in the range from 25 °C to 80 °C.

The system efficiency is calculated as the faradaic efficiency (η), defined as the ratio between the volume of hydrogen produced (V_{H₂}^R) in the cathode compartment during the electrochemical hydrogen evolution reaction (HER) and the ideal volume of hydrogen that should have been produced (V_{H₂}^T) if the measured charge had been completely used in the water electrolysis process:

$$\eta\% = \frac{V_{\text{H}_2}^{\text{R}}}{V_{\text{H}_2}^{\text{T}}} \times 100 \quad (4)$$

where V_{H₂}^R is the volume of hydrogen measured experimentally using the Hoffmann cell, and V_{H₂}^T is the theoretical volume of hydrogen calculated by the following equation:

$$V_{\text{H}_2}^{\text{T}} = \frac{Q}{2F} \frac{RT}{P} \quad (5)$$

where Q is the charge corresponding to the product of the current intensity and time (value measured by the equipment), R is the gas constant, T is the absolute temperature, P is the pressure and F is the Faraday constant.

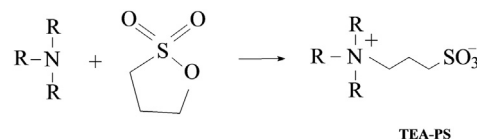
It is worth noting that the (1 – η) term corresponds only to the charge spent in parallel reactions, such as corrosion or electrolyte decomposition.

3. Results and discussion

The zwitterionic compound 3-triethylammonium–propanesulfonate (TEA–PS), a white powder with a melting point of 144 °C, is prepared by the reaction of the inexpensive materials 1,3-propanesultone and triethylamine (see Scheme 1). This compound has been described as active in acid catalysed reactions, including the dimerisation of olefins [18,19].

The good performance of TEA–PS/HCl in dimerisation reactions may have resulted from the Lewis and Brønsted acid characteristics of these types of compounds, suggesting that these candidates should be evaluated in the water electrolysis process using electrolyte [18]. Using a 0.1 M solution, initial tests indicated that these compounds had poor effectiveness in water electrolysis, producing current densities with potentials of –1.7 V and –2.0 V at 678 mA cm^{–2} and 862 mA cm^{–2}, respectively.

An alternative process to improve the behaviour of TEA–PS was developed by reacting TEA–PS and HBF₄, as shown in Scheme 2.



Scheme 1. Synthesis of TEA–PS precursor.

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