**Evaluation of acid doped PBI membranes for the SO2 depolarized electrolysis at high temperature**

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**Highlights**

* Electrochemical comparison of a commercial and a composite TiO2 PBI based membrane.
* Novel gas phase SO2 depolarized electrolysis.
* Study of the effect different operation conditions on the electrolysis process.
* SO2 depolarized electrolysis at temperatures higher than 100°C

Renewable energies are the alternative for a sustainable energy production future. Due to the weather dependence of these energies there is a need for its storage. For example, solar energy has a production peak during the day, however the production is zero at night. This production excess can be used to produce hydrogen, which can be transported and stored for later use.

Hydrogen has a strong potential to become one of the leadings energy carriers in all energy sectors such as fuel for electric vehicles, in combined heat and power plants or fuel cell applications. However, one of the main technical hurdles to overcome to make hydrogen economy [1] a real alternative is relative to hydrogen production. It is mainly produced from fossil fuels by steam reforming of natural gas or high energy consumption processes, which are not environmentally friendly [2]. Thus, new routes for hydrogen production are to be developed for a sustainable energy generation in the “hydrogen economy”. By using renewable energy sources, a “Green Hydrogen” can be produced, being water the ideal raw material. Hydrogen could be produced from water by a single thermal dissociation step, however, due to the considerably high energy consumption this process is not the best candidate [3]. Nevertheless, other routes combine a chemical step and a thermal step which are the most promising technologies for hydrogen production [4].

One of the leading thermochemical cycles to produce hydrogen with a high sustainability is the hybrid Sulphur cycle, also known as Westinghouse cycle. It is a hybrid electrochemical-thermochemical cycle. It was originally proposed in 1975 [5] and developed by Westinghouse electric corporation. The process is labelled “hybrid” because of the substitution of one thermochemical reaction by the electrochemical oxidation of SO2 with water to yield sulphuric acid and hydrogen [3]. The SO2 is electrochemically oxidized at the anode to form sulphuric acid, protons and electrons (E0 = 0.158 V vs SHE). The protons are conducted across a proton exchange membrane (PEM) that acts as a separator to the cathode where they recombine with the electrons to form hydrogen according to equations 1 and 2 [3].

SO2(aq) + 2 H2O → H2SO4(aq) + 2H+ + 2 e- (1)

2H+ + 2 e- → H2(g) (2)

The typical PEM used in the electrolysis cell is a Nafion membrane. However, Nafion based membranes show several limitations, including the inability to operate at elevated temperatures and the decreased performance observed when exposed to high acid concentrations [6].

This work is focused on the study of the SO2 depolarized electrolysis at high temperature (100-200°C) using acid doped PBI membranes as PEM. Two different membranes will be studied for the electrolysis, a commercial PBI membrane and a composite membrane modified with TiO2, this method is explained elsewhere [7], as inorganic filler with the aim to enhance the electrolyte conductivity, hence reducing the membrane resistance, by improving the acid uptake and retention. The tests are performed in a 25 cm2 SO2 depolarized electrolysis cell. A novel operation process consisting on working with SO2 in the gas phase and generating steam which will be mixed with the SO2 flow, with a determined molar ratio, before entering the electrolyzer will be tested. A platinum loading of 0.9 mg Pt/cm2 was employed on both electrodes (anode and cathode) using 40% Pt/Vulcan carbon XC72 as catalyst by spraying a catalytic ink on the electrode surface. Different operation conditions are evaluated such as temperature, SO2 flow and the SO2/H2O molar ratio. The acid uptake and the acid retention will be measured as well as the ion conductivity of the studied membranes. Polarization curves and impedance spectroscopy analysis are carried out to evaluate the performance of the cell and the ohmic and charge transfer resistances. A preliminary stability test will be performed to assess the stability of the different components of the cell (membrane and electrodes).

**References**

1. Winter, C.J.; Nitsch, J. Hydrogen as an Energy Carrier: Technologies, Systems, Economy; Springer Berlin Heidelberg, 2012.
2. R. M. Navarro, M. A. Peña and J. L. G. Fierro, Chem. Rev. 107 (2007) 3952–3991.
3. Sattler, C.; Roeb, M.; Agrafiotis, C.; Thomey, Sol. Energy 156 (2017) 30–47.
4. Gorensek, M.B.; Edwards, T.B., Ind. Eng. Chem. Res. 48 (2009) 7232–7245.
5. Brecher, L.E.; Wu, C.K. (Westinghouse Electric Corporation, Pittsburg, PA, United States). Pers. Commun. 1975.
6. Staser, J.A.; Gorensek, M.B.; Weidner, J.W., J. Electrochem. Soc. 157 (2010) 952–958.
7. J. Lobato, P. Cañizares, M.A. Rodrigo, D. Úbeda, F.J. Pinar, Journal of Membrane Science 369 (2011) 105-111

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