



## Composite membranes for alkaline electrolysis based on polysulfone and mineral fillers



Dariusz Burnat<sup>a, b, \*</sup>, Meike Schlupp<sup>a, b</sup>, Adrian Wichser<sup>c</sup>, Barbara Lothenbach<sup>d</sup>,  
Michal Gorbar<sup>a, \*\*</sup>, Andreas Züttel<sup>a, f</sup>, Ulrich F. Vogt<sup>a, b, e</sup>

<sup>a</sup> Empa – Swiss Federal Laboratories for Materials Science and Research, Hydrogen and Energy, Dübendorf, Switzerland

<sup>b</sup> Empa – Swiss Federal Laboratories for Materials Science and Research, Materials for Energy Conversion, Dübendorf, Switzerland

<sup>c</sup> Empa, Swiss Federal Laboratories for Materials Science and Research, Department for Analytical Chemistry, Dübendorf, Switzerland

<sup>d</sup> Empa, Swiss Federal Laboratories for Materials Science and Research, Department for Concrete and Construction Chemistry, Dübendorf, Switzerland

<sup>e</sup> Albert-Ludwigs-University of Freiburg, Faculty of Environment and Natural Resources, Department of Crystallography, Freiburg, Germany

<sup>f</sup> École Polytechnique Fédérale de Lausanne (EPFL), Institut des Sciences et Ingénierie Chimique, Lausanne, Switzerland

### HIGHLIGHTS

- Corrosion of forsterite, wollastonite, barite and chrysotile was tested in 5.5 M KOH at 85 °C.
- Barium sulphate showed an excellent corrosion stability after 8000 h.
- Calculated solubility limits of barite, wollastonite and chrysotile match the experimental data.
- Membrane's top layer has resistivity two orders of magnitude higher than the bulk microstructure.
- Membranes outperform commercial Zirfon 500upt and previously used chrysotile (asbestos).

### ARTICLE INFO

#### Article history:

Received 26 January 2015

Accepted 13 April 2015

Available online xxx

#### Keywords:

Alkaline electrolysis

Membrane gas separator

Phase inversion

Barite

Resistivity

Gas purity

### ABSTRACT

Mineral-based membranes for high temperature alkaline electrolysis were developed by a phase inversion process with polysulfone as binder. The long-term stability of new mineral fillers: wollastonite, forsterite and barite was assessed by 8000 h-long leaching experiments (5.5 M KOH, 85 °C) combined with thermodynamic modelling. Barite has released only 6.22 10<sup>-4</sup> M of Ba ions into the electrolyte and was selected as promising filler material, due to its excellent stability. Barite-based membranes, prepared by the phase inversion process, were further studied. The resistivity of these membranes in 5.5 M KOH was investigated as a function of membrane thickness and total porosity, hydrodynamic porosity as well as gas purities determined by conducting electrolysis at ambient conditions. It was found that a dense top layer resulting from the phase inversion process, shows resistivity values up to 451.0 ± 22 Ω cm, which is two orders of magnitude higher than a porous bulk membrane microstructure (3.89 Ω cm). Developed membranes provided hydrogen purity of 99.83 at 200 mA cm<sup>-2</sup>, which is comparable to previously used chrysotile membranes and higher than commercial state-of-the-art Zirfon 500outp membrane. These cost-effective polysulfone – barite membranes are promising candidates as asbestos replacement for commercial applications.

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\* Corresponding author. Empa – Swiss Federal Laboratories for Materials Science and Research, Materials for Energy Conversion, Dübendorf, Switzerland.

\*\* Corresponding author. ZHAW – Zurich University of Applied Sciences, Winterthur, Switzerland.

E-mail address: [dburnat@gmail.com](mailto:dburnat@gmail.com) (D. Burnat).

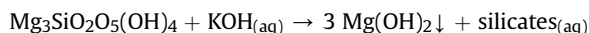
## 1. Introduction

Nowadays, 95% of total hydrogen is produced from hydrocarbon reforming with the drawback of high CO<sub>2</sub> emissions. Hydrogen utilization as an energy carrier requires environmentally-friendly technologies, which provide a clean and fossil fuel-free route from production to utilization [1]. Among all promising technologies, alkaline electrolysis appears to be the most attractive solution

for near-future commercial hydrogen production, because it is an existing and mature technology, which has been used for the last 50 years within the industrial sector [2]. Moreover, large scale electrolyzers show remarkable efficiencies of up to 80% [3,4], which makes them especially attractive for large scale on-site hydrogen production.

In the alkaline electrolysis cell, two electrodes are immersed in highly concentrated electrolyte lye of 25 wt%–33 wt% KOH (5.5 M–7.8 M [5]) at temperatures of up to 85 °C [4]. A membrane separates anode and cathode compartments in order to prevent a mixing of the H<sub>2</sub> and O<sub>2</sub> gases produced during electrolysis. Simultaneously the membrane requires a certain porosity to enable OH<sup>−</sup> migration to close the electric circuit between cathode and anode. The optimisation of membrane porosity and pore size distribution is crucial, since these parameters directly affect both ionic conductivity and gas separation properties. Other important requirements are chemical stability in the alkaline electrolyte (KOH) at operating conditions as well as mechanical stability, to ensure a reliable separation of the electrodes during installation and operation under industrial conditions.

For the last 50 years, chrysotile (asbestos) has served well as separation membrane for industrial alkaline electrolyzers, but it has recently been completely withdrawn from commercial use due to serious health hazards [6]. Furthermore, chrysotile membranes cannot withstand operating temperatures higher than 85 °C due to severe corrosion leading to membrane failure. Several studies address the instability of chrysotile, Mg<sub>3</sub>SiO<sub>5</sub>(OH)<sub>4</sub>, in KOH lye [7,8], which forms soluble silicates and poorly soluble brucite, Mg(OH)<sub>2</sub>, according to the following reaction:



As an alternative to chrysotile, the use of polymeric membranes with embedded ceramic fillers has been proposed. Such composite membranes with e.g. 85 wt.% of ZrO<sub>2</sub> powder are commercially available (Zirfon 500utp from Agfa [9]). They allow operation at temperatures up to 120 °C, which significantly increases the conductivity of KOH and therefore the efficiency of the electrolysis process [10]. The function of the ceramic filler in such composite membranes is to promote the hydrophilicity of the membrane by neutralizing the hydrophobic character of the polymer. A good wetting behaviour of the membrane is crucial to avoid the adhesion of gas bubbles to the surface, which would interfere with OH<sup>−</sup> ion migration through the membrane and thus decrease the efficiency of the electrolysis cell. ZrO<sub>2</sub> despite its high price and high impact on total membrane production cost is still the only filler used in alkaline electrolysis membranes, due to its good stability in alkaline conditions as well as strong patent protection of cheaper alternatives.

In this study we investigate alternatives to Zirfon membranes, based on polymeric polysulfone (PSF) binder combined with natural fillers. Polysulfone is known for its excellent stability in highly alkaline environments at temperatures of up to 170 °C and can be easily processed via a phase inversion process [11,12]. This simple and easily scalable technique is well known for the production of membranes for dry gas separation and water filtration [13–16] and allows a precise tuning of the membrane's microstructure and pore size distribution. By studying the relationship between microstructure, porosity and ionic conductivity of prepared membranes we are able to identify critical membrane parameters influencing the energy consumption of the electrolysis process. As membrane filler materials, natural and abundant minerals such as forsterite Mg<sub>2</sub>SiO<sub>4</sub>, wollastonite CaSiO<sub>3</sub> and barite BaSO<sub>4</sub> are investigated. Since the composite membranes contain up to 90 wt.% of inorganic particles, the application of low-cost filler materials (up to 20 times

cheaper than commercial zirconia) is expected to decrease the price of the electrolysis cell stack and make the technology more cost-attractive for large scale applications. The selected minerals show promising stabilities in mild alkaline environments [17–20] and contain significantly less Si per formula unit than chrysotile or are Si-free in the case of barite. The chemical stability under alkaline electrolysis conditions is assessed by long-term leaching experiments up to 8000 h and thermodynamic modelling based on the Karpov model [21], which is extrapolated to high ionic strengths (>5.5 M).

## 2. Experimental

### 2.1. Leaching experiments

Forsterite, wollastonite and barite powders as well as pieces of as-received chrysotile cloth (see Table 1.) were first investigated by X-ray diffraction followed by Rietveld refinement to determine the presence of secondary phases. Without any processing, minerals and chrysotile cloth were exposed to the corrosive environment of 5.5 M KOH at a temperature of 85 °C for up to 8000 h, in order to investigate the chemical stability under electrolysis conditions. Furthermore, the same minerals were subjected to leaching at 160 °C for 200 h to accelerate the corrosion process and increase the detectability of secondary phases by X-ray powder diffraction (XRD, see the Supplementary information). Potassium hydroxide solutions (5.5 M) were prepared by dissolving potassium hydroxide pellets (Sigma–Aldrich, Switzerland, 85% + H<sub>2</sub>O) in deionized water. The molar ratio between filler material (or chrysotile) and lye was set to 1:10 at a volume of 36.4 ml KOH. After the experiment, the extracted alkaline solution was centrifuged (4000 rpm for 15 min) to eliminate solid residues in the liquid samples. Inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES; Agilent 7500ce, H<sub>2</sub> as a reaction gas, *m/z* 28) was used to determine the concentration of dissolution products of the tested materials. A stock solution (Silicon plasma standard solution, 1000 mg L<sup>−1</sup>, Alfa Aesar) with acidified (1% HNO<sub>3</sub>) deionized water was used for external calibration of the system (10–1000 μg Si L<sup>−1</sup>). Materials used in this study are summarized in Table 1.

### 2.2. Thermodynamic modelling

Thermodynamic modelling was carried out using the Gibbs free energy minimization program GEMS [21]. GEMS is a broad-purpose geochemical modelling code, which computes equilibrium phase assemblage and speciation in a complex chemical system from its total bulk elemental composition. Chemical interactions involving solids, solid solutions, aqueous electrolyte and gas phase were considered simultaneously. The speciation of the dissolved species as well as the kind and amount of solids precipitated were calculated. The thermodynamic data for aqueous species as well as for solids were taken from the PSI-GEMS thermodynamic database [21–23], coupled with the SUPCRT database to allow temperature extrapolations. The molar mass of KOH and minerals used for calculations were the same as for the leaching experiments. The purity of minerals taken for the calculations was 100% except for forsterite, for which 7% impurity of fayalite was determined by Rietveld refinement. The data for chrysotile, wollastonite, barite, forsterite and fayalite (to mimic the impurity of forsterite) were taken from the SUPCRT database [24]. A summary of the data used is given in Table 2.

The activity coefficients of aqueous species *y<sub>i</sub>* were computed with the extended Debye–Hückel equation in the Truesdell–Jones

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