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Corrosion behavior analyses of metallic membranes in hydrogen iodide environment for iodine-sulfur thermochemical cycle of hydrogen production

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ARTICLE INFO

Article history:

Received 23 February 2018

Received in revised form

10 April 2018

Accepted 25 April 2018

Available online xxx

Keywords:

Metallic membrane

Corrosion

Membrane reactor

Hydrogen

IS thermochemical cycle

HI decomposition

ABSTRACT

HI decomposition in Iodine-Sulfur (IS) thermochemical process for hydrogen production is one of the critical steps, which suffers from low equilibrium conversion as well as highly corrosive environment. Corrosion-resistant metal membrane reactor is proposed to be a process intensification tool, which can enable efficient HI decomposition by enhancing the equilibrium conversion value. Here we report corrosion resistance studies on tantalum, niobium and palladium membranes, along with their comparative evaluation. Thin layer each of tantalum, palladium and niobium was coated on tubular alumina support of length 250 mm and 10 mm OD using DC sputter deposition technique. Small pieces of the coated tubes were subject to immersion coupon tests in HI-water environment (57 wt% HI in water) at a temperature of 125–130 °C under reflux environment, and simulated HI decomposition environment at 450 °C. The unexposed and exposed cut pieces were analyzed using scanning electron microscope (SEM), energy dispersive X-ray (EDX) and secondary ion mass spectrometer (SIMS). The extent of leaching of metal into liquid HI was quantified using inductively coupled plasma-mass spectrometer (ICP-MS). Findings confirmed that tantalum is the most resistant membrane material in HI environment (liquid and gas) followed by niobium and palladium.

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<https://doi.org/10.1016/j.ijhydene.2018.04.212>

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Introduction

The increasing demand of clean energy and long term solution for energy crisis has resulted in the faster evolution of Hydrogen economy [1]. There are various methods available for hydrogen production [2–4], but thermochemical water splitting processes are the best options where heat energy from nuclear power plants is available [5–8] for utilisation. Thermochemical water splitting from Iodine–Sulfur (IS) thermochemical cycle offers a clean and economical route for large scale hydrogen production [9–14]. This water splitting process consists of three coupled reactions [15]. The first reaction is Bunsen reaction in which sulfur dioxide (SO_2), water, and iodine (I_2) react to form sulfuric acid (H_2SO_4) and hydrogen iodide (HI). Sulfuric acid and hydrogen iodide are separated and decomposed separately at $\sim 850^\circ\text{C}$ and $\sim 300\text{--}450^\circ\text{C}$ respectively. HI decomposition section consists of acid mixtures of HI, H_2O and I_2 commonly known as HI_x . Hydrogen is produced in the HI decomposition section of the cycle. A critical challenge with this step is the low equilibrium conversion of HI decomposition reaction ($\sim 22\%$ at 700 K) which increases the amount of recycled HI, affecting the overall thermal efficiency of the cycle. Moreover, the reaction environment of HI_x is extremely corrosive in nature. It is, therefore, important that the material used in IS thermochemical cycle should be resistant to corrosive environment at 450°C . Hydrogen permselective membrane reactors can be used to remove hydrogen *in-situ* from the reaction mixture and push the reaction forward, enhancing the conversion of HI decomposition reaction [16,17], and the overall efficiency of the IS process. Though palladium and its alloys are widely used and studied for application of metal membranes in hydrogen separation [18–21], they cannot withstand the corrosive environment of HI_x processing section [22]. Very few literatures are available on corrosion resistance studies of potential materials for application in IS cycle [23–25]. Corrosion behavior of niobium and tantalum has been studied in acidic [26–28], chemical [29] and electrolyser (fuel cell) environments [30] along with that of tantalum base alloys [31,32]. Apart from tantalum, corrosion resistance of palladium films has also been widely studied. Role of palladium films in enhancing corrosion resistance of stainless steel [33,34] and titanium [35] have also been highlighted. Corrosion behavior of niobium in sulfuric and hydrochloric acid solutions [36], corrosion of niobium and tantalum in alkaline media [37], and effect of niobium on the corrosion resistance of nickel-base alloys [38] have also been reported. Though refractory materials like tantalum and niobium are envisaged as corrosion resistant materials with higher hydrogen permeabilities compared to palladium and its alloys [22], to the best of our knowledge, the corrosion resistance analysis of metals in view of membrane applications is rare in literature. In the present work, corrosion resistance studies of tantalum, niobium and palladium membranes have been carried out in HI liquid and gas environment, along with their comparative evaluation. The study includes two important analytical domains, namely the leaching studies of metal into liquid HI environment using inductively coupled plasma-mass spectrometer (ICP-MS)

studies, and iodine percolation behavior analysis using secondary ion mass spectrometer (SIMS) studies. Moreover, to the best of our knowledge, the said two studies (metal leaching and iodine percolation into the metals), and an in-depth analysis (HI in liquid and gas environment) of corrosion behavior of potential metal membrane materials for application in HI_x processing section have not been carried out in the literature.

Experimental details

Fabrication of metal membranes

Thin layers each of tantalum, niobium and palladium, of thickness $\sim 2.5\ \mu\text{m}$, was coated on tubular alumina support of length 250 mm and 10 mm OD using DC sputter deposition technique. The base pressure of sputtering chamber was 5.5×10^{-6} torr and deposition pressure was kept at 3.2×10^{-2} torr. The flow of ultra-pure Ar gas to the chamber was kept at 70 sccm and was regulated by a mass flow controller. DC power was kept at 200 W and substrate temperature was kept at 500°C . Membranes were annealed for 2 h after sputter coating. The morphological analysis of coated surface was carried out using scanning electron microscope (SEM). The surface layer images were recorded at an acceleration voltage of 30 kV and $\times 1000$ magnification when operated in secondary electron mode. The quantitative surface elemental analysis and mapping of membrane were carried out by an energy dispersive X-ray spectrometer (EDX) coupled with the SEM and a micro analysis system (INCA Oxford Instrument, UK).

Corrosion resistance studies

Corrosion resistance studies of metallic membranes were carried out using immersion coupon tests in liquid HI– H_2O environment, and simulated HI decomposition environment at 450°C , both upto 200 h of exposure. The coated tubes were cut into small pieces of 2 cm length and immersed in HI-water azeotrope (57 wt% HI in water) at a temperature range of $125\text{--}130^\circ\text{C}$ under reflux environment as shown in Fig. 1. The tubes were taken out after every 50 h of exposure in HI medium and were analyzed using SEM, EDX and SIMS. The extent of leaching of metal into liquid HI was analyzed by ICP-MS (VG PQ Ex Cell, Thermo Elemental). The elemental depth distribution analyses of iodine by SIMS in all the samples were carried out using magnetic sector based Cameca IMS-7f instrument equipped with both oxygen (O_2^+ and O^-) and cesium (Cs^+) primary ion beams. All the analyses were carried out using negative secondary ion detection mode, since iodine as negative ion (I^-) is more sensitive as compared to positive ion (I^+). Since, the samples were non-conducting, a thin film (thickness $\sim 50\text{ nm}$) of Au were deposited in all the samples using sputter deposition technique. Cs^+ primary ion beam at an impact energy of 15 keV (sample potential -5 keV) with negative secondary ion detection mode was opted for all the analyses. Primary ion beam current of $62 \pm 1\text{ nA}$ was raster over an area of $250\ \mu\text{m} \times 250\ \mu\text{m}$ and secondary ions were collected from an analysis region of $63\ \mu\text{m}$ in diameter by

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