

MEMBRANE ELECTROLYSIS FOR BUNSEN REACTION OF THE I-S THERMOCHEMICAL CYCLE

Submitted by

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CERTIFICATE

This is to certify that the thesis entitled **“MEMBRANE ELECTROLYSIS FOR BUNSEN REACTION OF THE I-S THERMOCHEMICAL CYCLE”**, being submitted by IMMANUEL. V to the Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy, is a record of bonafide research work carried out by him. IMMANUEL. V has worked under my guidance and supervision and has fulfilled the requirements for the submission of the thesis.

The results contained in this thesis have not been submitted in part or in full to any other University or Institute for the award of any degree or diploma.

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ABSTRACT

Thermo-chemical cycles are being investigated as an energy efficient way of producing hydrogen from water. Iodine-sulphur (I-S) is one of the most efficient among thermo-chemical cycles. In this cycle iodine and sulphur dioxide are used as recycling agents and consists of three main reactions. First is the Bunsen reaction where sulphuric acid and hydriodic acid are produced by reaction of iodine, sulphur dioxide and water. The other two are the sulphuric acid decomposition and hydriodic acid decomposition. In practice, thermal efficiency realized in I-S cycle is low compared to thermodynamic value because of heat required to remove excess iodine and water used in the Bunsen reaction. Membrane electrolysis is coming up as one of the alternatives to direct contact mode of carrying out Bunsen reaction of I-S cycle. It has potential to reduce the use of excess iodine and water.

Bunsen reaction was carried out in a two-compartment membrane electrolysis cell having Nafion117 as a separator between the compartments. Graphite electrodes, used in the membrane electrolysis cell, were characterized by using linear sweep voltammetry (LSV) and cyclic voltammetry (CV). Areal-resistance of the membrane was measured at different temperatures, and different concentrations of anolyte and catholyte. Areal-resistance of membrane in chemical environment of Bunsen reaction was about 50% more than the values reported in NaCl electrolyte and was found to increase with sulphuric acid concentration. Preliminary electrolysis experiments were carried out at 300 K, in constant current mode with current density in the range 1.5 to 4.7 A/dm². Aqueous solutions of $\times 5.0$ N HI containing dissolved iodine, with I₂/HI ratio in the ratio 0.25 to 1.25 were used as catholyte solution. Aqueous solution of 10 N sulphuric acid saturated with

dissolved SO_2 was used as anolyte solution. The concentration of dissolved SO_2 in the anolyte was maintained by continuously bubbling SO_2 in anolyte at atmospheric pressure in first set of experiments, and by maintaining a SO_2 -atmosphere at 2 bar in another set of experiments. Volume of the anolyte changed in the first set of experiments and so current efficiency determination became difficult. In the other set of experiments, the increase in concentration of acids in the two compartments compared well with the amount of charge supplied during electrolysis with current efficiency of the cathode in the range of 90 – 95% and that of anode in the range closed to 100%. Current-voltage characteristic of the electrolysis cell was determined and the cell voltage was found to vary linearly with an increase in current density. The cell voltage increased with increase in initial concentration of sulfuric acid in anolyte from 10 N to 14.3 N and decreased with increase in value of I_2/HI ratio in the catholyte.

Experimental setup was modified and a systematic study was carried out to determine effect of independent operating variables on performance of membrane electrolysis cell. Effect of six independent variables on cell voltage was determined for current density values of up to 80 A/dm^2 . The variables were anolyte pressure, catholyte pressure, temperature, sulphuric acid concentration, HI concentration, and I_2/HI molar ratio in catholyte. Flow rate of anolyte and catholyte were identified where mass transfer resistance was not significant before performing experiments with different values of independent variables. Cell voltage was analyzed by identifying three different regimes based on its variation with current density and current density ranges where electrode resistance or ohmic resistance dominated were identified. Current efficiency was measured for 1 A/dm^2 and was found to be close to 100% irrespective of the value of the independent variables.

Membrane electrolysis could be used to carry out Bunsen reaction at much lower levels of excess iodine as compared to the direct contact mode because the two acid phases (sulphuric acid rich and HI rich phases) are separated by an ion exchange membrane. However, undesired permeation of ions or dissolved SO_2 through membrane caused cross-contamination of the two acid phases. Cross-contamination affects the purity of solutions. Cross-contamination arising out of permeation of dissolved SO_2 and/ or sulphate ions from anolyte to catholyte and that of iodine/iodide ions from catholyte to anolyte was measured. Permeation was obtained even in absence of current density and the flux increased rapidly with current density. At 1 A/dm^2 , the permeated SO_2 and sulphate ions were $\times 12\%$ of total sulphate ions produced in electrolysis which was lower than about 20% of feed sulphuric acid appearing in HI_x phase in direct contact mode. The permeated iodine and iodide ions together were less than 3% of iodide ions produced in electrolysis.

Minimum amount of heat equivalent of electric energy required for membrane electrolysis was calculated and increase in its value with increase in sulphuric acid concentration was compared with an estimate of reduction in heat required for concentration of sulphuric acid. Based on the calculation and qualitative reasoning, best region for operation of membrane electrolysis cell, at low current densities, was found to be sulphuric acid concentration of 18.2 N in anolyte, 6.7 N HI in catholyte, I_2/HI ratio of 0.5, 2 bar anolyte pressure, 1 bar catholyte pressure, and 313 K.

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