# STUDIES ON ELECTRO-ELECTRODIALYSIS FOR CONCENTRATION OF HYDROIODIC ACID

by

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# CERTIFICATE

This is to certify that the thesis entitled **“STUDIES ON ELECTRO-ELECTRODIALYSIS FOR CONCENTRATION OF HYDROIODIC ACID”,** being submitted by PRADEEP KUMAR SOW to the Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy in Chemical Engineering, is a record of bonafide research work carried out by him. PRADEEP KUMAR SOW has worked under our 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 water splitting process that uses heat along with the chemical recycling agents to decompose water into hydrogen and oxygen. Among the numerous thermochemical cycles proposed Iodine-Sulphur (I-S) cycle has been found to provide with the highest theoretical efficiency. I-S cycle is a closed loop process where iodine and sulphur acts as the recycling agents and consists of three major reaction steps. The central part is the Bunsen reaction where hydroiodic acid (HI) and sulphuric acid are produced from the reaction between iodine and sulphur di-oxide in aqueous medium. The HI and the sulphuric acid are then concentrated and decomposed in HI decomposition section and the sulphuric acid decomposition section to give hydrogen and oxygen respectively. In practice the energy requirement is higher than the theoretical estimation. A major contribution towards the increased energy consumption is from the HI acid concentration process primarily due to formation of pseudo-azeotropic mixture of HI with water. Among the various processes being investigated electro-electrodialysis (EED) is coming up as a viable alternative to the HI concentration process.

EED was carried out in a two-compartment cell using graphite electrode and Nafion-117 as the separator. The cell and the components were characterized using electrochemical analysis techniques such as impedance spectroscopy, cyclic voltammetry, chronopotentiometry. Investigation on iodine-iodide redox system was carried out using cyclic voltammetry at graphite electrode in aqueous $HI_x$ solution. Prominent oxidation and reduction were identified using semi-quantitative relation between electroactive species concentration and post-peak diffusion limited current as due to tri-iodide ion redox reactions while the shoulder with oxidation peak was due to oxidation of iodide ion. Formation of iodate at higher electrode potential was confirmed by chemical analysis along with XRD identification of iodate on the electrode. Impedance spectroscopy analysis was done on the graphite electrode at varying temperature and in electrolyte solutions of different iodine and HI concentration. Theoretical modeling and simulation of the experimental data provided evidence for the presence of complex mass transfer impedance due to homogenous reaction between iodine, iodide and tri-iodide ions. The iodine-iodide equilibrium-limited homogeneous reaction interferes in the diffusion-driven development of concentration profile of the reactant and appears as another resistance to transport of reactant. Effect of temperature and iodine concentration on different transport resistances of the EED cell was found by equivalent circuit modeling of the measured impedance response of the cell. Equivalent circuit for the cell consisted of a resistor for ohmic resistance of the cell, a Warburg element for the resistance due to diffusion boundary layer and a constant phase element (CPE) for the resistance to transport of ions due to non-electroneutral heterogeneous transport (HT) layer at the membrane. The admittance of the HT layer was found to reduce with increase in temperature while it was found to increase with increase in the iodine concentration. The dependence of the transport resistances and the energy consumption on the time of EED operation was investigated using under-limiting current chronopotentiometry. Four different energy consumption modes were identified in the EED cell namely; the ohmic, the mass transfer, the electrodes reactions and open circuit voltage (OCV) which was calculated individually based on the potential drop contribution by each component. The potential drop and corresponding energy consumption, corresponding to the electrode reaction was found to be negligibly low as compared to the other potential drop components. Studies on the variation of different transport resistances with operation time of the

EED cell showed that first three energy consumption mechanisms change little with change in $HI_x$ concentration while the OCV increases significantly and becomes the major energy consumption mode especially at low current densities for the desired EED exit $HI_x$ concentration. Preliminary studies on the EED cell were conducted and HI was successfully concentrated beyond its azeotropic composition using EED. Current efficiency of the cell for the HI concentration process was found to be close to ~ 82.5% which compared well with the values reported in literature. EED process for HI concentration was studied for the effect of individual operating parameters such as $I_2$/HI ratio, concentration of HI ($x_{HI/H2O}$), temperature and pressure. Studies were conducted in an asymmetric system where the concentrations and pressure of anolyte and the catholyte were varied separately. Open circuit voltage (OCV) was found to be a contributor to the net potential drop across the EED cell. Ohmic resistance was found to decrease with increase in $I_2$/HI ratio in catholyte and was found to increase with increase in $I_2$/HI ratio in anolyte. Increase in $x_{HI/H2O}$ decreased the resistance for anolyte section where as caused an increase in resistance for catholyte section. Increase in temperature reduced the voltage drop and the resistance across the EED cell. A non-zero differential pressure between the two compartments of the cell increased the resistance across the cell without affecting the OCV value. Electrode potential studies at the graphite electrodes showed an increase in the electro potential with increase in the iodine concentration and decrease with the increase in the HI concentration. Energy required for concentrating acid increased linearly with current density favoring operation at low current densities. Energy consumed in overcoming OCV contributed substantial fraction of the total energy consumed in EED process at lower current densities. Simulation of the iodine circuit consisting of an EED, a

flash and a decomposer was carried out in Aspen plus$^{\text{TM}}$ simulation platform to study the effect of EED current density and outlet HI concentration on the efficiency of the cycle. Efficiency reduced strongly with increase in current density. For EED current density of 5 A/dm$^2$, maximum efficiency was ~35.9% with EED catholyte's exit HI mole fraction on iodine-free basis in the range of 0.19-0.20. Simulation results showed that reducing EED resistance was most effective, among all EED parameters, in increasing the cycle's thermal efficiency and the increased efficiency value was calculated as 39.4%. Maximum theoretical efficiency of the cycle containing EED cell and Bunsen reactor with ideal membrane and zero ohmic and charge trasnfer resistance was calculated to be close to 46.5%.

# Contents

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