

Fuel Exhaling Fuel Cell for Fuel Purification and Water Desalination



A Thesis submitted to
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in partial fulfillment of the requirements for the
BS-MS Dual Degree Programme

By

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Certificate

This is to certify that this dissertation entitled “**Fuel Exhaling Fuel Cell for Fuel Purification and Water Desalination**” towards the partial fulfilment of the BS-MS dual degree programme at the **Indian Institute of Science Education and Research, Pune** represents study/work carried out by **Deepraj Pandit (Reg.No.20141008)** at Indian Institute of Science Education and Research under the supervision of **Dr. Muhammed Mustafa O T, Assistant Professor, Department of Chemistry, IISER Pune** during the academic year 2018-2019.



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Declaration

I hereby declare that the matter embodied in the report entitled “**Fuel Exhaling Fuel Cell for Fuel Purification and Water Desalination**” are the results of the work carried out by me at the **Department of Chemistry, Indian Institute of Science Education and Research, Pune**, under the supervision of **Dr. Muhammed Mustafa O T** and the same has not been submitted elsewhere for any other degree.

A handwritten signature in black ink, appearing to read 'Deepraj Pandit', with a stylized flourish at the end.

Date: 30/3/2019

Place: Pune

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ABSTRACT

'Hydrogen economy' or sustainable production of hydrogen and its subsequent utilization for energy conversion offers a rejuvenating shift towards a carbon neutral economy. This is mainly because hydrogen fuel has long been touted as a clean alternative to gasoline and the utilization of hydrogen fuel for energy conversion is typically achieved with the help of a proton exchange membrane fuel cell (PEMFC); which is a potential zero emission technology. The steam reforming of alcohols and methane is the most popular method for hydrogen production but hydrogen produced by this method always contain impurities such as CO and CO₂ beyond the tolerance level to be directly utilized in a fuel cell. This necessitates energy intensive fuel separation methods such as pressure swing adsorption (PSA), temperature swing adsorption (TSA), cryogenic distillation and membrane based purification. We demonstrate a fuel cell concept driven by the energy of neutralization, which can purify the hydrogen fuel stream during electric power production. The gas chromatography and in-situ electrochemical mass spectrometry confirm the production of highly pure hydrogen as the cathodic half-cell chemistry and exclusive consumption hydrogen in the impure fuel stream as the anodic half-cell chemistry. The same fuel cell configuration is further extended for water desalination and half-cell water deionization during electric power production using the concept of bipolar membranes. The desalination studies show this fuel cell is able to desalinate highly saline water (4 M NaCl) during the production of ~26 mW/cm² of electric power and ~22.8 mL/h of hydrogen fuel.

CHAPTER 1. INTRODUCTION

The electricity is the foundation of the modern world and burning of fossils fuel is the conventional source for electricity production¹. But immoderate use of fossils fuels causes global warming and global climatic change so there is a need for better and cleaner sources of energy²⁻³. The present known reserves of oil, natural gas and coal will last for 41, 64 and 155 years respectively, if the consumption and production of this sources will continue at constant rate in the future⁴. So people have started looking for the alternate sources of energy. The sustainable and renewable sources for electricity production are hydroelectric, biomass, wind, solar, geothermal, and marine tidal⁵⁻⁶. However these sources of energy have got seasonal and geographical variations which demands their storage at the time of availability and conversion at the time of demand. The electrochemical storage and conversion technologies such as batteries, supercapacitors, solar cells and fuel cell play an important role in sustainable energy landscape as these can bridge the existing gap between energy availability and energy demand.

1.1 Battery

Battery is energy storage device which stores energy in the chemical form and converts it to electrical energy when needed. Battery is composed of one or more electrochemical cell which are connected in series or parallel to produce the voltage. It consist of anode (positive electrode) and cathode (negative electrode) where the redox reactions takes places. The electrodes are separated by electrolyte which enables the transfer of ions towards the electrodes⁷. Once the electrodes are connected externally redox reaction happen near the electrode/electrolyte interface, producing electrons and creates a potential difference between anode and cathode⁷⁻⁹. Due to this potential difference electrons flow from electrode having low reduction potential to the electrode having high reduction potential. So, the cell convert chemical energy to electrical energy during discharge chemistry and the process is reversed during the charging process¹⁰.

Primary and secondary battery are two different categories of battery. Primary battery is the non-chargeable whereas secondary battery is chargeable⁹.

Example of primary battery is zinc carbon. Lithium ion battery, nickel hydride battery and lead acid battery are examples for secondary batteries.

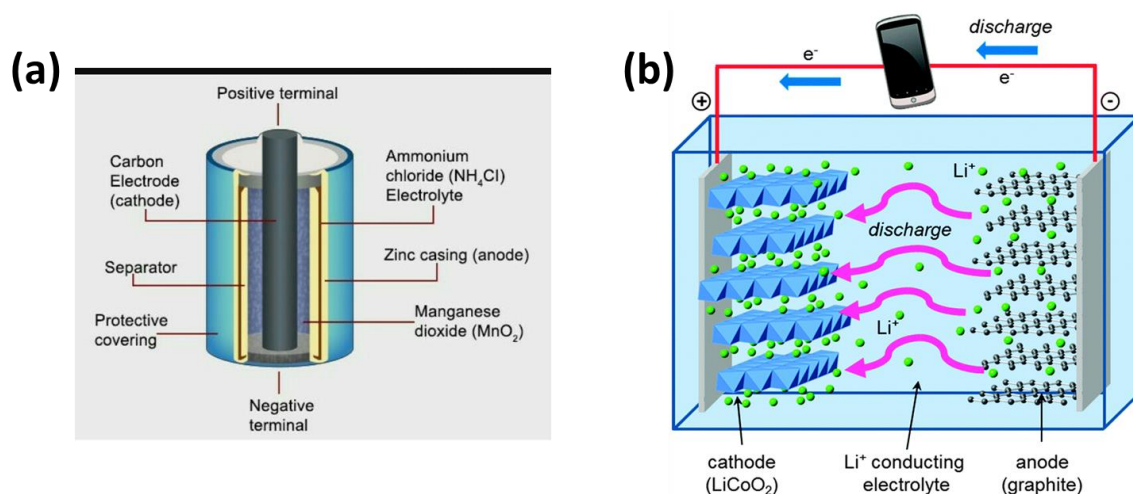


Figure 1.1 Schematic of (a) zinc-carbon battery and (b) Li - ion battery

(a) <https://brainly.in/question/7294569>

(b) <https://www.extremetech.com/extreme/212388-accidental-nanoparticles-could-let-lithium-ion-batteries-live-another-day>

1.2 Capacitor

Capacitors are the energy storage devices with high power density but with low energy density. Capacitor is formed by separating two electrodes or metal plates by

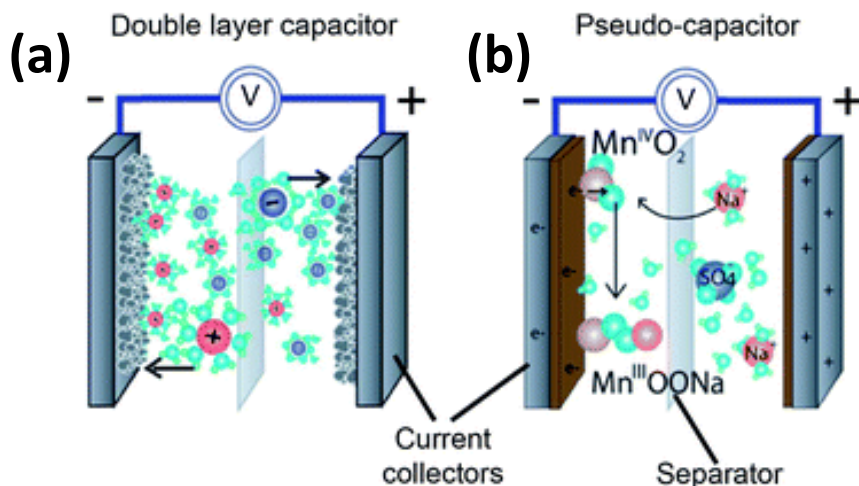


Figure 1.2 Schematic of (a) electrochemical double layer capacitor (b) pseudo capacitor

J. Mater. Chem. A, 2016, 4, 16771-16800

a dielectric material. Capacitor physically store electrical charge without any chemical or phase change and the process is highly reversible¹¹. The opposite charges are collected on the electrode surface upon applying voltage and kept separated with the help of dielectric material, thus producing an electric field¹⁰.

The electrochemical double layer capacitors (EDLC) and pseudo capacitors are two types of electrochemical supercapacitors. The EDLC are based on nano porous carbon material and store charge by non-faradic adsorption of ion at the electrode/electrolyte interface. Whereas pseudo capacitors are made up of conducting polymer or metal oxide based electrodes and store charge using fast redox reaction at the surface by faradic mechanism¹²⁻¹³.

1.3 Solar cell

A solar cell is an electrical device that converts the light directly into electricity by the photovoltaic effect¹⁴⁻¹⁵. Silicon semiconductors are commonly used for the fabrication of the solar cell. The generation of current in a solar cell involves two key processes. First, when the light with sufficient energy is incident on the solar cell, the electrons are excited from lower energy levels to higher energy levels and creates electron-hole pairs in the solar cell.

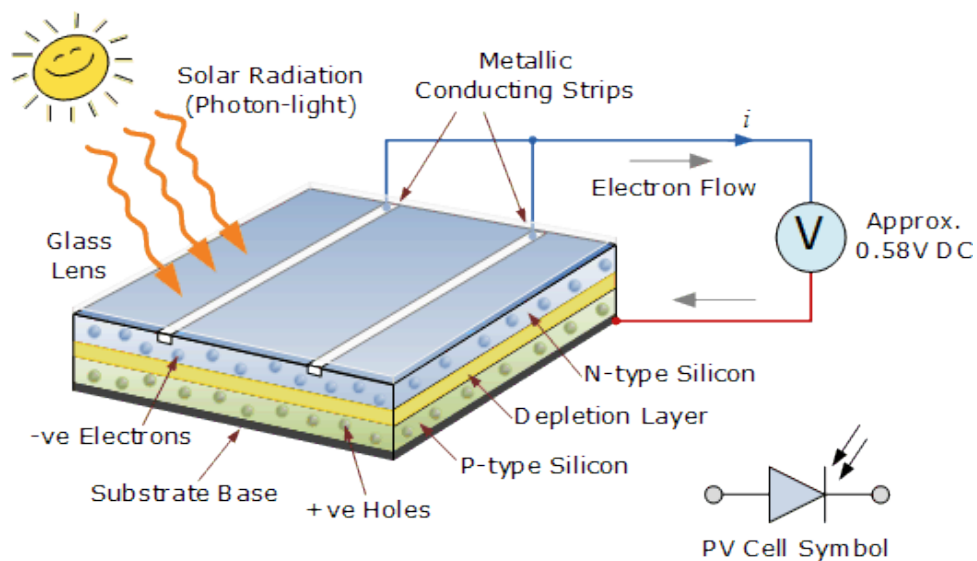


Figure 1.3 Schematic representation of solar cell

<http://www.alternative-energy-tutorials.com/solar-power/photovoltaics.html>

Second, the electron-hole pair are further separated by p-n junction to prevent their recombination¹⁴⁻¹⁵. This electron flow through the external circuit and produce electricity. The holes move in opposite direction and eventually will combine with electrons.

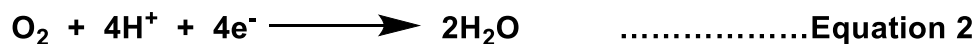
1.4 Fuel cell

Fuel cell is an electrochemical energy conversion device which convert the chemical energy stored in the form of fuel to electricity¹⁰. Direct methanol, hydrazine, borohydride, phosphoric acid and proton exchange membrane fuel cell (PEMFC) are some of the popular fuel cells¹⁰. The PEMFCs are the most popular fuel cell among all since byproduct is only water while converting chemical energy into electricity and therefore it is a potential zero emission technology¹⁶⁻¹⁸. In PEMFC chemical energy of H₂ and O₂ is converted to electricity, H₂ undergoes oxidation at the anode forming protons and electrons¹⁹. The electrons flows through the circuit and protons flow across the proton exchange membrane towards cathode where oxygen undergoes reduction by accepting electrons and protons forming water as the only byproduct (equations 1-3)¹⁹.

Oxidation Reaction :



Reduction Reaction:



Net Reaction

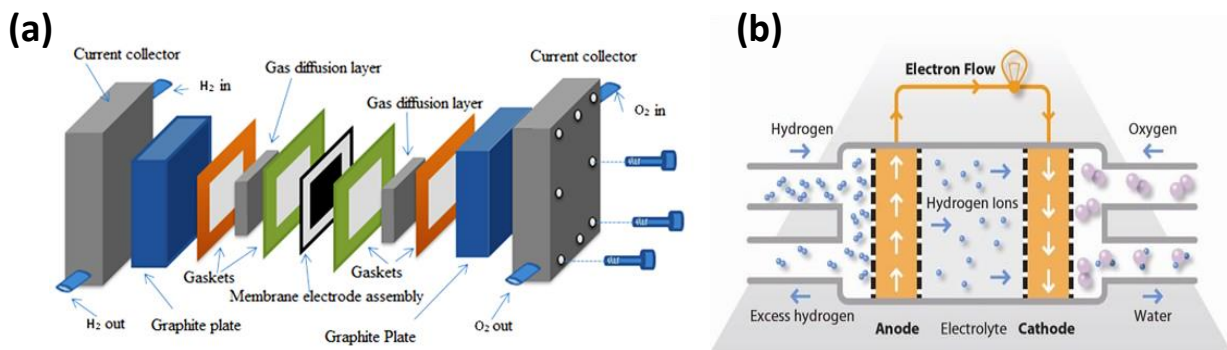


Figure 1.4 Scheme of (a) fuel cell assembly and (b) a PEMFC

<https://nptel.ac.in/courses/103102015/introduction>

Hydrogen is a potential energy carrier molecule of the future and hydrogen based PEMFC fuel cell are the cleanest option electricity production since water is the only byproduct. In the sustainable energy landscape thus fuel cells are integral part of hydrogen economy²⁰⁻²¹. ‘Hydrogen economy’ can be defined as sustainable production of hydrogen and its subsequent utilization for energy conversion which offers a rejuvenating shift towards a carbon neutral economy. This is mainly because hydrogen fuel has long been touted as a clean alternative to gasoline and the utilization of hydrogen fuel for energy conversion is typically achieved with the help of a proton exchange membrane fuel cell (PEMFC); which is a potential zero emission technology. All these suggest that the first part of hydrogen economy or sustainable production of hydrogen is extremely important for realizing a robust hydrogen economy.

1.5 Hydrogen production

Hydrogen is typically produced from biomass and natural gas²⁰. Steam reforming is the most popular method for hydrogen production. Methane is mostly used in steam reforming but other hydrogen carrier molecules such methanol, ethanol, propane, or even gasoline can be used. This method involves production of hydrogen by reacting hydrocarbon with high temperature steam (700°C–1,000°C) under 3–25 bar pressure in the presence of a catalyst to produce hydrogen, carbon monoxide and carbon dioxide (equation 4). Further, the carbon monoxide and steam react in the presence of catalyst to produce more hydrogen (equation 5)²²⁻²⁴. Since, carbon monoxide and carbon dioxide are intermediate in this process, the impure hydrogen stream can adversely affect the performance of PEMFC as carbonaceous impurities are poisonous for platinum based electrocatalysts employed in fuel cells²⁵⁻²⁶. So produced hydrogen needs a separation module before it can be used in PEMFC.

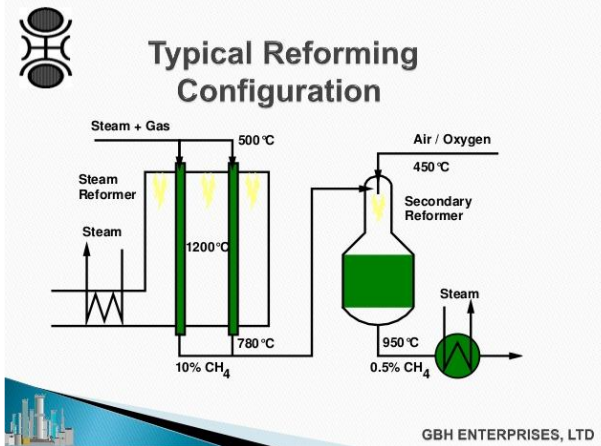
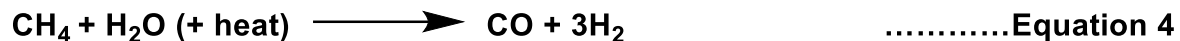


Figure 1.5 Scheme for steam reforming of methane

<https://www.slideshare.net/GerardBHawkins/steam-reforming-the-basics-of-reforming>

Steam-methane reforming reaction



Water-gas shift reaction



1.6 Hydrogen separation

Hydrogen separation is important for sustainable use of hydrogen as an energy carrier. Conventionally hydrogen separation is done by pressure swing adsorption (PSA)²⁷, temperature swing adsorption (TSA)²⁸, cryogenic process²⁹ and membrane based separation³⁰⁻³¹. In PSA, other gaseous impurities such as CO₂ is captured by adsorbent bed at higher pressure allowing only hydrogen to pass through the column. The desorption of captured impurities is carried out at low pressure. TSA is similar to PAS where the adsorbent bed capture impurities at low temperature and releases it at higher temperature but it is time consuming since cooling and heating requires time. Cryogenic process are also used for hydrogen separation where the gaseous mixture is brought down to subzero temperature using external energy. At this subzero temperature other gaseous impurities undergoes phase change from gas to liquid or solid and hence can be easily separated from mixture. Membrane based separation is also popular method for hydrogen separation in which only hydrogen permeate through the membrane to other side because of inherent properties of the membrane. Different types of membrane such as dense polymer, microporous ceramic, dense ceramic, porous carbon and dense

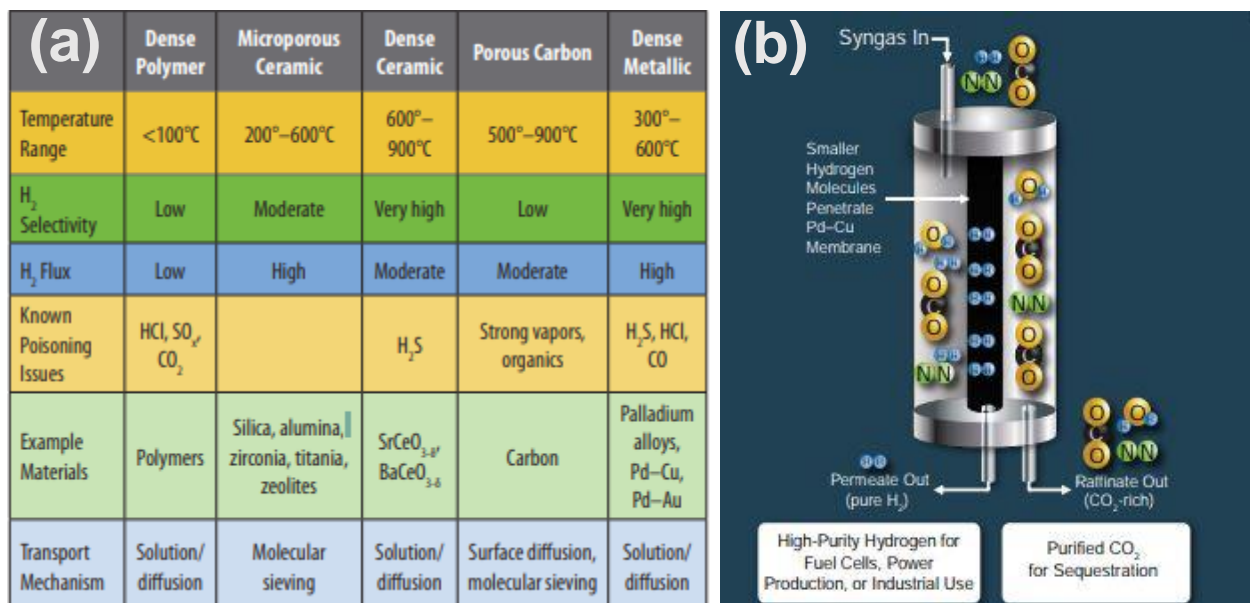


figure 1.6 (a) Properties of hydrogen-selective membranes. (b) Schematic representation for membrane based hydrogen separation

<https://www.undeerc.org/ncht/pdf/eercmh36028.pdf>

metallic are used for hydrogen separation and each one has its own advantages and disadvantages. Apart from these electrochemical methods are also used for hydrogen separation. It is done by electrochemical cell which contains an ion transport membrane in which first H₂ is dissociated at metal electrode, then these protons diffuse across the membrane to other side and produce H₂ on other side of the membrane³².

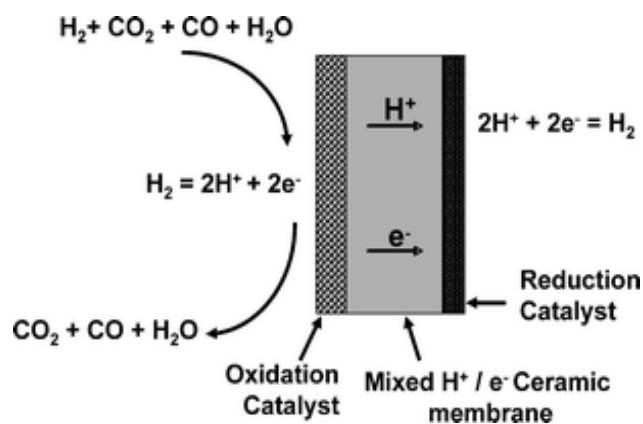


Figure 1.7 Scheme for hydrogen separation using ion transport membrane

Phair, J.W. & Badwal, S.P.S. *Ionics* (2006) 12: 103

1.7 Water desalination

With the exponential increase in global population and industrialization there is ever increasing demand for fresh water. Even though nearly 75% of the earth surface is covered with water but very limited accessible resources are available to get fresh water, all of this resources are dependent on the amount of rain in that region³³. The inconsiderate exploitation of water and changing the rain pattern causes water shortage and today water scarcity is one of the major global issue. The ultimate solution for this problem is seawater. However, seawater is highly saline (salinity is approximately 35 g/L)³⁴, and cannot be used for household or irrigation purposes. So to reduce the salinity of seawater and make it useful for drinking purposes desalination methods play an important role. Desalination is the process of removing salt from saline water³⁵⁻³⁶. The state of the art process for the water desalination is sea water reverse osmosis (SWRO). In the SWRO desalination is carried out by applying an external pressure across the semipermeable membrane to overcome the osmotic pressure so that the water molecules diffuse across the semipermeable membrane to other side leaving behind salt³⁷⁻³⁸. It a highly energy intensive process. Membrane fouling is the serious problem with this method and need frequent cleaning which increases the effective cost of this method³⁹⁻⁴². There are also other methods used for desalination such as multistage flash distillation⁴³⁻⁴⁴, capacitive deionization⁴⁵, electro-dialysis⁴⁶, shock electro-dialysis⁴⁷ and ion concentration polarization⁴⁸. All these methods are energy intensive. Capacitive deionization and electro-dialysis are electrochemical methods for water desalination. Among these capacitive deionization is emerging as a very efficient methods for water desalination.

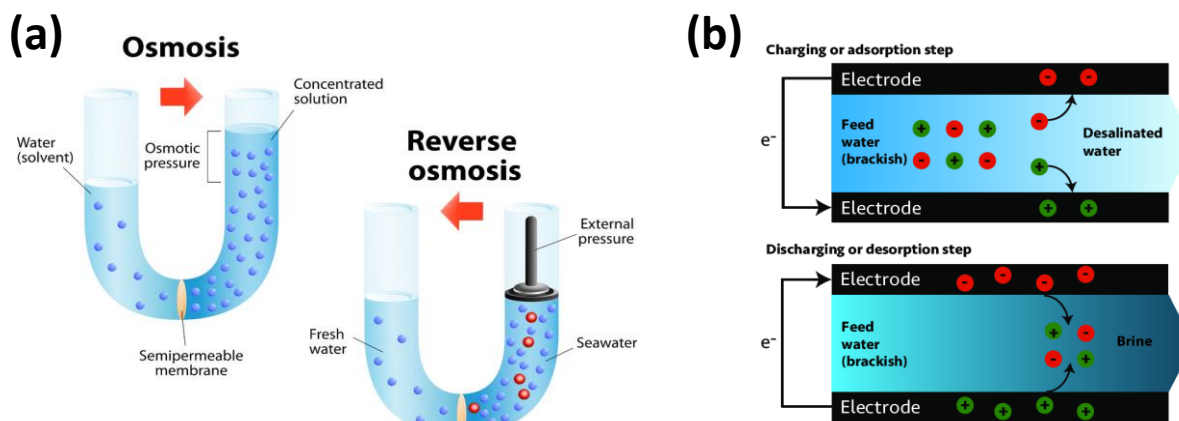


Figure 1.8 Scheme for (a) reverse osmosis and (b) capacitive deionization

(a) <https://puretecwater.com/reverse-osmosis/what-is-reverse-osmosis>

(b) Dykstra, Jouke. (2018). Desalination with porous electrodes.

We have attempted to address the two issues of water desalination and H_2 purification by developing a fuel cell concept which can couple electric power production with fuel exhalation. To achieve this target we interconvert energy of neutralization as electromotive force by decoupling the direct acid-alkali chemistry. This device can purify the hydrogen fuel stream and desalinate water during electric power production.

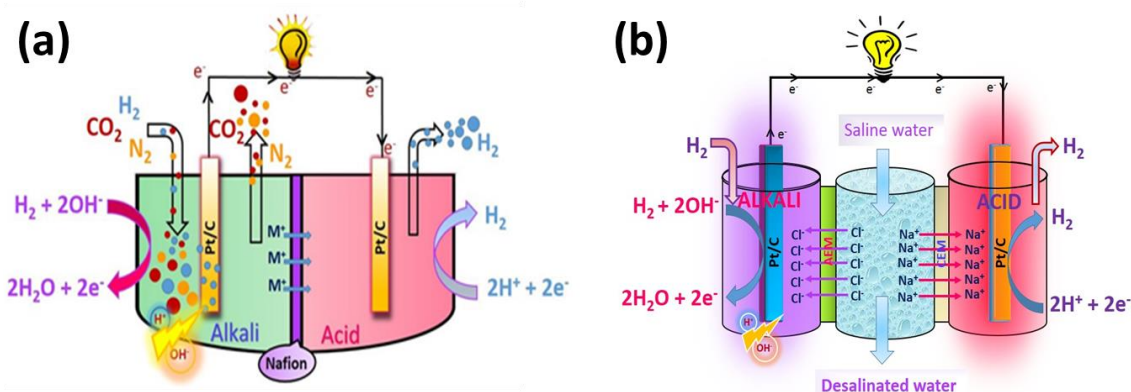


Figure 1.9 Schematic representation for (a) hydrogen purifying fuel cell (b) desalination fuel cell

CHAPTER 2. EXPERIMENTAL SECTION

2.1 Chemicals

Sodium hydroxide (97%), sulfuric acid (98%), Sodium chloride (99%) potassium hydrogen phosphate (98%), Phosphoric acid (99.9%), potassium phosphate (99%), acetic acid (99.7%), sodium acetate (99%), and potassium sulfate (99%), potassium carbonate (99%) were bought from Sigma-Aldrich India and were used as such. Pt@C was obtained from Fuel Cell Store (USA). Nafion@ 117 and Fumasep membrane was obtained from Fuel Cell Store (USA).

2.2 Characterization techniques

Electrochemical measurement were performed by using the VMP-300 Electrochemical Workstation (Biologic, France). The cleaning of all the electrode was done with 0.05-micron alumina powder and then cycling the electrode in 0.5 M H₂SO₄. The Desalination studies were done by conductivity (Conductivity Meter 306) and Microwave Plasma Atomic Emission Spectroscopy (4200 MP-AES) measurement and H₂ separation was confirms by Mass Spectroscopy (Agilent 5973N MSD) and Gas Chromatography (Agilent 7693 G4514A).

a. Cyclic voltammetry

Cyclic voltammetry (CV) is a powerful electrochemical technique used to investigate the redox properties of molecular species. It is a current vs potential curve of the response current recorded at the working electrode to the applied excitation potential across it⁴⁹. CV is generally performed in three electrode configurations.

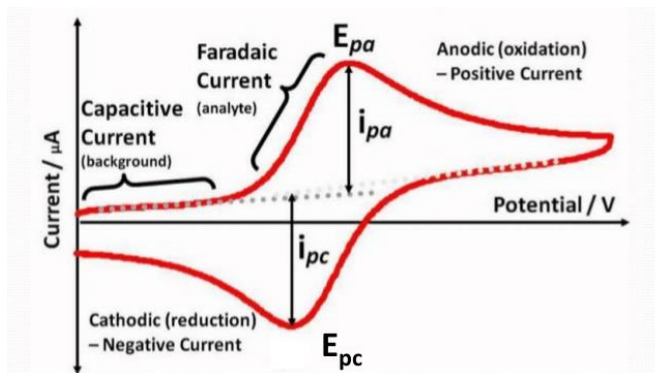


Figure 2.1: Schematic representation of cyclic voltammogram

<https://www.slideshare.net/AfrinNirfa1/cyclic-voltammetry>

The potential of the working electrode (WE) is monitored using a reference electrode (RE). The controlling potential applied across the WE and the counter electrodes is the excitation signal. The excitation signal shows linear variation with time at a specific sweep rate (in volt / second); first scan positively and then the potential is scanned in reverse direction, making a complete cycle hence the name cyclic voltammetry⁴⁹. The Hydrogen evolution reaction (HER) and Hydrogen oxidation reaction (HOR) were studied as a function of pH using a Pt disk (2 mm diameter) as the working electrode, platinum mesh as the counter electrode and an Ag/AgCl (Cl⁻) (3.5 M KCl) as a reference electrode. The buffer solutions with different pH were made and pH was confirmed by pH meter. First, the solution was saturated with hydrogen by purging for 15 minutes and then cyclic voltammograms were recorded by scanning the potential from 0.4 V to -1.2 V at scan rate of 20 mV/s with continuous head space purging of hydrogen.

b. Chronopotentiometry

Chronopotentiometry is a technique in which constant potential is applied on working electrode and current is measured as a function of time using proper reference electrode.

c. Chronoamperometry

Chronoamperometry is an important technique usually used for the electroplating where constant current is applied on the working electrode and potential of the working electrode is monitored as a function of time using a reference electrode⁵⁰.

d. Microwave plasma atomic emission spectroscopy (MPAES)

The MPAES technique used for multi-analyte determination of minor and major element. Microwave energy is used to produce plasma discharge. Samples are typically nebulized prior to interaction with the plasma and then this atomized sample passes through the plasma and electrons are promoted to the excited state. The excited electrons return to the ground state with emission of light which is separated into a spectrum. The intensity of each emission line is measured at the detector⁵¹. It provides the concentration of specific analyte corresponding to that intensity of emission line. This technique was used for understanding the extent of desalination studies. The three compartment fuel cell, initially with 4 M NaCl in the middle chamber was discharged completely and then the solution from middle chamber was analyzed by MP-AES analysis to determine the concentration of sodium ions.

e. Titration method

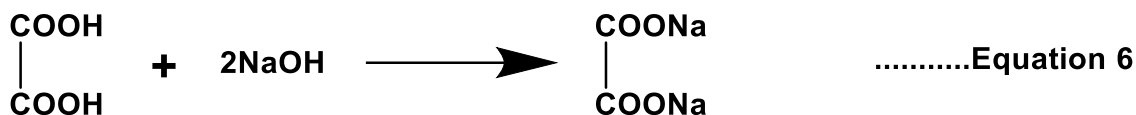
Titration is a method to determine the concentration of unknown solution using the solution of known concentration.

e.1 Acid-base titration

This titration is used to determine the concentration of unknown acid or base. We used phenolphthalein as an indicator for the end point of acid base neutralization reaction. It is colorless in acidic and turn to magenta in basic solution. We have used this method to determine the concentration of anolyte (NaOH) and catholyte (H₂SO₄) of the discharge product to confirm energy of neutralization is the driving force for the fuel cell we have proposed. The anolyte and catholyte was titrated against 0.5 M oxalic acid and 1 M NaOH respectively. Since, NaOH is highly hygroscopic, we first standardized the 1 M NaOH solution using 0.5 M oxalic acid and then used the standardized NaOH solution for determination of catholyte (H₂SO₄) concentration⁵⁴⁻⁵⁵.

For catholyte titration

Step 1 Standardization of NaOH using oxalic acid



Step 2 Titration unknown acid against standardize NaOH

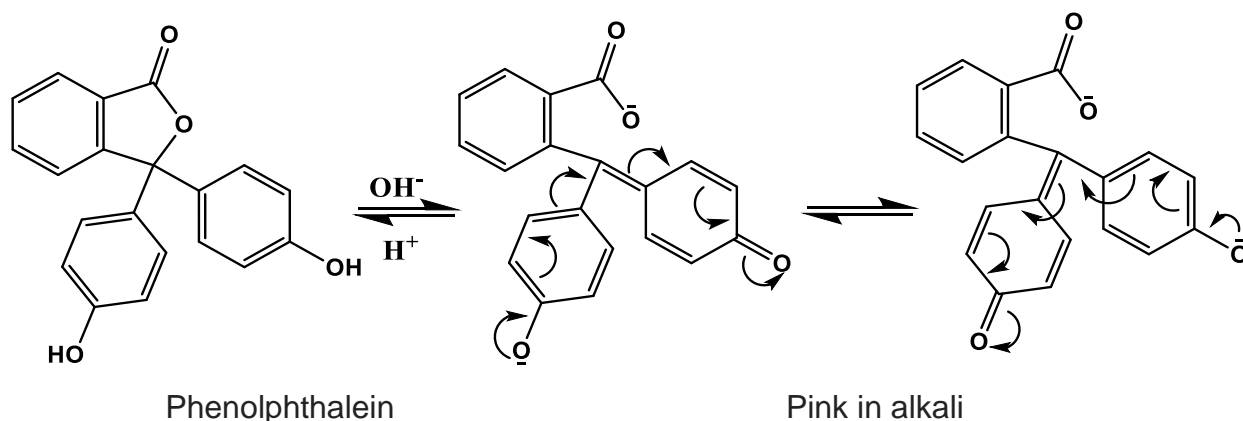


The concentration of unknown solution can be calculated using following formula,

$$a_1 \cdot M_1 \cdot V_1 = a_2 \cdot M_2 \cdot V_2$$

where a_1 , M_1 , V_1 are respectively basicity, molarity and volume of acid used and a_2 , M_2 , V_2 are acidity, molarity and volume of base used in the titration.

At the end point of the reaction



e.2 Mohr's method

This method used to determine the chloride ions concentration of a solution by titrating against the silver nitrate. Potassium chromate is used as an indicator for end point detection. When silver nitrate solution is added slowly to the chloride solution, a white precipitate of silver chloride is formed. At the point when all chloride ions are precipitated and the excess silver reacts with chromate ions of the indicator and form red-brown precipitate of silver chromate⁵⁶⁻⁵⁷.

Titration reaction



End point reaction



e.3 Gravimetric analysis of sulphate

The gravimetric analysis is an analytical method used for quantitative determination of analyte based on the mass of an analyte. The gravimetric analysis of sulphate is used to determine the amount of Sulphate in solution. When aqueous solution of barium chloride is added slowly to sulphate ion solution under constant stirring an insoluble white precipitate of barium sulphate is formed which is then collected by centrifugation. It is washed with cold water and then with acetone, dried and weighed. Based on the weight of BaSO_4 , amount of sulphate in the solution was quantified which is used for confirming deionization in the cathodic compartment of fuel cell⁵⁸⁻⁸⁹.

Titration reaction



f. Gas chromatography

The gas chromatography is used to separate the different chemical compounds. Based on the differential interaction of compound with chromatography column the separation of different compounds takes place. The compound with lowest affinity for chromatography column elute first followed by lower affinity compounds. We have used this method to check the purity of hydrogen and the purity of hydrogen collected from cathodic compartment is found to be 100%.

$$\text{Purity of Hydrogen} = \frac{\text{intensity of peak corresponding to Hydrogen}}{\text{total intensity of all peak}} \times 100$$

g. CO (carbon monoxide) stripping

This experiment was carried out to show the platinum electrode poisoning by carbon monoxide. The Pt/C catalyst ink was prepared by mixing Pt/C (5 mg) in 0.5 mL isopropanol with 5 wt% Nafion binder and sonicated for 30 minutes. The Pt/C catalyst ink was drop casted onto the glassy carbon electrode. First the CO was purged into the 1 M KOH solution for 40 minutes after that N₂ was purged into the same solution for 20 minutes. Then by using three electrode configuration with Pt/C coated glassy carbon electrode as working, platinum mesh as counter and Hg/HgO (1M NaOH⁻) as a reference electrode, the cyclic voltammetry was recorded by scanning the potential from - 0.7 V to 0.4 V and reversed scan to -0.85 V with respect to standard hydrogen potential⁵²⁻⁵³.

h. Fuel cell assembly

All the fuel cell experiments were done in a 3 compartment fuel cells. The three compartment fuel cell was assembled by using Pt/C (40 wt% Pt) as an anode electrode and platinum mesh as a cathode electrode. Pre-treatment of Nafion membrane as follows. A Nafion@117 membrane is pre-treated with H₂O₂ and water solution taken in 1:3 ratio respectively and the solution is heated at 80 °C for 30 minutes. After washing with distilled water, Nafion membrane is again heated at 80 °C for 30 minutes in H₂SO₄ solution⁶⁰ to make it proton conducting.

1 M H₂SO₄ and 2 M NaOH were used as a catholyte and anolyte respectively, and 4 M NaCl was used in middle chamber for desalination. 1 M NaCl was used in the middle chamber while deionizing the half-cells. The anodic and cathodic compartment were separated by anion exchange membrane and cation exchange membrane respectively and the middle chamber housed the water for desalination. This configuration cause's desalination in the middle chamber and by interchanging the interfacial chemistry of membrane the same configuration can be used for water deionization in both anodic and cathodic compartment. The hydrogen was purged in anodic compartment which undergoes oxidation and there is regeneration of pure hydrogen back from cathodic compartment by utilizing the energy of neutralization. We have subsequently used this fuel cell for separating a mixture of gaseous species in the anodic compartment and collected the 100% pure hydrogen from the cathodic

compartment whose purity is confirmed by gas chromatography and in-situ mass spectrometry. After discharge, solution from the middle chamber was collected and desalination studies were carried out.

CHAPTER 3. RESULTS AND DISCUSSION

3.1 Abstract

'Hydrogen economy' or sustainable production of hydrogen and its subsequent utilization for energy conversion offers a rejuvenating shift towards a carbon neutral economy. This is mainly because hydrogen fuel has long been touted as a clean alternative to gasoline and the utilization of hydrogen fuel for energy conversion is typically achieved with the help of a proton exchange membrane fuel cell (PEMFC); which is a potential zero emission technology. The steam reforming of alcohols and methane is the most popular method for hydrogen production but hydrogen produced by this method always contain impurities such as CO and CO₂ beyond the tolerance level to be directly utilized in a fuel cell. This necessitates energy intensive fuel separation methods such as pressure swing adsorption (PSA), temperature swing adsorption (TSA), cryogenic distillation and membrane based purification. We demonstrate a fuel cell concept driven by the energy of neutralization, which can purify the hydrogen fuel stream during electric power production. The gas chromatography and in-situ electrochemical mass spectrometry confirm the production of highly pure hydrogen as the cathodic half-cell chemistry and exclusive consumption hydrogen in the impure fuel stream as the anodic half-cell chemistry. The same fuel cell configuration is further extended for water desalination and half-cell water deionization during electric power production using the concept of bipolar membranes. The desalination studies show this fuel cell is able to desalinate highly saline water (4 M NaCl) during the production of ~26 mW/cm² of electric power and ~22.8 mL/h of hydrogen fuel.

3.2 Introduction

Air pollution and water scarcity are two major problems faced by 21st century. We have to shift from fossils fuels to sustainable energy solutions such as hydrogen to address global warming and paramount pollution. To enable sustainable drinking water supply desalination of seawater is the ultimate solution³⁵.

Hydrogen fuel is an integral part of sustainable energy chain as water is the only byproduct during hydrogen energy conversion, therefore shifting from present hydrocarbon economy to hydrogen economy has long been touted as an energy pathway to reduce the carbon foot print substantially. However, because of hydrogen's peculiar physic chemical properties, low molecular weight alcohols were employed as hydrogen carrier molecules²⁰. The extraction of hydrogen from alcohols to be used in indirect alcohols fuel cell is typically achieved by steam reforming technique²². This technique invariably requires very high temperature and pressure and it is well known to carbonize hydrogen streams beyond tolerance level to be directly utilized in fuel cells²⁵. So hydrogen fuel purification is important for sustainable use of hydrogen as an energy carrier. Conventionally, hydrogen separation is carried out by by pressure swing adsorption (PSA)²⁷, temperature swing adsorption (TSA)²⁸, cryogenic process²⁹ and membrane based separation³⁰⁻³¹. In PSA, other gaseous impurities such as CO₂ is captured by adsorbent bed at higher pressure allowing only hydrogen to pass through the column. The desorption of captured imputies is carried out at low pressure. TSA is similar to PAS where the adsorbent bed capture impurities at low temperature and releases it at higher temperature but it is time consuming since cooling and heating require time. Cryogenic process are also used for hydrogen separation where the gaseous mixture is brought down to subzero temperature using external energy. At this subzero temperature other gaseous impurities undergoes phase change from gaseous to liquid or solid states and hence can be easily separated from the mixture. Membrane based separation is also popular method for hydrogen separation in which only hydrogen permeate through the membrane to other side because of inherent properties of the membrane. Different types of membrane such as dense polymer, microporous ceramic, dense ceramic, porous carbon and dense metallic are used for hydrogen separation and each one has its own advanantages and disadvantages. Apart from these electrochemical methods are also used for hydrogen separation. It is carried out by electrochemical cell which contains an ion transport membrane in which first H₂ is dissociated at the metal electrode, then this protons diffuse across the mebrane to other side and produce H₂ on other side of the membrane³².

The ocean contains nearly 97% of earth water so obtaining potable water from sea can address the global water scarcity problem. However, seawater is highly saline (salinity is approximately 35 g/L)³⁴, and cannot be used for household or irrigation purposes. So to reduce the salinity of seawater and make it useful for drinking purposes desalination methods play an important role. Desalination is the process of removing salt from saline water. It is an energy intensive process. The state of the art process for the water desalination is sea water reverse osmosis (SWRO). In the SWRO, desalination is carried out by applying a pressure so as to increase the osmotic pressure across the semipermeable membrane which makes it a highly energy demanding process. There are other methods used for desalination such as multistage flash distillation, capacitive deionization, electro-dialysis, shock electro-dialysis and concentration polarization. However, all these methods are equally energy demanding. Here in we report a fuel cell concept which can purify impure hydrogen stream during electric power production. The same fuel cell concept can be extended for water desalination during electric power production and hydrogen fuel exhalation. Both the fuel cell concept interconvert energy of neutralization as electromotive force.

3.3 Results and Discussion

The hydrogen evolution reaction (HER) and hydrogen oxidation reaction (HOR) are proton coupled reactions whose potential shifts with pH (shown in Figure 3.1). The potential shift is ~ 60 mV negatively for both HER and HOR with unit change in pH. This will generate a potential difference if direct acid alkali chemistry is decoupled in such a way that HOR will occur in alkaline medium and HER in acidic solution (equation 11-13). Therefore electricity production is mainly by interconverting the energy of neutralization reaction. When direct acid alkali chemistry is decoupled, the anodic half-cell possessed a negative redox potential relative to the cathodic half-cell, Figure 3.2, making simultaneous electric power production and hydrogen exhalation from the cathode feasible. Since there is exclusive oxidation of hydrogen at anode and generation of pure hydrogen at cathode, it can be used for purifying impure hydrogen stream as shown in Figure 3.3.

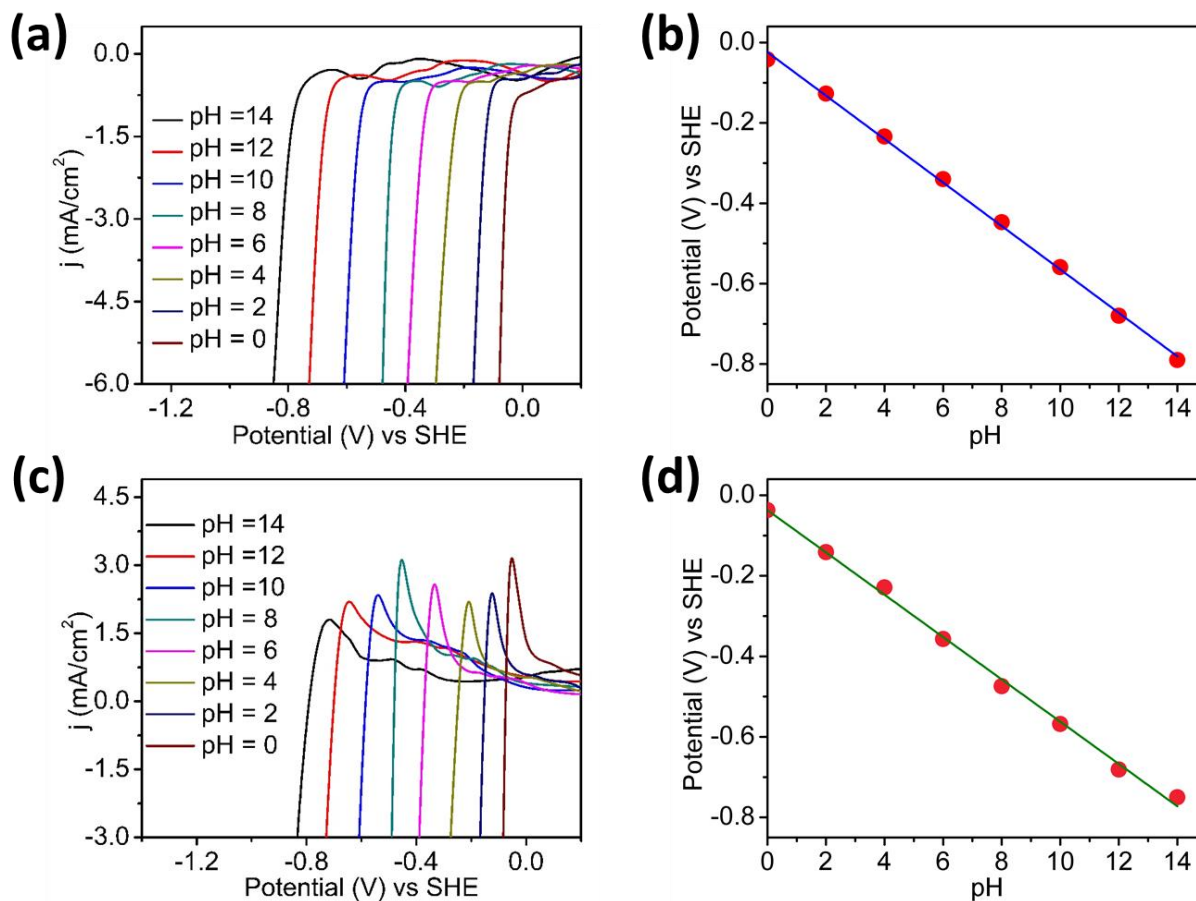
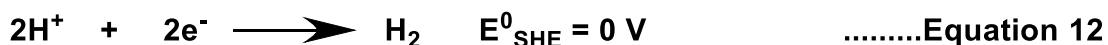


Figure 3.1: (a) Linear sweep voltammogram for hydrogen evolution reaction at different pH at a scan rate of 20 mV/s and (b) corresponding Pourbaix diagram for hydrogen evolution reaction. (c) Linear sweep voltammogram for hydrogen oxidation reaction at different pH at a scan rate of 20 mV/s and (d) corresponding Pourbaix diagram for hydrogen oxidation reaction.

In alkaline compartment



In acidic compartment



Total cell reaction



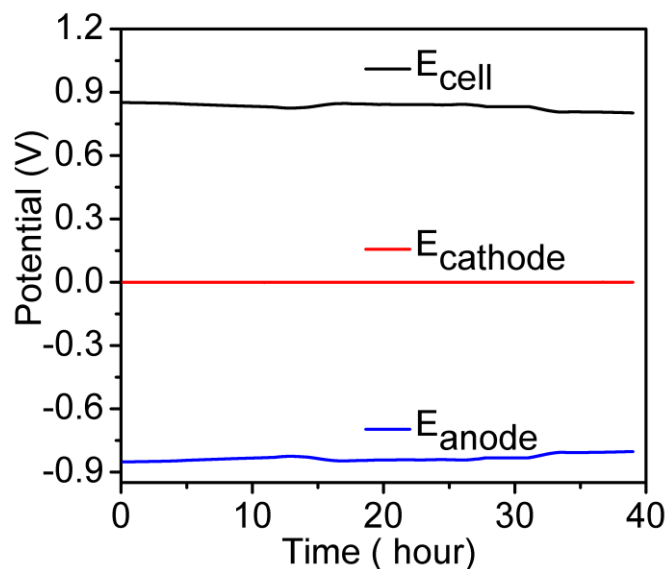


Figure 3.2: Cathodic and anodic half-cell potentials with time for hydrogen exhaling fuel cell.

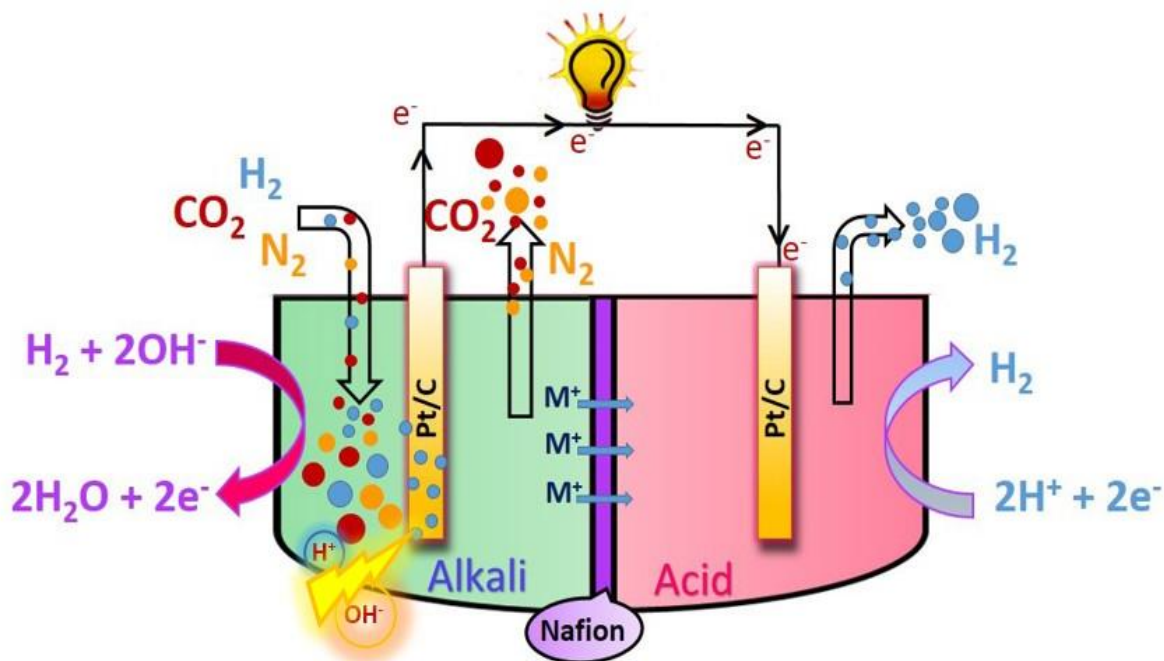


Figure 3.3: Schematic representation of hydrogen purifying fuel cell.

This fuel purification is extremely important because of the well-known poisoning of Pt based electrocatalyst by carbon containing impurities such as CO. This poisoning of Pt domains by CO is investigated by cyclic voltammetry, Figure 3.4, and it suggest a sharp

CO stripping peak on Pt domains evidencing its blocking by carbonaceous impurities. This CO removal can be accelerated by alloying Pt with Ru due to the operation of bifunctional mechanism, Figure 3.4, where CO stripping occurs at more negative potential compared to Pt.

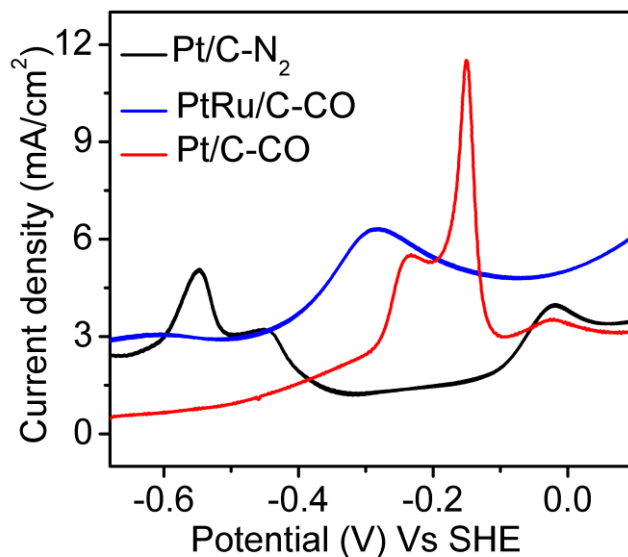


Figure 3.4: Linear sweep voltammogram showing CO poisoning of Pt and PtRu electrocatalysts. These catalysts are widely employed in fuel cells and therefore the presence of carbonaceous impurities can affect the performance of fuel cells.

3.3.1 Fuel Purifying Fuel Cell

Since in the anodic half-cell of proposed fuel cell, there is exclusive hydrogen oxidation even in the presence of a mixture of gaseous species containing hydrogen, this fuel cell offers opportunities for hydrogen fuel purification, Figure 3.3. When pure hydrogen is bubbled to the anodic half-cell, the polarization demonstrated ~60 mW/cm² at ~140 mA/cm² peak current density, Figure 3.5a. When impure hydrogen is bubbled into the anodic half-cell, the peak power and peak current densities are decreased suggesting hydrogen is the fuel for the fuel purifying fuel cell, Figure 3.5a. This is further clear from the long term discharge at the same current density where the time of discharge is reduced by half when 50:50 mixture of H₂ and N₂ is passed to the anodic

half-cell, Figure 3.5b. Therefore, hydrogen oxidation in the impure mixture is the anodic half-cell chemistry (equation 14). The cathodic half-cell chemistry is monitored by gas chromatographic technique and it evidence the presence of pure hydrogen (Figure 3.5c), indicating HER as the exclusive cathodic half-cell chemistry (equation 15). Therefore the overall cell reaction involves the purification of impure hydrogen and hence it offers opportunities for fuel purification during electric power production, equation 16.

3.3.1.1 Fuel Cell Performance

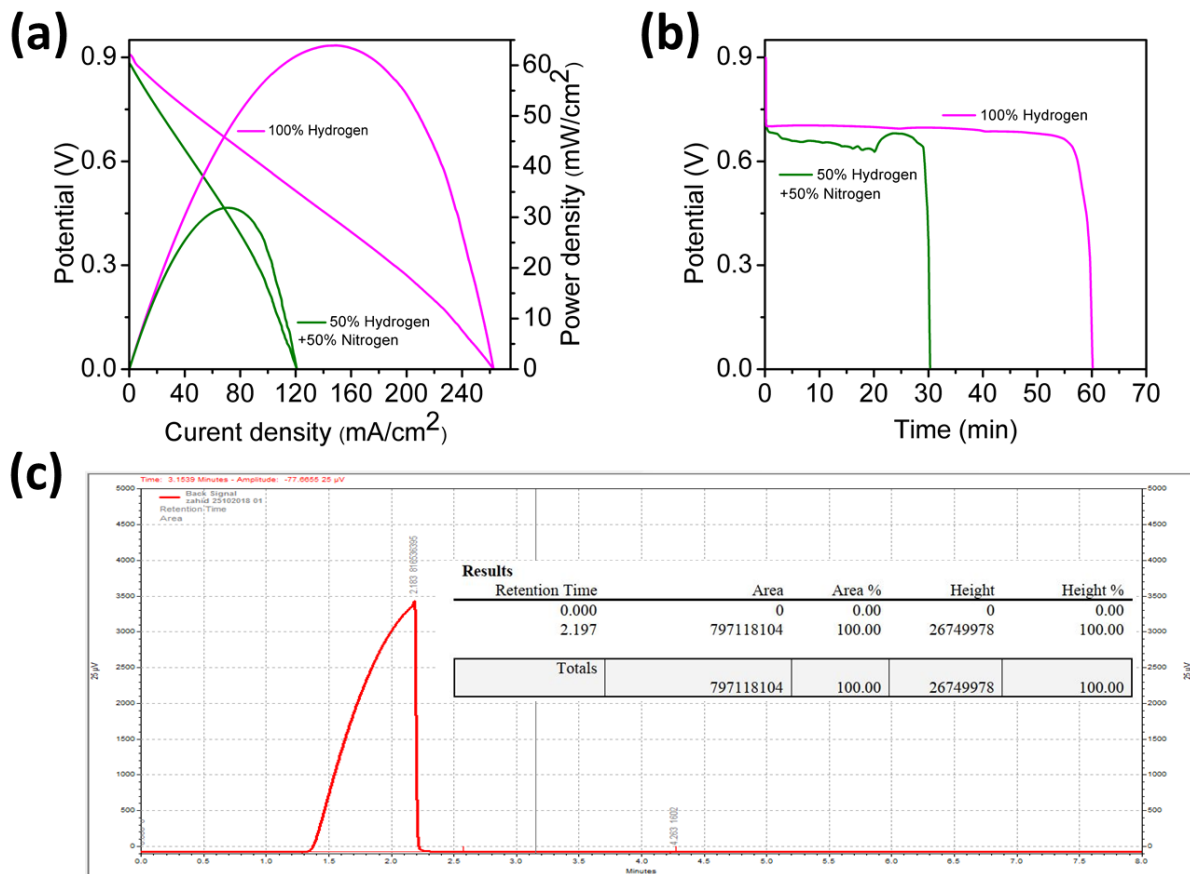
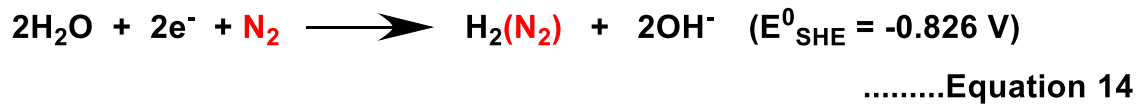
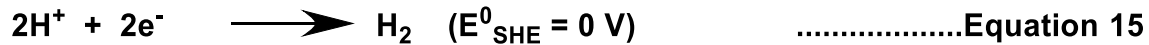


Figure 3.5: (a) Polarization curve for hydrogen purifying fuel cell, (b) galvanostatic polarization of hydrogen purifying fuel cell at 40 mA/cm² and (c) gas chromatogram for the gaseous species collected from the cathodic compartment.

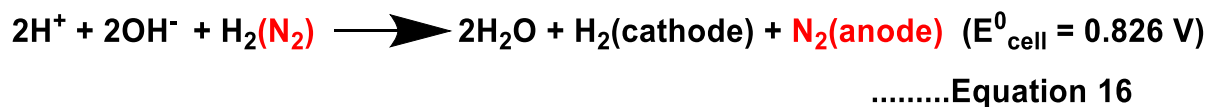
Anodic half-cell reaction



Cathodic half-cell reaction



Total cell reaction:



3.3.2 Water Desalination Fuel Cell

The same two compartment H_2 separation fuel cell configuration is extended to three compartment fuel cell configuration for water desalination. Here, the middle compartment house the water for desalination and anodic and cathodic half-cells are separated from the middle compartment by anion exchange membrane (AEM) and cation exchange membrane (CEM) respectively, Figure 3.6. When direct acid alkali chemistry is decoupled the anodic half-cell possessed a negative redox potential relative to the cathodic half-cell, Figure 3.2, making simultaneous electric power production and hydrogen exhalation from the cathode feasible (equation 11-13). Therefore, anodic and cathodic half-cell reactions involve the consumption of OH^- ions and H^+ ions respectively. This will generate a net positive and a net negative charge in anodic and cathodic compartment respectively. So if anodic and cathodic compartment were separated by anion and cation exchange membranes, then chloride ions will migrate to anodic compartment through AEM and sodium ions will migrate to cathodic compartment through CEM from the middle chamber to balance the net charges generated. This process of removing ions from the solution is known as desalination and here it occurs during simultaneous electric power generation and fuel exhalation.

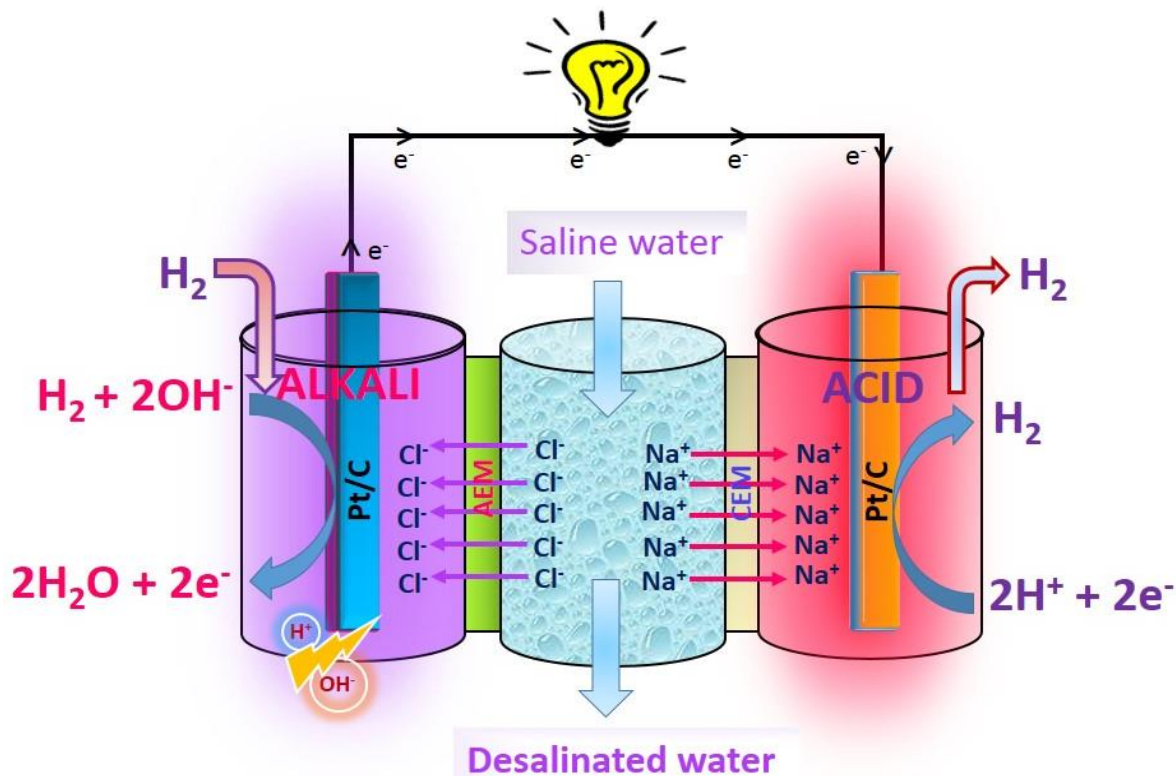


Figure 3.6: Schematic representation of desalination fuel cell. AEM is anion exchange membrane and CEM is cation exchange membrane.

3.3.2.1 Fuel Cell Performance

The experimental studies indicates three compartment fuel cell shows good performance with power density of $\sim 26 \text{ mW/cm}^2$ at current density of 150 mA/cm^2 , Figure 3.7a. It takes nearly 22 hours for the complete discharge of the fuel cell and the H_2 collected from cathodic compartment shows nearly 100 % faradic efficiency, Figure 3.7b and Figure 3.7c. The open circuit voltage (OCV) measurements shows long term stability of fuel cell with very less decrease in OCV even after 40 hours (Figure 3.7d) suggesting diffusion driven neutralization reactions are negligible with in this time limit. The desalination studies were carried out using MP-AES (Microwave Plasma Atomic Emission Spectroscopy) and conductivity measurement by collecting the solution from the middle chamber after the complete discharge of the fuel cell.

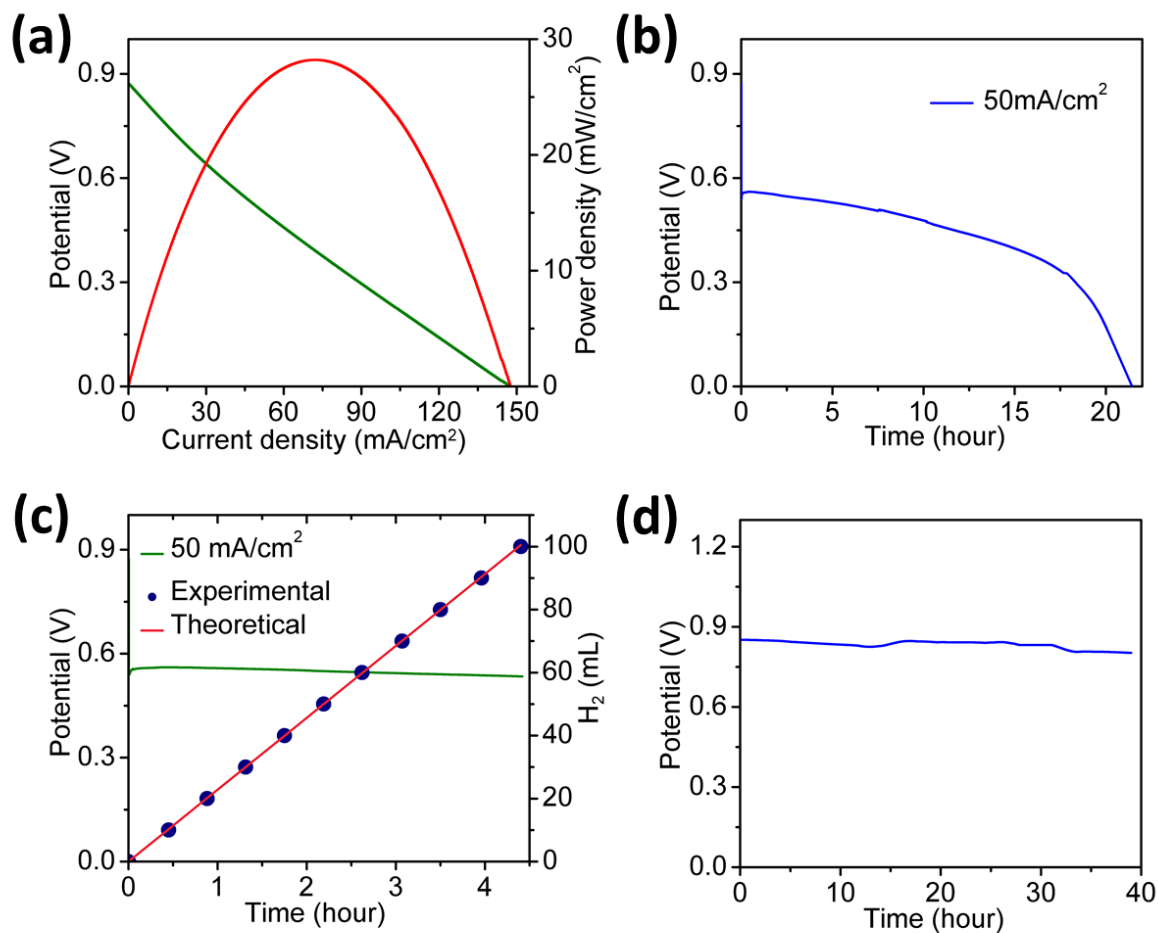


Figure 3.7 (a) Polarization curve for fuel exhaling water desalination fuel cell (FEWDFC), (b) galvanostatic polarization of FEWDFC at 50 mA/cm², (c) galvanostatic polarization at a current density of 50 mA/cm² with H₂ quantification at the cathode and (d) open circuit voltage measurement with time.

3.3.2.2 Desalination Studies

The desalination studies confirm the removal of salt from the middle chamber during the discharge process, Figure 3.8. The analyte OH⁻ concentration and catholyte H⁺ concentration decreased after discharge because of their consumption during electrochemical reactions, Figure 3.8a. This change in concentration of acid and base after discharge indicates that the heat of neutralization is the driving force for this fuel cell, Figure 3.8a. The decrease in sodium ion concentration from 4 M to 1 M measured using the MP-AES, the decrease in Cl⁻ ion concentration from 4 M to 1.2 M by Mohr's method and sharp decrease in conductance values suggest desalination

capability of fuel cell for highly saline water (Figure 3.8b-c) during electric power production. The desalination is happening by balancing the charge generated in anodic and cathodic compartment during the electrochemical reaction by movement of ions from middle chamber to respective compartments (equation 17-18).

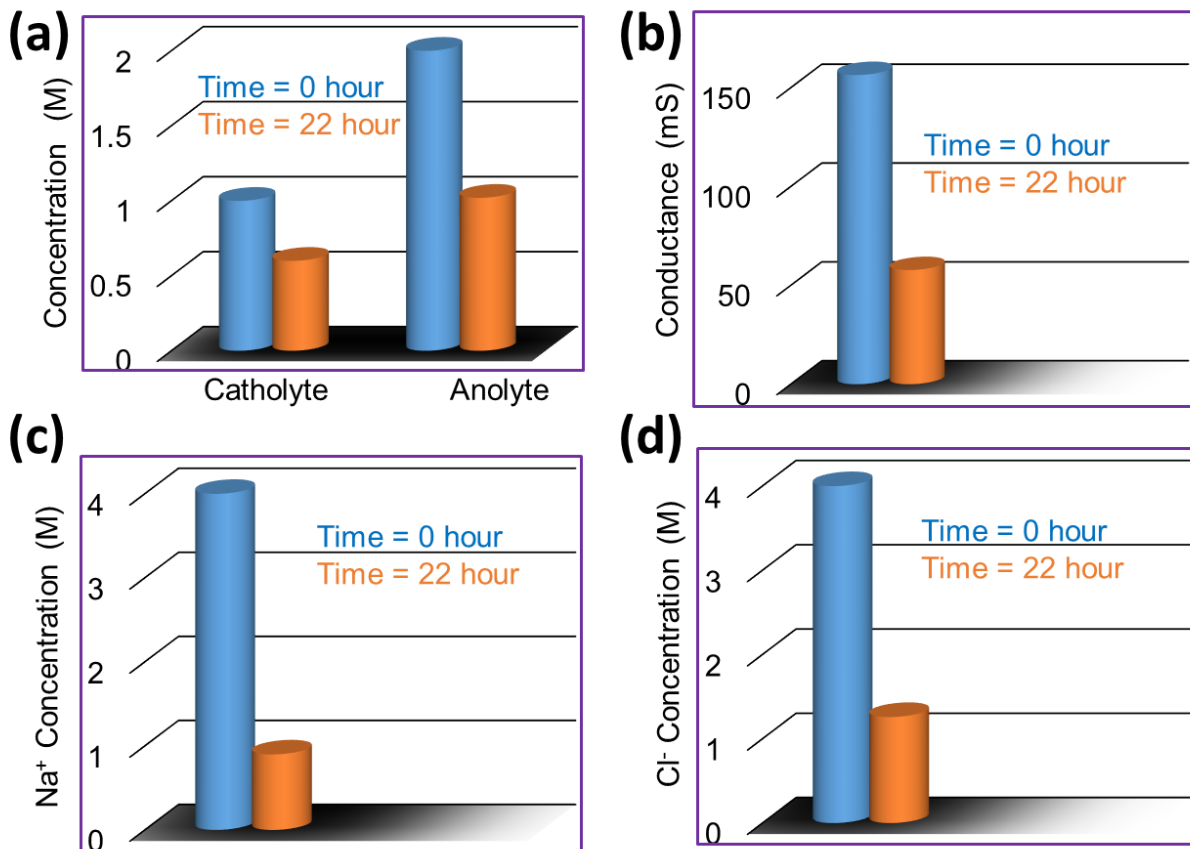


Figure 3.8 (a) Concentration of anolyte and catholyte before and after discharge, (b) conductance measurement (c) sodium ion concentration estimated by MP-AES and (d) chloride ion concentration estimated by precipitation titration before and after discharge of the fuel cell.

3.3.3 Water Deionization Fuel Cell

Deionization is the process of removing ions from a given solution. We have extended the same three compartment water desalination configuration further for water deionization. By changing the interfacial chemistry of membrane we are able to do deionization in the half cells of three compartment fuel cell. For achieving this target, we have separated the anodic and cathodic half-cells from the middle saline compartment (1 M NaCl) by CEM and AEM respectively. This should reverse the ion flow during electric power production as shown in Figure 3.9 and equation 19-21.

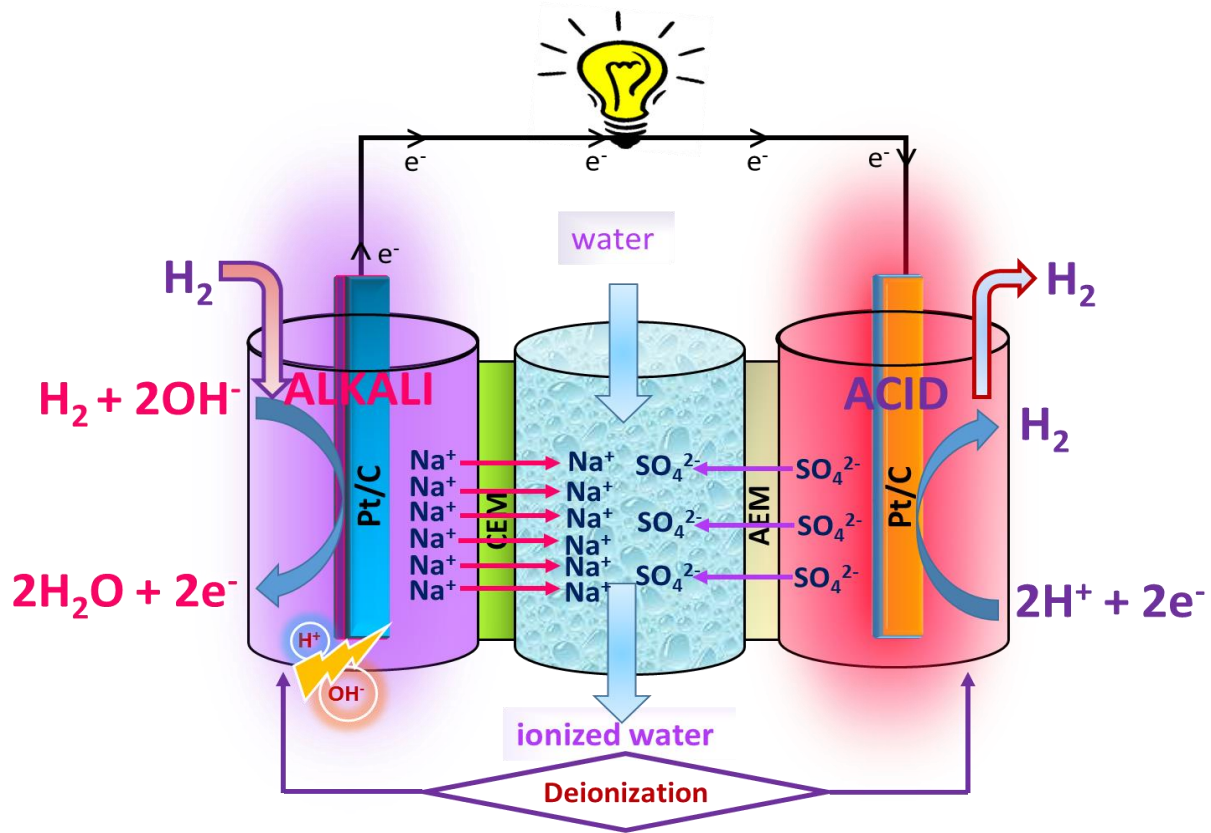
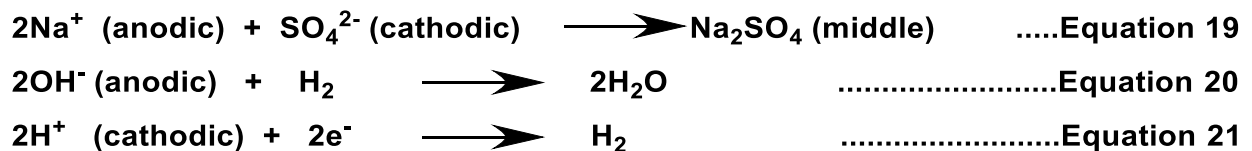


Figure 3.9: Schematic representation of water deionization fuel cell. CEM and AEM are cation exchange membrane and anion exchange membrane respectively.



3.3.3.1 Fuel Cell Performance

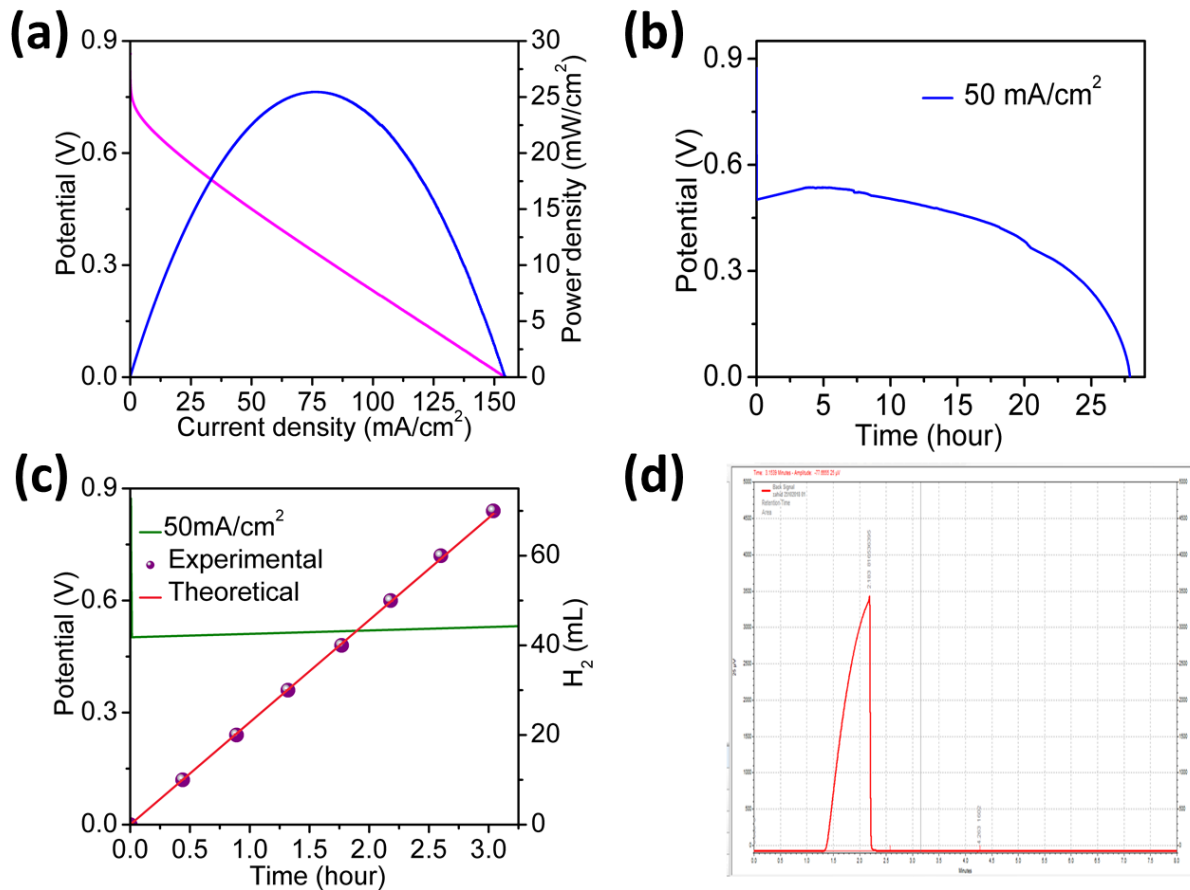


Figure 3.10 (a) Polarization curve for fuel exhaling water deionization fuel cell (FEWDFEC), (b) galvanostatic polarization of FEWDFEC at 50 mA/cm², (c) galvanostatic polarization at a current density of 50 mA/cm² with H₂ quantification at the cathode and (d) gas chromatography for gaseous species collected at the cathode.

The fuel exhaling water deionization fuel cell shows decent performance with power density of ~25 mW/cm² at current density of ~160 mA/cm² with nearly 100 % efficiency for hydrogen production during discharge chemistry (Figure 3.10a-c). The gas chromatogram of collected gaseous species from the cathode shows it is pure hydrogen, Figure 3.10d.

3.3.3.2 Deionization Studies

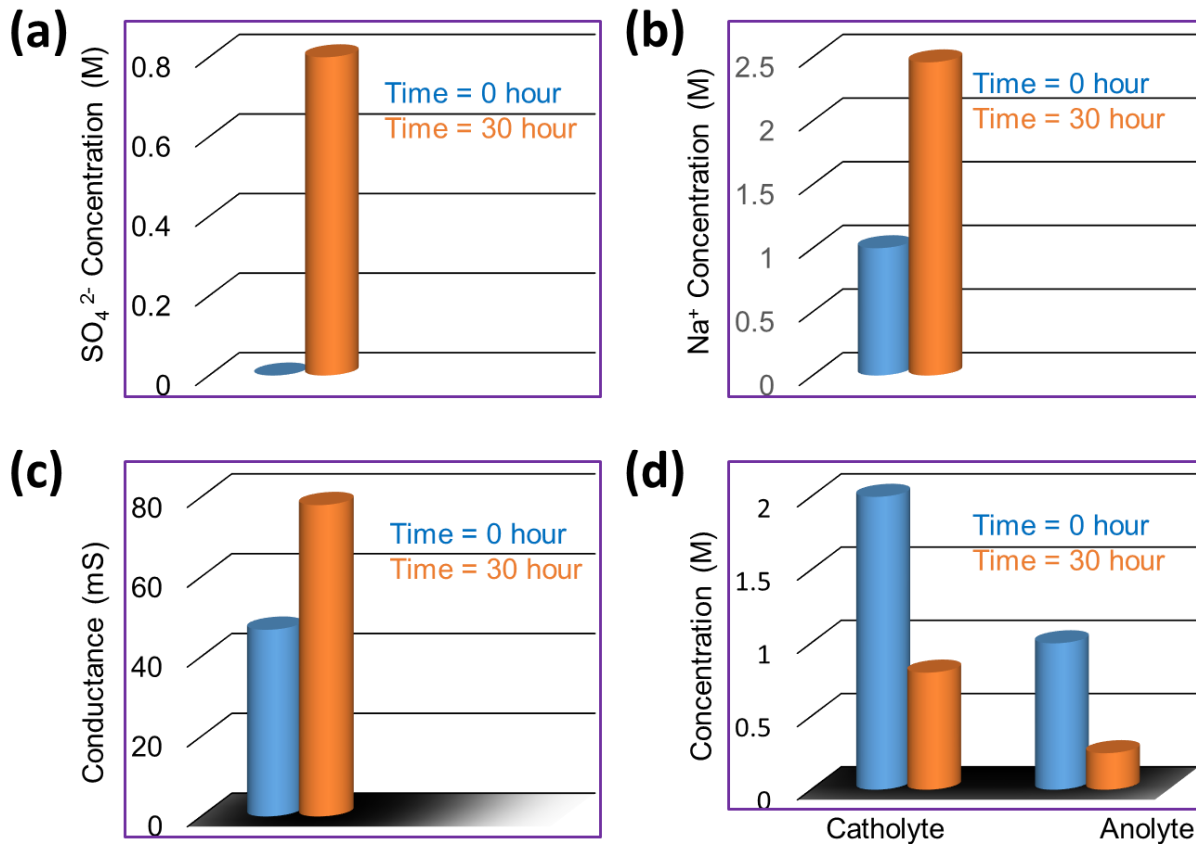


Figure 3.11 (a) Sulphate ion concentration in the middle chamber before and after discharge and (b) sodium ion concentration in the middle chamber before and after discharge. (c) Conductance measurement before and discharge in the middle compartment. (d) Concentration of OH^- in the anolyte and H^+ in the catholyte before and after discharge of the fuel cell.

The increase in concentration of sodium and sulphate ions in the middle chamber after complete discharge of the fuel cell confirms the deionization process in both the half-cells (Figure 3.11a-b). The increase in conductance of middle chamber further suggest migration of ions to the middle chamber from the other two half-cells (Figure 3.11c). The decrease in concentration of catholyte (acid) and anolyte (base) after the discharge indicate that the heat of neutralization is the driving force for the operation of fuel cell (Figure 3.11d). Over all the fuel cell concept driven by energy of neutralization can be exploited for hydrogen fuel purification during electric power production. Using

bipolar membrane architecture, it is possible to achieve desalination of highly saline water. By controlling the interfacial chemistry of bipolar membranes, overall water purification in the half-cells could be achieved.

CHAPTER 4. CONCLUSION AND FUTURE OUTLOOK

We have successfully shown that fuel exhaling fuel cell driven by energy of neutralization can be used for hydrogen purification, water desalination and water deionization during electric power production. Because of the presence of bipolar electrolytes and bipolar membranes, the fuel cell demonstrated multiple capabilities of fuel production, water deionization and desalination during electricity generation. The pH gradients allowed purification of impure hydrogen stream with the production of nearly 100 % pure hydrogen in the cathodic half-cell. The employment of bipolar membrane configuration allows water desalination of highly saline water (4 M NaCl) during electric power generation which is confirmed by microwave plasma atomic emission spectroscopy and conductivity measurement. By changing the interfacial chemistry of the bipolar membrane, the same fuel cell can be used for water purification in the half-cells. As a future direction, the same principle can be used for low voltage water electrolyzer, which can produce clean chemical fuels during the desalination process. Further, water desalination can be carried out with evolution of chlorine and hydrogen in cathodic and anodic half-cells respectively using a unipolar membrane configuration.

REFERENCES

- (1) Dresselhaus, M. S.; Thomas, I. L. Alternative Energy Technologies. *Nature* **2001**, *414*, 332.
- (2) Larcher, D.; Tarascon, J. M. Towards Greener and More Sustainable Batteries for Electrical Energy Storage. *Nature Chemistry*. **2015**.
- (3) Poizot, P.; Dolhem, F. Clean Energy New Deal for a Sustainable World: From Non-CO₂ Generating Energy Sources to Greener Electrochemical Storage Devices. *Energy Environ. Sci.* **2011**, *4* (6), 2003–2019.
- (4) Goldemberg, J. Ethanol for a Sustainable Energy Future. *Science (80-.)*. **2007**, *315* (5813), 808–810.
- (5) Chu, S.; Majumdar, A. Opportunities and Challenges for a Sustainable Energy Future. *Nature* **2012**, *488* (7411), 294–303.
- (6) Panwar, N. L.; Kaushik, S. C.; Kothari, S. Role of Renewable Energy Sources in Environmental Protection: A Review. *Renew. Sustain. Energy Rev.* **2011**, *15* (3), 1513–1524.
- (7) Bruce, D.; Haresh, K.; Jean-Marie, T. Electrical Energy Storage for the Grid: A Battery of Choices. *Science (80-.)*. **2011**, *334* (6058), 928–935.0
- (8) Chapter 2 Electrode / Electrolyte interface: Structure and Characteristics. **1900**
- (9) Goodenough, J. B.; Park, K. S. The Li-Ion Rechargeable Battery: A Perspective. *J. Am. Chem. Soc.* **2013**, *135* (4), 1167–1176.
- (10) Winter, M.; Brodd, R. J. What Are Batteries, Fuel Cells, and Supercapacitors? *Chem. Rev.* **2004**, *104* (10), 4245–4270.
- (11) Miller, J. R.; Simon, P. Fundamentals of Electrochemical Capacitor Design and Operation. *Electrochem. Soc. Interface* **2008**, *17* (1), 31–32.
- (12) González, A.; Goikolea, E.; Barrena, J. A.; Mysyk, R. Review on Supercapacitors: Technologies and Materials. *Renew. Sustain. Energy Rev.* **2016**, *58*, 1189–1206.
- (13) Wang, Y.; Song, Y.; Xia, Y. Electrochemical Capacitors: Mechanism, Materials, Systems, Characterization and Applications. *Chem. Soc. Rev.* **2016**, *45* (21), 5925–5950.

- (14) Kannan, N.; Vakeesan, D. Solar Energy for Future World: - A Review. *Renew. Sustain. Energy Rev.* **2016**, *62*, 1092–1105.
- (15) Lee, T. D.; Ebong, A. U. A Review of Thin Film Solar Cell Technologies and Challenges. *Renew. Sustain. Energy Rev.* **2017**, *70* (December), 1286–1297
- (16) Therdthianwong, A.; Saenwiset, P.; Therdthianwong, S. Cathode Catalyst Layer Design for Proton Exchange Membrane Fuel Cells. *Fuel* **2012**, *91* (1), 192–199.
- (17) Hsieh, C. Y.; Nguyen, X. V.; Weng, F. B.; Kuo, T. W.; Huang, Z. M.; Su, A. Design and Performance Evaluation of a PEM Fuel Cell - Lithium Battery-Supercapacitor Hybrid Power Source for Electric Forklifts. *Int. J. Electrochem. Sci.* **2016**, *11* (12), 10449–10461.
- (18) San Martin, J. I.; Zamora, I.; San Martin, J. J.; Aperribay, V.; Torres, E.; Eguia, P. Influence of the Rated Power in the Performance of Different Proton Exchange Membrane (PEM) Fuel Cells. *Energy* **2010**, *35* (5), 1898–1907.
- (19) FuelCellToday(<http://fuelcelltoday.com/>).Fuel Cell Basics, **2012**.
- (20) Hosseini, S. E.; Wahid, M. A. Hydrogen Production from Renewable and Sustainable Energy Resources: Promising Green Energy Carrier for Clean Development. *Renew. Sustain. Energy Rev.* **2016**, *57*, 850–866.
- (21) Ball, M.; Weeda, M. The Hydrogen Economy – Vision or Reality? *Int. J. Hydrogen Energy* **2015**, *40* (25), 7903–7919.
- (22) Nikolaidis, P.; Poullikkas, A. A Comparative Overview of Hydrogen Production Processes. *Renew. Sustain. Energy Rev.* **2017**, *67*, 597–611.
- (23) Iulianelli, A.; Liguori, S.; Wilcox, J.; Basile, A. Advances on Methane Steam Reforming to Produce Hydrogen through Membrane Reactors Technology: A Review. *Catal. Rev.* **2016**, *58*, 1–35.
- (24) <https://www.energy.gov/eere/fuelcells/hydrogen-production-natural-gas-reforming>
- (25) Shi, G. Y.; Yano, H.; Tryk, D. A.; Watanabe, M.; Iiyama, A.; Uchida, H. A Novel Pt-Co Alloy Hydrogen Anode Catalyst with Superlative Activity, CO-Tolerance and Robustness. *Nanoscale* **2016**, *8* (29), 13893–13897.
- (26) He, J.; Shen, Y.; Yang, M.; Zhang, H.; Deng, Q.; Ding, Y. The Effect of Surface Strain on the CO-Poisoned Surface of Pt Electrode for Hydrogen Adsorption. *J. Catal.* **2017**, *350*, 212–217.
- (27) Seshan, K. Pressure Swing Adsorption. *Appl. Catal.* **1989**, *46* (1), 180.

- (28) Hedin, N.; Andersson, L.; Bergström, L.; Yan, J. Adsorbents for the Post-Combustion Capture of CO₂ Using Rapid Temperature Swing or Vacuum Swing Adsorption. *Appl. Energy* **2013**, *104*, 418–433.
- (29) Agrawal, R.; Auvil, S. R.; DiMartino, S. P.; Choe, J. S.; Hopkins, J. A. Membrane/Cryogenic Hybrid Processes for Hydrogen Purification. *Gas Sep. Purif.* **1988**, *2* (1), 9–15.
- (30) Adhikari, S.; Fernando, S. Hydrogen Membrane Separation Techniques. *Ind. Eng. Chem. Res.* **2006**, *45* (3), 875–881.
- (31) Ockwig, N. W.; Nenoff, T. M. Membranes for Hydrogen Separation. *Chem. Rev.* **2009**, *110* (4), 2573–2574.
- (32) Phair, J. W.; Badwal, S. P. S. Review of Proton Conductors for Hydrogen Separation. *Ionics (Kiel)*. **2006**, *12* (2), 103–115.
- (33) Dai, S.; Unocic, R. R.; Smirnov, S. N.; Veith, G. M.; Vlassioux, I. V.; Mahurin, S. M.; Surwade, S. P. Water Desalination Using Nanoporous Single-Layer Graphene. *Nat. Nanotechnol.* **2015**, *10* (5), 459–464.
- (34) Desai, D.; Beh, E. S.; Sahu, S.; Vedharathinam, V.; Van Overmeere, Q.; De Lannoy, C. F.; Jose, A. P.; Völkel, A. R.; Rivest, J. B. Electrochemical Desalination of Seawater and Hypersaline Brines with Coupled Electricity Storage. *ACS Energy Lett.* **2018**, *3* (2), 375–379.
- (35) Phillip, W. A.; Elimelech, M. The Future of Seawater Desalination: Energy, Technology, and the Environment. *Science (80-.)*. **2011**, *333* (6043), 712–717.
- (36) Henthorne, L.; Boysen, B. State-of-the-Art of Reverse Osmosis Desalination Pretreatment. *Desalination* **2015**, *356*, 129–139.
- (37) Henthorne, L.; Boysen, B. State-of-the-Art of Reverse Osmosis Desalination Pretreatment. *Desalination* **2015**, *356*, 129–139.
- (38) Lee, K. P.; Arnot, T. C.; Mattia, D. A Review of Reverse Osmosis Membrane Materials for Desalination-Development to Date and Future Potential. *J. Memb. Sci.* **2011**, *370* (1–2), 1–22.
- (39) Bar-Zeev, E.; Elimelech, M. Reverse Osmosis Biofilm Dispersal by Osmotic Back-Flushing: Cleaning via Substratum Perforation. *Environ. Sci. Technol. Lett.* **2014**, *1* (2), 162–166.
- (40) Matin, A.; Khan, Z.; Zaidi, S. M. J.; Boyce, M. C. Biofouling in Reverse Osmosis Membranes for Seawater Desalination: Phenomena and Prevention. *Desalination* **2011**, *281* (1), 1–16.

- (41) Al-Karaghoul, A.; Kazmerski, L. L. Energy Consumption and Water Production Cost of Conventional and Renewable-Energy-Powered Desalination Processes. *Renew. Sustain. Energy Rev.* **2013**, *24*, 343–356.
- (42) Semiat R. Energy Issues in Desalination Processes. *Environ. Sci. Technol.* **2008**, *42* (22), 8193–8201.
- (43) Khawaji, A. D.; Kutubkhanah, I. K.; Wie, J. M. Advances in Seawater Desalination Technologies. *Desalination* **2008**, *221* (1–3), 47–69.
- (44) Qiblawey, H. M.; Banat, F. Solar Thermal Desalination Technologies. *Desalination* **2008**, *220* (1–3), 633–644.
- (45) Suss, M. E.; Porada, S.; Sun, X.; Biesheuvel, P. M.; Yoon, J.; Presser, V. Water Desalination via Capacitive Deionization: What Is It and What Can We Expect from It? *Energy Environ. Sci.* **2015**, *8* (8), 2296–2319.
- (46) Strathmann, H. Electrodialysis, a Mature Technology with a Multitude of New Applications. *Desalination* **2010**, *264* (3), 268–288.
- (47) Schlumpberger, S.; Lu, N. B.; Suss, M. E.; Bazant, M. Z. Scalable and Continuous Water Deionization by Shock Electrodialysis. *Environ. Sci. Technol. Lett.* **2015**, *2* (12), 367–372.
- (48) Kim, S. J.; Ko, S. H.; Kang, K. H.; Han, J. Direct Seawater Desalination by Ion Concentration Polarization. *Nat. Nanotechnol.* **2010**, *5* (4), 297–301.
- (49) Elgrishi, N.; Rountree, K. J.; McCarthy, B. D.; Rountree, E. S.; Eisenhart, T. T.; Dempsey, J. L. A Practical Beginner's Guide to Cyclic Voltammetry. *J. Chem. Educ.* **2018**, *95* (2), 197–206.
- (50) Hyk, W.; Nowicka, A.; Stojek, Z. Direct Determination of Diffusion Coefficients of Substrate and Product by Chronoamperometric Techniques at Microelectrodes for Any Level of Ionic Support. *Anal. Chem.* **2002**, *74* (1), 149–157.
- (51) <http://www.cbrnetechindex.com/Chemical-Detection/Technology-CD/Elemental-Analysis-CD-T/Microwave-Plasma-Atomic-Emission-Spectroscopy-CD-EA>
- (52) Vidaković, T.; Christov, M.; Sundmacher, K. The Use of CO Stripping for in Situ Fuel Cell Catalyst Characterization. *Electrochim. Acta* **2007**, *52* (18), 5606–5613.
- (53) Eichhorn, B.; Tsykin, M.; Seland, F.; Rønning, M.; Ochal, P.; Garcia, S.; Chen, D.; Muthuswamy, N.; Alayoglu, S.; Gomez de la Fuente, J. L.; et al. CO Stripping as an Electrochemical Tool for Characterization of Ru@Pt Core-Shell Catalysts. *J. Electroanal. Chem.* **2011**, *655* (2), 140–146.

- (54) <https://courses.lumenlearning.com/introchem/chapter/acid-base-titrations/>
- (55) <https://vlab.amrita.edu/?sub=2&brch=193&sim=352&cnt=1>
- (56) Doughty, H. W. Mohr's Method for the Determination of Silver and Halogens in Other than Neutral Solutions. *J. Am. Chem. Soc.* **1924**, *46* (12), 2707–2709. (57)
- (57) Belcher, R.; Macdonald, A. M. G. On Mohr's Method for the. *Anal. Chim. Acta* **1957**, *16*, 524–529.
- (58) <https://studymoose.com/quantitative-determination-of-sulfate-by-gravimetric-analysis-essay>
- (59) <http://www5.csudh.edu/oliver/che230/labmanual/gravsulf.htm>
- (60) Chen, C.; Levitin, G.; Hess, D. W.; Fuller, T. F. XPS Investigation of Nafion® Membrane Degradation. *J. Power Sources* **2007**, *169* (2), 288–295.