

**Electrochemical Characterization Of MnO_2 , Fuel Cell
Electrode For Renewable Energy, Using Glucose And
Alcohol Based Biofuels Synthesized From Woody
Biomass**

A thesis submitted in partial fulfillment of the requirement for
the award of the degree of

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In

Industrial Metallurgy

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CERTIFICATE OF RECOMMENDATION

This is to certify that the thesis entitled “**ELECTROCHEMICAL CHARACTERIZATION OF MnO₂, FUEL CELL ELECTRODE FOR RENEWABLE ENERGY, USING GLUCOSE AND ALCOHOL BASED BIOFUELS SYNTHESIZED FROM WOODY BIOMASS**” is a bonafide record of work carried out by **Upendra Kumar (Exam roll on: M4MET1601)** under the guidance of **Prof. Subir Paul** of Department of Material Engineering during the academic session 2015-16 for partial fulfillment of the degree of **Master of Engineering in Industrial Metallurgy** from Jadavpur University. In my opinion the work fulfils the requirement for which it is going to be submitted.

It is also certified that neither this nor any part of it has been submitted to any other university of institute for the award of any degree or diploma.

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I hereby declare that the thesis contains literature survey and original research work by the undersigned candidate as a part of his Master of Metallurgical Engineering curriculum.

All information in this document have been obtained and presented in accordance with the academic rules and ethical conducts.

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ABSTRACT

The demand for energy is increasing global forcing more facile fuel to burn and this gives to raise huge environment pollution and thread humane life. There is huge amount of forest woody residue. The project aims at utilization this forest waste to green energy by converting it to bio fuel which electrochemically oxidized on high energetic and inexpensive. The MnO_2 is such an electrode developed by by electro chemical deposition on 304 stainless steel plate. The electro chemical oxygen characterizations of the above fuel cell perform on MnO_2 and Pt electrode by cyclic voltammetry and potential dynamic polarization. The electro chemical oxygen produces high current and energy on MnO_2 surface. The scanning electron microscope is study of MnO_2 surface show more high energetic 3D surface of MnO_2 which accounts for increase current and energy.

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CHAPTER 1:

INTRODUCTION

INTRODUCTION

With fast urbanization, automation, high tech cities, the demand for energy is increasing and the resource of fossil fuel and oil reserve are diminishing. The use of fossil fuels also creating huge environmental pollution and greenhouse gas effects on earth. The need of hour is to find more resource of alternative energy: green energy with little or no pollution. The above facts lead to an increase in oil price, more dependence on foreign currency, inflation and negative impact on national economy. India being an agriculture based country produces a huge amount of agriculture waste in the form of woody biomass which is a good source of biofuel.

The project aims at producing clean electrical energy from Biofuel derived from agriculture biomass, which is the source of stored solar energy. Energy is produced by oxidizing the fuels to heat energy, which in turn is used to rotate turbine to generate electricity. The energy conversion by this step (limited by Carnot cycle, 2nd law of thermodynamics) is about 25%,. The products of combustion are polluting gases. Whereas in fuel cell, the same biofuel can be electrochemically oxidized in the anode chamber, the electron released at anode goes to external load, fuels such as H₂ is ionized as H⁺, move to cathode chamber through membrane, unite with O₂ from the atmospheric air to pure H₂O. Since the electrochemical oxidation of the fuel directly produces electron or electrical energy, the energy efficiency of conversion is over 80%. Electrochemical oxidation of the biofuel in a fuel cell can deliver clean electrical energy with no pollution and maximum energy conversion efficiency. The cell potential and current developed from the fuel cell can be used as renewable battery with no recharging required. Thus the project aims at producing pollution free renewable energy in village, rural and agriculture sectors using alternative route by developing fuel cells using inexpensive Electrode, MnO₂ so that buying this energy producing unit is not a burden for common man and this brings down the energy demand from the fossil fuel and reducing global pollution from the greenhouse gases.

Pretreated wood floor of mango tree was depolymerized by different treatments, followed by enzymatic saccharification and fermentation. Two types of bio fuel were developed: glucose based and alcohol based. The capacity of these biofuel to produce renewable electrical energy was investigated by cyclic voltammeter and polarization studies on

MnO₂ electrode which was produced by the electrode position technique from MnSO₄ bath. The morphology of the electrode surface was studied in scanning electron microscope.

CHAPTER 2:

LITERATURE REVIEW

LITERATURE REVIEW

2.1 Biofuel waste

India is an agriculture based country and produce huge amount of agriculture/forest waste in the form of woody biomass. This biomass can be synthesize to produce bio-oil.

Biofuel

Biofuel is a type of energy whose energy comes from biological carbon fixation. Biofuels are derived from biomass conversion, such as solid biomass, liquid fuels and various biogases. However fossil fuels have their source in ancient carbon fixation, they are not considered biofuel by the generally accepted definition because they contain carbon that has been "out" of the carbon cycle for a very long time. Biofuels are gaining increased public and scientific attention, driven by factors such as oil price spikes, the need for increased energy security, concern over greenhouse gas emissions from fossil Fuels and government subsidies.

Bioethanol is a high-octane, water-free alcohol produced from the fermentation of sugar or converted starch. It is a clear pellucid liquid with mild odour in its purest form. The boiling point is 78°C and it freezes at -112°C. It cannot be used in combustion engines either on its own nor blended with petroleum. Hydrous bioethanol is usually used for blending with gasoline.

Cellulosic biomass comes from non-food sources such as trees and grasses. It is also being researched as a raw material for ethanol production. Bioethanol facilities often are linked to sugar or starch factories and use the by-products from that industry as substrates.

In its pure form, ethanol can be used as a fuel for automotive vehicles, but it is usually used as an additive of gasoline to increase octane and enhance vehicle emissions. Bioethanol is widely used in the United States and Brazil. It produces relatively the same amount of carbon dioxide as plants bound while growing.

Eventually, bioethanol could considerably reduce the climate relevant greenhouse gas emissions from transport and vehicle. Biodiesel is derived from vegetable oils, animal fats or recycled greases. The pure biodiesel can be used as a fuel for vehicles, but

eventually it is used to reduce levels of particulates carbon monoxide, and hydrocarbons from diesel-powered vehicles as a diesel additive. Biodiesel is produced from oils or fats using transesterification.

Bio ethanol

Nowadays, ethanol fuel becomes the most common bio-fuel worldwide, especially in Brazil. Ethanol fuels are produced by fermentation of sugars comes from wheat, corn, sugar beets, sugar cane, molasses and any sugar or starch that alcoholic beverages can be made from potato and fruit waste. The methods of producing ethanol used are enzyme digestion, fermentation of the sugars, distillation and drying. The distillation process requires significant energy input for heat.

Ethanol can be used in petrol engines to replace gasoline; it could be mixed with gasoline to any percentage. From now, most car petrol engines can run on mixture of up to 15% bio-ethanol with petroleum/gasoline. Ethanol has a smaller energy density than gasoline, so it takes more fuel to produce the same amount of work. An advantage of ethanol is that it has a higher rating of octane than non-ethanol gasoline available at normal gas stations which allows an increase of an engine's compression ratio for improved thermal efficiency. In high altitude region, some states mandate a mix of gasoline and ethanol as a winter oxidizer to reduce atmospheric pollution emissions.

In the current alcohol-from-corn production model in the United States, allowing for the total energy consumed by farm equipment, cultivation, planting, fertilizers, pesticides, herbicides, and fungicides made from petroleum, irrigation systems, harvesting, transport of feedstock to processing plants, fermentation, distillation, drying, transport to fuel terminals and retail pumps, and lower ethanol fuel energy content, the net energy content value added and delivered to consumers is very small. And, the net benefit does little to reduce imported oil and fossil fuels required to produce the considered) does little to reduce imported oil and fossil fuels required to produce the ethanol.

Even ethanol-from-corn and other food stocks have implications both on world food prices and limited, but positive energy yield, the technology has to cause the development of cellulosic ethanol. In terms of a joint research agenda conducted through the U.S. Department of Energy, the fossil energy ratios for cellulosic ethanol, corn ethanol, and gasoline are 10.3, 1.36, and 0.81, respectively.

As dry ethanol has roughly one-third lower energy content per unit of volume compared to gasoline, so larger / heavier fuel tanks are required to travel the same distance, or more fuel stops are required. With large current unsustainable, non-scalable subsidies, ethanol fuel still costs much more per distance travelled than current high gasoline prices.

Cellulosic ethanol

Cellulosic ethanol is a type of bio-fuel produced by wood, grasses, or the non-food plants.

The cellulosic ethanol is derived from lignocellulose. Lignocellulose is a structural material that comprises much of the mass of plants. Cellulose, hemicellulose and lignin are the main three parts to compose lignocellulose. Many cellulosic materials could be used for ethanol production as feedstock, such as corn straw, switch grass, miscanthus, woodchips and lawn and tree maintenance. The cellulosic ethanol has many advantages and diverse raw material compared to source like corn and cane sugars, but requires a complicated processing to make the sugar monomers to the microorganisms that are used to make ethanol by fermentation. Cellulose, however, is contained in nearly every natural, free-growing plant, tree, and bush, in meadows, forests, and fields all over the world without agricultural effort or cost needed to make it grow.

According to U.S. Department of Energy studies conducted by Argonne National Laboratory of the University of Chicago, one of the benefits of cellulosic ethanol is that it reduces greenhouse gas emissions (GHG) by 85% over reformulated gasoline. By contrast, starch ethanol (e.g., from corn), which most frequently uses natural gas to

provide energy for the process, may not reduce GHG emissions at all depending on how the starch-based feedstock is produced.

Fossil versus renewable energy resources

Serious geopolitical implications are caused by the fact that the human society is heavily dependent on only a few energy resources such as petroleum, mainly produced in politically unstable oil-producing countries and regions. Indeed, according to the World Energy Council, about 82% of the world's energy needs are currently covered by fossil resources such as petroleum, natural gas and coal. Also ecological damages have come into prominence as the use of fossil energy sources suffer a number of ill consequences for the environment, including the greenhouse gas emissions, air pollution, acid rain, etc.

Moreover, the supply of these fossil resources is fixed finite. It is generally agreed that the petroleum will be exhausted within 50 years, natural gas within 65 years and coal in about 200 years at the present tempo of consumption. With regard to the depletion of petroleum supplies, the human has to face with the austere situation that the world is using petroleum faster than ever before, and nevertheless the "proven petroleum reserves" will still stop at the same level for 40 years, mainly as a result of new oil findings [18].

This fact is often used as an argument against the "prophets of doom", as there is seemingly still plenty of petroleum around for the time being. However, those "proven petroleum reserves" are increasingly found in places that are poorly accessible, inevitably resulting in an increase of extraction costs and hence, oil prices.

On the contrary, the agricultural raw materials such as wheat or corn have been continuously descending in price caused by the increasing agricultural yields. Agricultural crops such as corn, wheat and other cereals, sugar cane and beets, potatoes etc. can be treated in a bio-refinery into correlatively pure carbohydrate feedstock's, the pre-treating raw material for fermentation process. The fermentation process can transform those feedstock's into bio-fuels such as bio-ethanol.

Economic Impact

Along with technical development, from the economic perspective, the renewable resources are gradually replacing the fossil resources as a raw material. However, this is also be used as a reality for the generation of energy, considering of number of chemicals, increasingly produced from agricultural merchandises in place of petroleum.

Based on the local conditions such as distance to production site and local availability, the price of materials may vary rather widely from one place to another. All prices were converted into Euros per metric tonne (dry weight) for a number of fossil or renewable raw materials, similarly momentous feedstock intermediates like ethylene and sugar, for the only purpose of a clear indicative cost comparison of fossil versus renewable resources.

One deduction is that the renewable agricultural resources cost about half of the fossil resources based on the dry weight. At the present price of crude oil, petroleum costs about three times the price of corn. It is interesting that it notes the cost of sugar, a highly refined very pure feedstock (>99.5% purity); and very crude and unrefined mixture of chemical substances. It is cleared that agriculture feedstocks are cheaper than fossil today and are easily available in large quantities. Whereas the chemical technology based on switch fossil feedstocks into a bewildering variety of useful products very efficiently, the technology for converting agricultural raw materials into chemicals, materials and energy is still in its infancy.

It is broadly admitted that new technologies will need to be exploited and optimized to harvest the benefits of the bio-based economy. Especially industrial biotechnology is regarded a very crucial technology in this area, as it is excellently capable to utilize agricultural merchandises as a feedstock. The agricultural feedstocks processing into useful products emerge in so-called bio-refineries. However, the gradual transition from a fossil-based society to a bio-based society will take time and effort, the raw materials will

win over fossil resources in the future. This is expressly true in taking into account the viewpoint of increasingly rarer, extraction problem and more expensive fossil resources.

Utilization

The energy content of energy carrier is only one aspect in the total contrast. The value of an energy carrier is not only defined through its energy content and yield per hectare, but also equally by its physical shape and convenience in utilization. The aspect of an energy sources is expressly important for auto applications, like transportation. In Europe, the transport part delegates 32% of all energy consumption. In practice, liquid bio-fuels are much better suited for such an application. It is authentic that almost all cars and trucks are powered by liquid fuels such as gasoline and diesel. These fuels are readily and stanchly used in classic explosion engines. They are easy to store, transport and transfer and their utilization just requires non-storage technology at all.

The liquid fuels such as bio-ethanol and biodiesel from renewable sources is based strongly on the fact that these bio-fuels show all the advantages of the classic motor fuels. They are produced by agricultural petrol and diesel, with no engine recreation required. The utilization of bio-ethanol or biodiesel hence fits perfectly within the current concept of mobility.

Fleety growing wood species such as willow or poplar as a general renewable energy sources, are also included.

The gross energy yield per hectare is the highest for fast growing trees like willow or poplar. Although the liquid fuel is restricted by our selves, there remain big differences between the different bio-energy options to be interpreted.

Future of bio-fuel

The positive use of bio-ethanol coming from agricultural crops is a technically doable replacement for fossil-based gasoline. Furthermore, their use fits perfectly in the future concept and technology of our mobility. Liquid energy supporters are an expensive but very useful energy supporter for mobile applications such as transportation. It is obvious that energy sources for mobile applications can not only be compared on the basis of simple energy balances or costs, but also on the basis of their practical usefulness, quality, environmental impact and convenience in use of the obtained energy carrier. As the discussion about the sense or nonsense of bio-fuels is under way, the transition process from a fossil-based to a bio-based society is clearly moving along, with prominent growth in the United States, Brazil, China and Europe finally gaining ground. The large-scale introduction of bio-fuels can improve the interests of environment, mobility and agriculture and could be regard as a very important step with high symbolic value towards the sustainable society of the future.

2.2 Bio-oil to energy

Energy produce by burning of bio-oil to heat energy and to mechanical energy evolves lot of polluting gases like CO_2 , CO , H_2S etc. Secondary, the energy conversion from chemical to thermal to mechanical is a long process and efficiency of energy conversion is 25% to 35%

The same bio-oil can be used in fuel cell as a fuel .This fuel is electrochemically oxidised to release electron at anode and hence produce current, potential and energy. The theoretically energy conversion efficiency over 80%.

Fuel cells are electrochemical devices that convert chemical energy in fuels into electrical energy directly, promising power generation with high efficiency and low environmental impact. In a typical fuel cell, fuel is fed continuously to the anode and an oxidant is fed continuously to the cathode. The electrochemical reactions take place at the electrodes to produce an electric current through the electrolyte, while driving a complementary electric current that performs work on the load. Because the intermediate are not limited by thermodynamic limitations of heat engines such as the Carnot

efficiency. In addition, because combustion is avoided, fuel cells produce power with minimal pollutant.

Most fuel cell power systems comprise a number of components:

- Unit cells, in which the electrochemical reactions take place
- Stacks, in which individual cells are modularly combined by electrically connecting the cells to form units the desired output capacity.
- Balance of plant which comprises components that provide feedstream conditioning, thermal management, and electric power conditioning among other ancillary and interface functions.

2.3 Principle of fuel cell

A fuel cell is an electrochemical cell, which can continuously and directly convert the chemical energy of a fuel and an oxidant to electrical energy by a process involving essentially electrode-electrolyte system. The basic principles of a fuel cell are those of the electrochemical batteries. The big difference is that, in the case of batteries, the chemical energy is stored in the substances located inside them. When this energy has been converted to electrical energy, the battery must be thrown away or recharged appropriately. In a fuel cell, the chemical energy is provided by a fuel and an oxidant stored outside the cell in which the chemical reactions take place. As long as the cell is supplied with the fuel and oxidant, electrical power can be obtained.

2.4 Types of fuel cells

Alkaline Fuel Cell (AFC)

Phosphoric Acid Fuel Cell (PAFC)

Molten Carbonate Fuel Cell (MCFC)

Solid Oxide Fuel Cell (SOFC)

Proton Exchange Membrane Fuel Cell (PEMFC)

Alkaline Fuel Cell (AFC)

Alkaline Fuel Cells (AFC) consists of two porous electrodes with liquid KOH electrolyte between them. The hydrogen fuel is supplied to the anode electrode, while oxygen from air is supplied to the cathode. The working temperature ranges from 293 to 363 K. The electrical voltage between the anode and the cathode of a single fuel cell is between 0.9 V and 0.5 V depending on the load and the electrochemical reactions taking place at these electrodes. The hydrogen is usually compressed and the oxygen is obtained from the air. It uses a circulating liquid alkaline electrolyte, potassium hydroxide (30-45% KOH). This is an effective heat transfer and water management medium. The fuel cell can produce power at ambient temperatures but is designed to deliver full power at about 343 K, which, with electrical heating, it will normally reach within 10 min of a cold start.

The cell reactions are as follows:

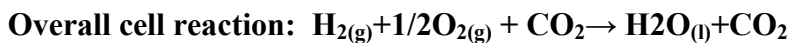
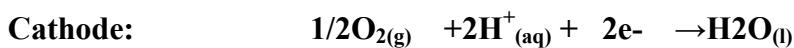
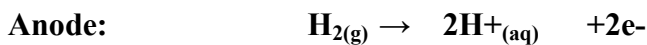


Phosphoric Acid Fuel Cell (PAFC)

The Phosphoric Acid fuel cell (PAFC) is in a mature state in terms of technological advancement. Acid fuel cells with phosphoric acid as electrolyte use relatively clean, reformed fuels. Phosphoric acid has the advantages of good thermal, chemical and electrochemical stability, good capillary properties and low vapour pressures though it is a poor ionic conductor. Among the common acids, it has the lowest volatility and this property allows PAFCs to operate at 463K to 473K for several thousand hours. Other inorganic acids such as HCl, HF, H₂SO₄ and HClO₄ have lower thermochemical stability and higher vapour pressures and therefore not suitable for operations at high temperatures (>473K). H₃PO₄ is the only inorganic acid that is suggested for its utility in fuel cell applications for these reasons. The concept of employing "super acids" was discussed many times in the past, but did not progress beyond research age. The water vapour -pressure-concentration characteristics are almost ideal. It permits wide change of vapour pressure across the face of the cell and as a function of current density, without showing a tendency to dry out or become too dilute, this is in marked contrast to KOH solutions, which tend to dry out; electrolyte circulation is essential in alkaline cells. It exhibits high tolerance for reformed hydrocarbons, removal of CO is possible by a shift reaction, and CO₂ is rejected naturally.

The major limitation of this acid is that oxygen reduction is very slow even at high temperatures and pressures.

The cell reactions are as follows:



Phosphoric acid with the function of the electrolyte is fixed in a porous layer between the electrodes. The advantage of this type of fuel cells is their relatively simple construction, mainly based on the use of carbon, PTFE and SiC which all can be processed by methods which are well-known from the origin of the fuel cell technology and could be easily adjusted to the demands of the fabrication of PAFC fuel cell components.

Molten Carbonate Fuel Cell (MCFC)

Fuel cells are approaching the early stages of commercialization, having been under study and development for more than 40 years. The high operating temperatures of MCFCs offer the prospect of being able to internally reform fuels such as natural gas. Long start-up times are implied, expensive materials are needed, and a number of design challenges are encountered due to leakage, corrosion, and loss through vaporization of the electrolyte. One of the most promising aspects of molten carbonates is the possibility of using, apart hydrogen, low cost fuels, as methanol, gaseous carbon. CO+H₂ (syngas) resulting from methane conversion by thermal cracking or reforming reaction. The oxidant is constituted by a mixture of air and carbon dioxide in the proportions of 70% and 30% respectively.

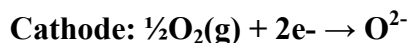
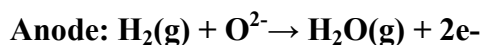
In operating MCFC, electrons are transferred from the anode through an external circuit to a cathode, where they participate in reduction reactions. Negative charges are conducted by carbonate anions from the cathode through the molten electrolyte to an anode. At the anode, electrons are produced by oxidation. MCFCs differ in many respects from

PAFCs because of their higher operating temperature and the nature of the electrolyte. The higher operating temperature of MCFCs provides the opportunity for achieving higher overall system efficiencies and greater flexibility in the use of available fuels. On the other hand, the higher operating temperature places severe demands on the corrosion stability and life of cell components, particularly in the aggressive environment of the molten carbonate electrolyte. Another difference between PAFCs and MCFCs lies in the method used for electrolyte management in the respective cells. In a PAFC, PTFE serves

as a binder and wet-proofing agent to maintain the integrity of the electrode structure and to establish a stable electrolyte/gas interface in the porous electrode. The phosphoric acid is retained in a matrix of PTFE and SiC between the anode and cathode. There are no materials available for use in MCFCs that are comparable to PTFE. Therefore, a different approach is required to establish a stable electrolyte/gas interface in MCFC porous electrodes. The MCFC relies on a balance in capillary pressures to establish the electrolyte interfacial boundaries in the porous electrodes.

Solid Oxide Fuel Cell (SOFC)

In the operation of SOFC, negative charges are conducted through the anode through an external circuit to the cathode; it is conducted by negative ions (O^{2-}) from the cathode through the electrolyte to the anode. Its typical operating temperature is 1273 K; at this temperature, the electrolyte is an oxygen-ion conductor, and the free energies of the overall reactions are substantially lower than at lower temperatures. The heat of reaction is almost independent of temperature; therefore the potential (ideal efficiency) reduced by the high temperature operation



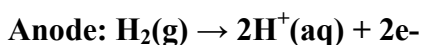
Different SOFC designs have been developed to implement the fuel cell and reformers into the stack and, ultimately, the complete system. Three main designs are encountering rapid development in SOFC technology: tubular, planar and monolithic configurations. Tubular SOFC designs are closer to commercialization and are being produced by several companies around the world. Demonstrations of tubular SOFC technology have produced

as much as 220 kW. Since SOFC requires high operating temperatures, their most common application is in large, stationary power plants. The high temperatures open the opportunity for “cogeneration”-using waste heat to generate steam for space heating, industrial processing, or in a steam turbine to make more electricity. Although they require inverters to change their direct current to alternating current, they can be manufactured in relatively small modular units. The compact size and cleanliness of SOFCs make them especially attractive for urban settings.

Proton Exchange Membrane Fuel Cell (PEMFC)

Proton exchange membrane fuel cells (PEMFCs) have reached the stage of being in the forefront among the different types of fuel cells. In 1950's Grubb suggested the use of ion-exchange polymeric membrane as the electrolyte for fuel cells. The membrane is non permeable to the reactant gases, hydrogen and oxygen but permeable to hydrogen ions, which are the current carriers in the electrolyte.

Electrochemical reaction occurring at the electrodes is as follows:



Hydrogen from the fuel gas stream is consumed at the anode, yielding electrons and hydrogen ions, which enter the electrolyte. At the cathode, oxygen combines with electrons from the cathode and hydrogen ions from the electrolyte to produce water. Water does not dissolve in the electrolyte and instead it is carried out of the fuel cell by excess oxidant flow.

2.5 Electrode materials

2.5.2 MnO₂ coating:-

Electrochemical capacitors, known as super capacitors or ultra-capacitors, with high power density, fast power delivery and long cycle life, promise to complement in energy storage applications such as uninterruptible back-up power supplies, load-leveling, portable electronics, hybrid electronic vehicles and renewable energy systems [22,23]. To achieve high power and high energy density, suitable electrode materials are required to undergo fast reversible redox reactions. Metal oxides like MnO₂ [24], RuO₂ [25], VO [26], Fe₂O₃ [27] offer high pseudo capacitance through fast and reversible redox reactions near the surface of active materials. Because of its high specific capacitance [25], RuO₂ is one of the most promising candidates for electrochemical capacitors. However, commercialization of RuO₂ is unlikely because of its high material cost, which derives from the scarcity of Ru. Conversely, MnO₂, with low cost, low toxicity, and most importantly high theoretical specific capacitance [28] has attracted much attention as a pseudo capacitive electrode material. However, its poor electric conductivity and its tendency to function capacitively in thin surface layers create practical challenges to realizing its high theoretical capacitance [28]. Nonetheless, numerous studies aimed at realizing favourable new microstructures on MnO₂-based composites for use as electrodes have been reported on both flexible and rigid substrates [29-37].

Carbon materials like carbon nano tubes [24,38], carbon fibers [39], activated carbon [40], graphene [41-43] are widely studied as super capacitor electrodes due to high specific area, high conductivity and low mass density. Among these, vertical graphene nanosheets or graphitic petals directly grown on carbon cloth or Ni foil without any binder have shown promising results as active electrode materials in electrochemical capacitors [44-46]. However, to date, this highly conductive and two-dimensional carbon nanosheet structure as a nanotemplate has not yet been systematically studied and optimized to exploit the electrochemical properties of the pseudo capacitive materials.

We report the electrochemical capacitors performance of vertical graphitic petals grown by microwave plasma chemical vapor deposition on flexible commercial buck paper. The buckpaper provides a light, flexible, and mechanically robust substrate for graphitic

petals growth. This substrate, when coated with a thin MnO₂ layer, forms an architecture referred to as a MnO₂ composite electrode. The graphitic petals/ buckypaper architecture offers an effective scaffold for exploiting the outstanding electrochemical behaviour of MnO₂, realizing high energy and power density characteristics for electrochemical super capacitor applications.

Density functional theory calculations were carried out to provide further insight on the interfacial electrical nature of the MnO₂ on the surface of graphitic petals. The Density functional theory results show a MnO₂/graphene interface capable of electron transport during the charge/discharge process.

The MnO₂ are most attractive materials because of its ion exchange, molecular adsorption, magnetic properties, catalytic, and electrochemical properties. MnO₂ nanoparticles were several different structures, including α -, β -, γ -MnO₂. The properties of MnO₂ depend not only on the manganese oxidation state, but also on the structure type of MnO₂ nanoparticles.

There are large numbers of potential applications of MnO₂ metal nanoparticles such as in the field of electrode materials in different rechargeable batteries, biosensors, coatings, nanofibers, nanowires and also in specific biogenic and bioscience applications. Effect of organic solvents on nanoparticles of metals hydroxide or oxide formation during chemical precipitation was used for developing effect of nanodimensional materials. This is the important way for chemists to expand their activity into Nanoscience. The nanoMnO₂ particles have excellent adsorption material for treatment of several pollutants in water environment.

Material used

Stainless steel was used as substrate on which MnO₂ alloy was electrodeposited. The substrate was polished by 2/0 and 3/0 gradation emery paper then it is rinsed by soap water and double distilled water.

The pretreated samples were electrodeposited by the solutions of 0.2 to 2.0 mole/litre of MnSO₄ and 0.1 to 1.0 mole/litre of H₂SO₄ at 120°C temperature and 0.5mA/cm²,

100mA/cm² 150mA/cm² current density respectively. The coated sample was rinsed by acetone and methanol one by one and then dried in an oven at 80°C 1 hour.

2.5.1 Ni-Co, coatings

The development in the field of surface treatment of metallic materials leads to an increase of their wear and corrosion resistance. The operating conditions and increases of process efficiency require an improvement of tools and equipment quality [3, 5, 6]. The increase of the surface quality is necessary for decorative as well as functional coatings. Surface treatments, which meet these requirements, include electro deposition of alloy coatings. Authors [1, 7, 8] observed that nickel-based coatings are used in a broad range of practical applications due to their good properties, such as magnetic and thermal conductivity, mechanical properties and resistance to abrasion and corrosion. Increased hardness and strength can be achieved by alloy coatings. Nickel and cobalt build solid solutions in the whole range of concentrations. The ability of nickel and cobalt to produce alloys at all ratios allows one to utilize their magnetic properties under various conditions [9, 10]. In the work [2] have described an increasing interest in electro deposition of alloy coatings, particularly due to their application in the area of surface treatment.

Production of coatings of required adhesiveness is conditional on adequate preparation of material surface. Microstructure and properties of electrodeposited simple and alloy coatings depend on chemical composition, pH and temperature of the bath, intensity of its mixing and physical parameters of the process, particularly current density [4]. In the work [11] has been found that changes in deposition conditions can result in coatings of different chemical composition, structure or phase composition. Important aspects of deposition of alloy coatings, according to [9] include concentration and stability of the other component (cobalt) in an electrolyte Authors in the work [12,3] in their work noticed that current density is one of the essential factors affecting structure and morphology of electrodeposited coatings. Current density affects not only the deposition rate and intensity of coating growth but also the size and distribution of individual crystallites.

The present work deals with the effect of current density on the microstructure, morphology, chemical composition and mechanical properties of Ni – Co alloy coating. The increase of current density showed a decrease of the current efficiency of electro deposition process and the content Co in alloy coating.

Material used

Ni-Co alloy coating was electrodeposited from a sulphate bath, which contained 640 g.l-1 nickel sulphate, 20 – 45 g.l-1 cobalt sulphate; 10 – 20 g.l-1 nickel chloride and 30 g.l-1 boric acid. Ni-Co alloy coating was deposited to a copper substrate at current densities of 1, 2, 4 and 6 A.dm-2, and bath temperature of 55 °C [13, 14]. The pH of the bath was maintained at 4.0 owing to the presence of boric acid. Before coating, the copper substrate was prepared by a procedure used under real operational conditions, namely by steel grit blasting and mechanical grinding to a mean roughness of about 3.8 μ m. The following steps involved degreasing by agents based on sodium hydroxide and rinsing with demineralised water. The surface was then activated by a mixture of sodium hydrogen sulphate and sodium fluoride and by an activating salt consisting of sodium hydrogen sulphate and sodium hydrogen fluoride [15, 16]. Demineralised water was used for final rinsing. The Ni-Co coating of thickness of approximately 30 μ m was then deposited onto the prepared surface. The content of cobalt sulphate, the major component of the sulphate bath, was determined by atomic absorption spectrometry [7]. Morphology of electrodeposited coatings was examined and photographed by an electron microscope JEOL JSM 7000F. Chemical composition of the Ni-Co coat was determined by a micro analyser INCA x Sight (Oxford Instruments), which was a part of the electron microscope.

Hardness of the Ni-Co coat was measured by a Vickers using 100 g loading [3, 6].

2.5.2 MnO₂ coating

MnO₂ are most attractive materials because of its ion exchange, molecular adsorption, magnetic properties, catalytic, and electrochemical properties. MnO₂ nanoparticles were several different structures, including α -, β -, γ -MnO₂. The properties of MnO₂ depend

not only on the manganese oxidation state, but also on the structure type of MnO₂ nanoparticles.

There are large numbers of potential applications of MnO₂ metal nanoparticles such as in the field of electrode materials in different rechargeable batteries, biosensors, coatings, nanofibers, nanowires and also in specific biogenic and bioscience applications. Effect of organic solvents on nanoparticles of metals hydroxide or oxide formation during chemical precipitation was used for developing effect of nanodimensional materials. This is the important way for chemists to expand their activity into Nanoscience. The nanoMnO₂ particles have excellent adsorption material for treatment of several pollutants in water environment.

Material used

Stainless steel was used as substrate on which MnO₂ alloy was electrodeposited. The substrate was polished by 2/0 and 3/0 gradation emery paper then it is rinsed by soap water and double distilled water.

The pretreated samples were electrodeposited by the solutions of 0.2 to 2.0 mole/litre of MnSO₄ and 0.1 to 1.0 mole/litre of H₂SO₄ at 120°C temperature and 0.5mA/cm², 100mA/cm² 150mA/cm² current density respectively. The coated sample was rinsed by acetone and methanol one by one and then dried in an oven at 80°C 1 hour.

2.5.3 Chemical Oxygen Demand (COD)

The COD (Chemical Oxygen Demand) test represents the amount of chemically digestible organics. COD measures all organics that were biochemically digestible as well as all the organics that can be digested by heat. It is used in the same applications as BOD [51]. COD has the advantage over BOD in the analysis can be completed within a few hours whereas BOD requires 5 days. The major drawback of the COD test is the presence of hazardous chemicals and toxic waste disposal.

COD Theory:

Like the BOD test, oxygen is used to oxidize the organics to carbon dioxide and water. However, instead of free dissolved oxygen, chemically bound oxygen in potassium Dichromate $K_2Cr_2O_7$ [52] is used to oxidize the organics. As the potassium dichromate is used up the Cr^{+3} ion is produced. The amount of dichromate used is proportional to the amount of organics present. Likewise, the amount of Cr^{+3} ions present is proportional to the amount of organics digested. Organics + $K_2Cr_2O_7$ Cr^{+3} (Orange) (Green) [53]. Most labs use the Hach Method to measure COD. This method uses test tubes with premeasured amounts of potassium dichromate, sulfuric acid, and catalyst. For the digestion to occur, the reaction needs acid, heat, and a catalyst. The acid is sulfuric acid and is already in the tube. The sample will get very hot when the sample is added to the acid and mixed. Be sure the cap is on tight before mixing and mix just prior to placing in the digestion reactor.

Safety:

Be very careful when adding water to acid. This is contrary to normal safety procedure. Be sure to wear goggles, gloves, apron, etc. and do not mix until the cap is tightened on the test tube. The heat will be provided by the digestion reactor [54] which is set at 150°C. The sample is refluxed (digested) for 2 hours. During the 2 hours, the organics are oxidized by the acid, potassium dichromate and catalyst. The catalyst is silver. However, silver must be soluble and will precipitate if chlorides are present in the sample. To prevent silver precipitation, mercury has been added to the reagents in the tube. The mercury will remove the chloride interference. Once the 2 hour refluxing period is finished, the remaining potassium dichromate is measured using the spectrophotometer

Spectroscopy:

Many compounds and elements absorb light in the ultra-violet or visible region of the spectrum. Spectrometers that send a beam of light at a specific wavelength through a sample can measure the amount of that light absorbed by the sample using a photocell [55]. The amount of light transmitted or absorbed will generate a varying electrical signal that can be displayed on a meter or digital display [56]. Spectrometers must be calibrated before each use and after each change of wavelength of light. This is usually done setting the display to read zero absorbance or 100% transmittance for a blank and maximum absorbance or 0% transmittance when the beam is completely blocked. Your instructor will show you how to do this for your spectrophotometer. The absorbance of light is directly proportional to the concentration of a solution according to the following Beer-Lambert Law:

$$\mathbf{A = \hat{\epsilon}dc}$$

$$\mathbf{Or: A = kc}$$

where "A" is the absorbance, " $\hat{\epsilon}$ " is the extinction coefficient, "d" is the path length in decimeters, and "c" is the concentration in moles/liter. The extinction coefficient and the path length can be combined into a single constant "k". If you measure the absorbance of several standard solutions for which you know the concentration [57], you can calculate an average "k" value. Then you can measure the absorbance of an unknown solution, divide by this average "k" value to get the concentration [58]. It is usually easier to read the percent transmittance on the spectrophotometer and convert it to absorbance [59]. This can be done using the following:

$$\mathbf{A = \log (100/\%T)}$$

Sample Handling

The sample volume used for the COD test is 2.0 ml so measuring the sample volume is critical. Be sure to mix the sample well and homogenize if necessary. Pipet quickly to avoid strength is greater than 1650 mg/L, the sample must be diluted. Make a 1:2 dilution by measuring 50 ml of sample and adding to 50 ml of deionizer water, then add 2.0 ml of well mixed dilution to the test tubes.

CHAPTER 3:

EXPERIMENTAL PROCEDURE

EXPERIMENTAL DETAILS

3.1 Pre-treatment

Goals of Pretreatment.

The beneficial effects of pretreatment of lignocellulosic materials have been recognized for a long time [21]. The goal of the pretreatment process is to remove lignin and hemicellulose, reduce the crystallinity of cellulose, and increase the porosity of the lignocellulosic materials. Pretreatment must meet the following requirements: (1) improve the formation of sugars or the ability to subsequently form sugars by hydrolysis, (2) avoid the degradation or loss of carbohydrate, (3) avoid the formation of byproducts that are inhibitory to the subsequent hydrolysis and fermentation processes, and (4) be cost-effective. Pretreatment methods can be roughly divided into different categories: physical, chemical, biological, or a combination of these. The following pretreatment technologies have promise for cost-effective pretreatment of lignocellulosic biomass for biological conversion to fuels and chemicals.

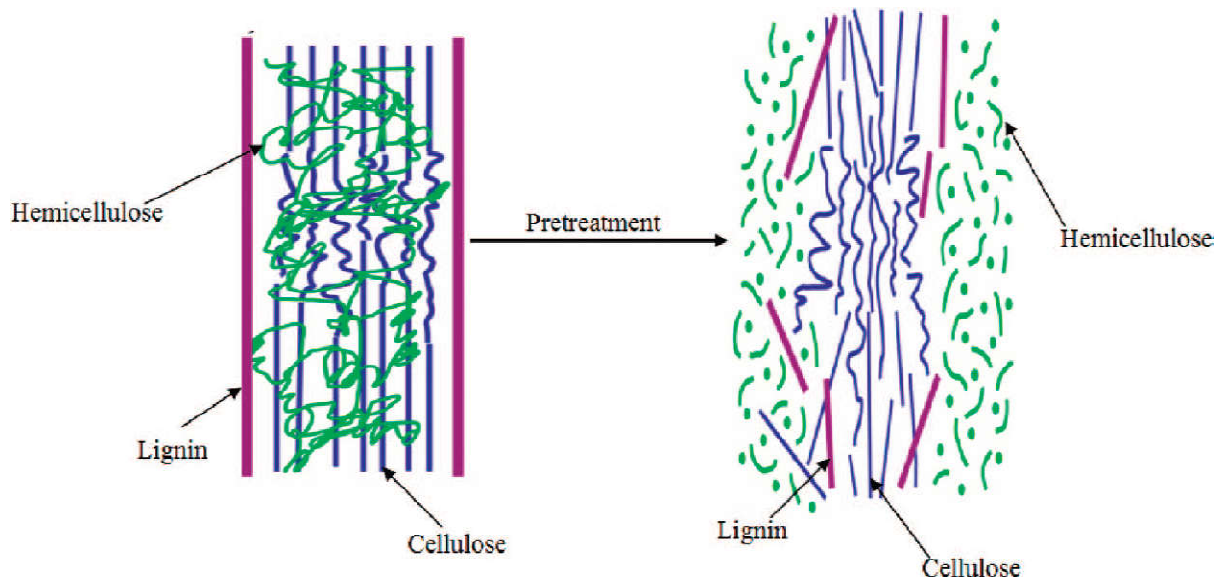


Figure no 3.1

Schematic of the role of pretreatment in the conversion of biomass to fuel

3.1.1 Mechanical Pre-treatment

Reduction of particle size of mango wood is often needed to make material handling easier and to increase surface/ volume ratio. The size of particle make to uniform of 1-2 mm..This can be done by grinding. Mechanical pretreatment is usually carried out before a processing step, and the desired particle size is dependent on these subsequent steps. For mechanical pretreatment factors like capital costs, operating costs, scale-up possibilities.

3.1.2 Heating Pre-treatment

After mechanical pretreatment, mango wood contain some atmospheric or physically absorbed moisture. These physically absorb moisture is remove to be dried at 160⁰c for one hour.

3.1.3 Chemical Pre-treatment

Since woody agriculture waste or forest waste contain some alkali or alkaline earth metal. These alkali or alkaline earth metal is harmful for electrode material or machinery parts. So remove this metals by soaking in 0.25-wt % Nitric acid at 80⁰c for one hour.

3.2 Hydrolysis to depolymerise

Lignocellulose is the primary building block of plant cell walls. Plant biomass is mainly composed of cellulose, hemicellulose, and lignin.

Cellulose

Cellulose is the main structural constituent in plant cell walls and is found in an organized fibrous structure. The long-chain cellulose polymers are linked together by

hydrogen and van der Waals bonds, which cause the cellulose to be packed into microfibrils. Hemicelluloses and lignin cover the microfibrils.

Hemicellulose

Hemicellulose from cellulose is that hemicellulose has branches with short lateral chains consisting of different sugars. These monosaccharides include pentose, hexoses, and uronic acids. The backbone of hemicellulose is either a homopolymer or a heteropolymer with short branches linked by glycosidic bonds and occasionally glycosidic bonds.

Lignin

Lignin is a complex, large molecular structure containing cross-linked polymers of phenolic monomers. It is present in the primary cell wall, imparting structural support, impermeability, and resistance against microbial attack [17]. The biomass is in very complex form, so we need to break the biomass into simpler form by using different hydrolysis processes.

3.2.1 Acid hydrolysis

Acid pretreatment can be used as diluted acids to solubilize the hemicellulose and make the cellulose more accessible to enzymes.

Initially, the biomass of 20g and the aqueous sulfuric acid solution of 3%, 5%, and 8% were loaded into a 500-ml stainless-steel container, which was kept on an oven. It was heated with an electrical heater for one hour at 100^o C. After removing the cap from the container, the cellulosic hydrolysate was quantitatively separated from the pretreated solids by filtration. After filtration it is neutralized by adding NaOH and pH is recorded as 6.9, 7 and 6.9. There are different types of samples shown in figure 3.2.1, 3.2.2 and 3.2.3 for experiment no. AE1, AE2 and AE3 respectively.

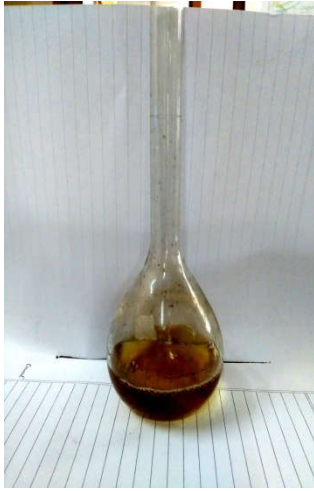


Figure no 3.2.1



Figure no 3.2.2



Figure no 3.2.3

3.2.2 Lime treatment

Lime pretreatment is one of the promising technologies for grassy feedstocks. Lime pretreatment increases cellulose digestibility and are very effective in lignin removal, exhibiting minor cellulose and hemicellulose solubilization as compared to acid processes [19]. They are more effective on agricultural residues than on woody materials [20].

Lime has been used to pretreat mango wood. Initially, the mango wood of 20g and aqueous solution of 0.13g, 0.15g, and 0.17g CaO /g of mango wood were loaded into a 500-ml stainless-steel container, which was kept on oven. It heat with electrical heater for one hour at 100⁰ c. After removing the cap from the container, the cellulose hydrolysate was quantitatively separated from the pretreated solids by filtration. After filtration, ph. are recorded as 9, 10.6, and 12. There are different types of sample are shown in figure 3.3.1, 3.3.2 and 3.3.3 for experiment no. LE1, LE2 and LE3 respectively.



Figure no 3.3.1



Figure no 3.3.2



Figure no3.3.3

3.3 Formation Of Glucose

3.3.1 Enzymatic saccharification to form glucose molecule

The hydrolysis of cellulose to soluble sugars makes it available as feedstock in alcoholic fermentation, single cell protein production. Pretreatment of cellulose opens up the structure and removes secondary bonds between glucose chains. Treatment with alkali can remove lignin, thus promoting hydrolysis and improving the glucose recovery from cellulose. Enzymatic hydrolysis of such cellulosic material by cellulase enzymes is the most promising approach to get high product yields. Fungi produce extracellular cellulase enzymes that break down cellulose into two or three glucose units which are readily degraded and assimilated as glucose monomers. On bioconversion of some lignocellulosic substrates, and to examine the ability of this organism to induce cellulase and saccharification on alkali and enzyme treated substrates. The alcohol based biofuel by acid treatment are shown in fig 3.3.4, 3.3.5 and 3.3.6 for experiment no. AF1, AF2 and AF3 respectively and also alcohol based bio-fuel by lime treatment are shown in figure 3.3.7, 3.3.8 and 3.3.9 for experiment no. LF1, LF2 and LF3 respectively.

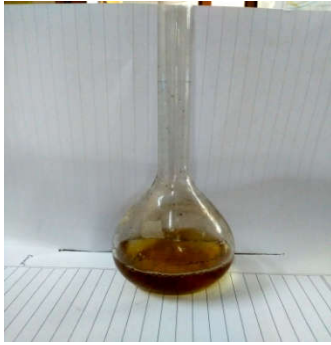


Figure no 3.3.4

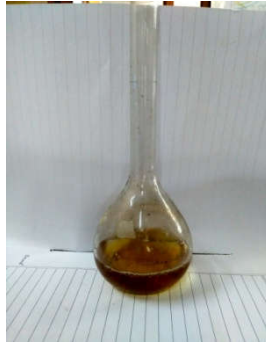


Figure no 3.3.5

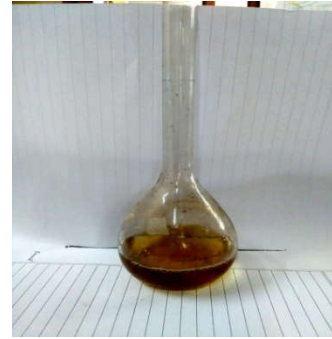


Figure no 3.3.6



Figure no 3.3.7

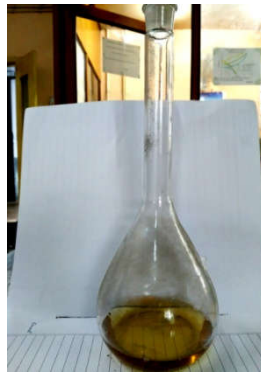


Figure no 3.3.8



Figure no 3.3.9

Material used

Dissolve a commercial enzyme of 100mg in 200ml pretreated mango wood and shaking gently at 60⁰c for 4 hours to achieve maximum sugar recovery.

3.3.2 Fermentation to Alcohol by Yeast

Fermentation process used in producing bio-oil which is made for the conversion of sugars to alcohol. When same process is followed by distillation, it can be used to obtain bio-ethanol for use as a transport biofuel.

Ethanol is manufactured by fermentation of the sugar. Fermentation only work directly with sugars. Two major components of plants, starch and cellulose, are both made up of sugars, and can be converted to alcohol for fermentation. Generally, only the sugar and

starch portions can be economically converted. There is much activity in the part of cellulosic ethanol, where the cellulose part of a plant is broken down to sugars and subsequently converted to ethanol.

One mole of glucose is converted into two moles of ethanol and two moles of carbon dioxide:



The second stage is the fermentation process to convert glucose into ethanol and CO₂. Fermentation ethanol is a change of a mole of glucose into 2 moles of ethanol and 2 moles of CO₂. The yeasts will mainly metabolize glucose and fructose to form alcohol.

Material used

Dissolved 0.1g tryptone and 5g yeast in 100ml extract sugar solution .The mixed solution is kept in seal packet in vessel. The fermentation is done after two days at 30⁰C.

3.4 Electrode preparation

3.4.1 Coating of MnO₂ on stainless steel

Stainless steel is used as substrate on which MnO₂ was electrodeposited. The substrate was polished by 2/0 and 3/0 gradation emery paper then it is rinsed by soap water and double distilled water.

The MnO₂ becomes deposited on the anode and accumulates for 10 minutes.

The pretreated samples were electrodeposited by the solutions of 2.0 mole/litre of MnSO₄ and 1.0 mole/litre of H₂SO₄ at 60°C temperature and 2.857mA/cm² current

density with potential 2.0 volte for 10 minutes. The P^h. is recorded as 2.7. The coated sample was rinsed by acetone and methanol one by one and then dried in an oven at 80°C 1 hour.

3.4.2 Coating of Ni-Co alloy on stainless steel

The stainless used as a substrate was polished by 2/0 and 3/0 gradation emery paper then it is rinsed by soap water and double distilled water.

The Ni-Co alloy becomes deposited on the cathode for 10 minutes.

Ni-Co alloy coating was electrodeposited from sulphate bath, which contain 640g/l nickel sulphate 45g/l cobalt sulphate, 20g/l nickel chloride and 30g/l boric acid.

The deposition of Ni-Co on substrate occurs at current density 115.853mA/cm² and the bath temperature was maintained at 55⁰ c. The ph. of the bath was maintained at 4.0 owing to the presence of boric acid.

CHAPTER 4:

RESULTS AND DISCUSSIONS

4.1 Pre-Treatment

4.1.1 Acid treatment

4.1.1.1 Glucose based biofuel

Depolymerisation					Enzymatic Saccharification			
Exp. No.	H ₂ SO ₄ (%)	PH (Solution+ NaOH)	Heating time (m)	Heating temperature (°C)	Enzyme (100mg/20ghydrolysed product)	Shaking time (hour)	Shaking temperature (°c)	CO D
AE1	3	6.9	90	100	100	4	60	58
AE2	5	7	90	100	100	4	60	73
AE3	8	6.9	90	100	100	4	60	99

Table No 1: Various controlling parameter of production of glucose based biofuel of three different experiments using acid treatment

4.1.2 Lime Treatment

Depolymerisation					Enzymatic saccharification			
Exp.No	CaO (g/g biomass)	PH	Heating time (m)	Heating temperature (⁰ C)	Enzyme (100mg/20g hydrolysed product)	Shaking time (hour)	Shaking temperature (⁰ c)	COD
LE1	0.13	9	90	100	100	4	60	29
LE2	0.15	10.6	90	100	100	4	60	39
LE3	0.17	12	90	100	100	4	60	78

Table no 4.2: Various controlling parameter of production of glucose based biofuel of three different experiments using lime treatment

4.1.2.1 Glucose based biofuel

Two type of pre-treatment is given Acidic and Alkali pre-treatment to break the complex polymer into simple polymer or monomer.

For Acid treatment H_2SO_4 is used

For Alkali treatment Lime (CaO) IS used

Table no 4.1 illustrate the various controlling parameter to produce glucose based biofuel with acid treatment and table no 4.2 illustrate the similar data for the biofuel with lime treatment. It say that in each treatment (tab. no 4.1) there is COD percent (%) COD is the chemical oxygen demands of fuel it that means determined using UV spectrometer at wave length (600nm). The COD indicates the some amount of biofuel has form, it vary with the type of treatment. It is also seen that with lime treatment (table no 4.2) there is good value of COD which indicates that even with lime treat men the biofuel has been produce.

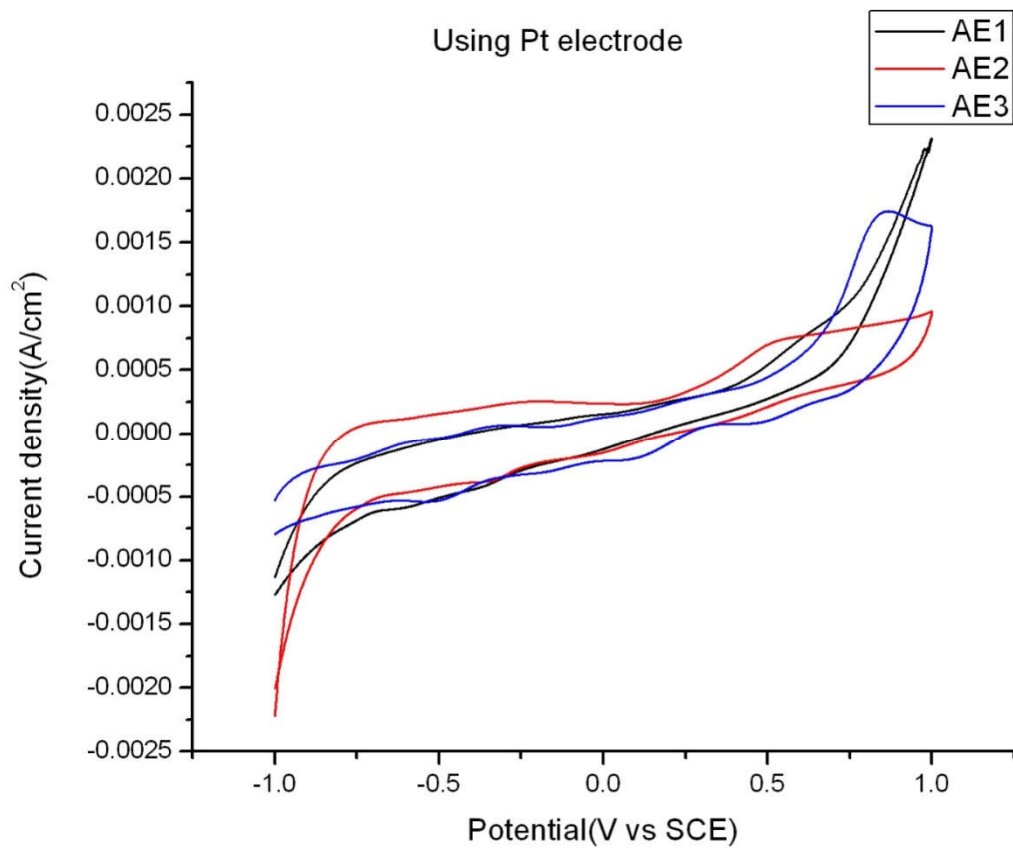


Figure no 4.1.1 Comparison of cyclic voltmeter of glucose based biofuel with three different acid treatment using Pt electrode

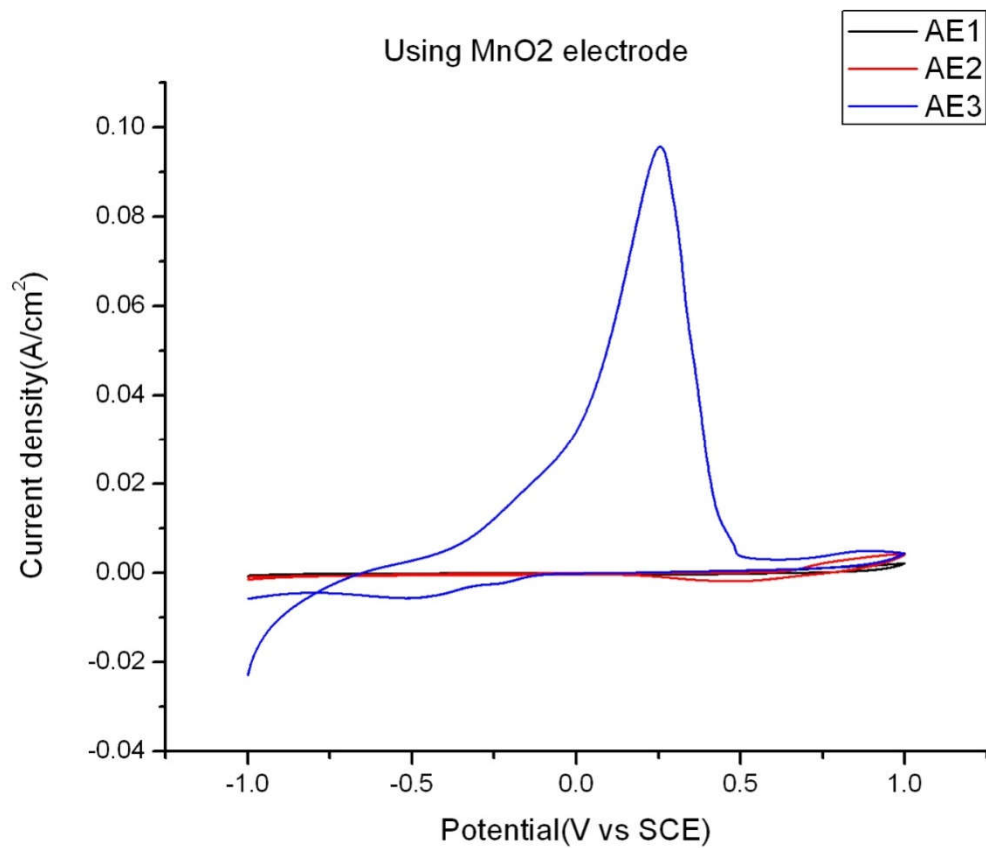


Figure no 4.1.2: Comparison of cyclic voltmeter of glucose based biofuel with three different acid treatment using MnO₂ electrode

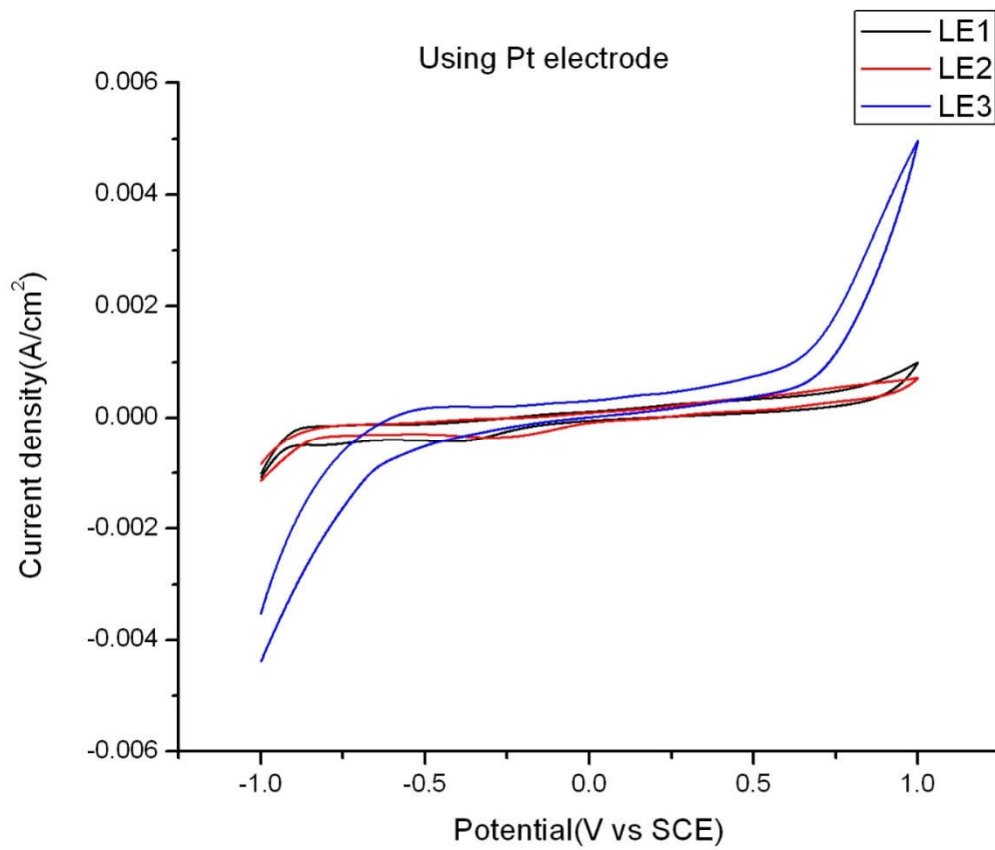


Figure no 4.1.3 : Comparison of cyclic voltmeter of glucose based biofuel with three different lime treatment using Pt electrode

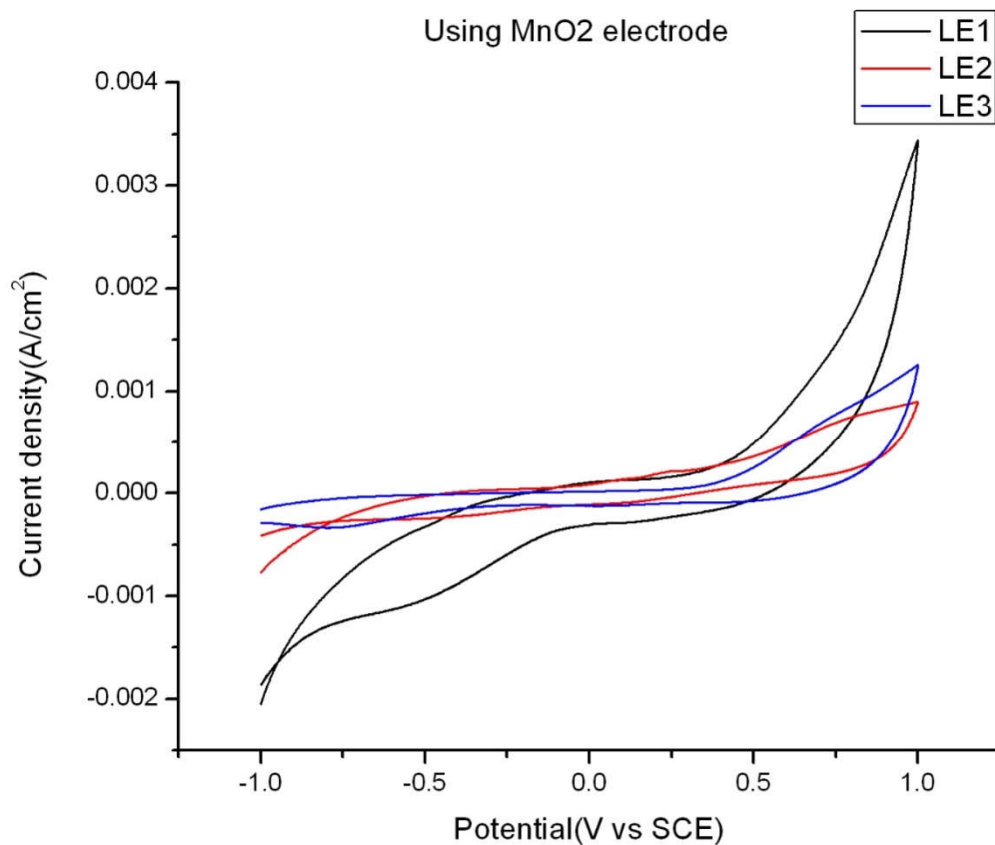


Figure no 4.1.4: Comparison of cyclic voltmeter of glucose based biofuel with three different lime treatment using MnO₂ electrode

The electrochemical oxygen of the above biofuel has been tested on two electrodes, pure Pt foil and MnO₂ electrode produced by electro deposition as described in experimental method section 3.4.

Figure no 4.1.1 shows the cyclic voltmeter of different biofuel as described in table no 4.1 on Pt surface.

It is see that all the fuel exhibit Jump is the current at a particular potential b/t 0.5 V to 1V vs. SCE. The maximum current is vary between 1 mA/cm² to 2.5 mA/cm² depending on various treatments (AE to AE3). It is seen AE3 is the best which is given more enclose area which indicate the energy given. If you see AE3 is the highest. So higher concentration of acid is needed to break the complex polymer to the simple polymer or monomer.

The same treatment on MnO₂ electrode is shown in figure no 4.1.2. It is see also here then treatment AE3, the higher acid concentration the highest current as well as energy produce. It is to be noted the highest current on MnO₂ electrode coming 80 to 90 mA/cm². This comes out as the much better fuel cell electrode than the Pt. Which commonly known as very good electrochemical material. A fuel cell fabricated with MnO₂ electrode of 100 cm² is expected to deliver a maximum current of 80Ma.

Similar curve for the biofuel with Lime treatment on Pt as shown in figure 4.1.3. Here also higher percentage of lime corresponds to higher current. But compare to acid treatment Lime treatment has not produce the very high quantity of fuel oil as shown in figure 4.1.3 which produce only 4Ma current.

Similar curve on MnO₂ electrode in figure 4.1.4. It is seen that the energy contain of electrochemical oxygen fuel is better on MnO₂ than on Pt surface.

4.1.3 Acid Treatment

4.1.3.1 Alcohol based biofuel

Depolymerisation					Enzymatic saccharification				
Exp.No	H ₂ SO ₄	PH (Solution+ NaOH)	Heating time (m)	Heating temperature (°C)	Enzyme (100mg/20g hydrolysed product)	Shaking time (hour)	Shaking temperature (°c)	Yeast(mmg)	COD
AF1	3	6.9	90	100	100	4	60	5	235
AF2	5	7	90	100	100	4	60	5	331
AF3	8	6.9	90	100	100	4	60	5	516

Table no 4.3: Various controlling parameter of production of alcohol based biofuel of three different experiments using acid treatment

4.1.4. Lime Treatment

4.1.4.1 Alcohol based biofuel

Depolymerisation					Enzymatic saccharification				
Exp. No	CaO (g/g biomass)	PH	Heating time (m)	Heating temperature (⁰ C)	Enzyme (100mg/20g hydrolysed product)	Shaking time (hour)	Shaking temperature (⁰ c)	Yeast(mmg)	COD
LF1	0.13	9	90	100	100	4	60	5	268
LF2	0.15	10.6	90	100	100	4	60	5	371
LF3	0.17	12	90	100	100	4	60	5	492

Table no 4.4 Various controlling parameter of production of alcohol based biofuel of three different experiment using acid treatment

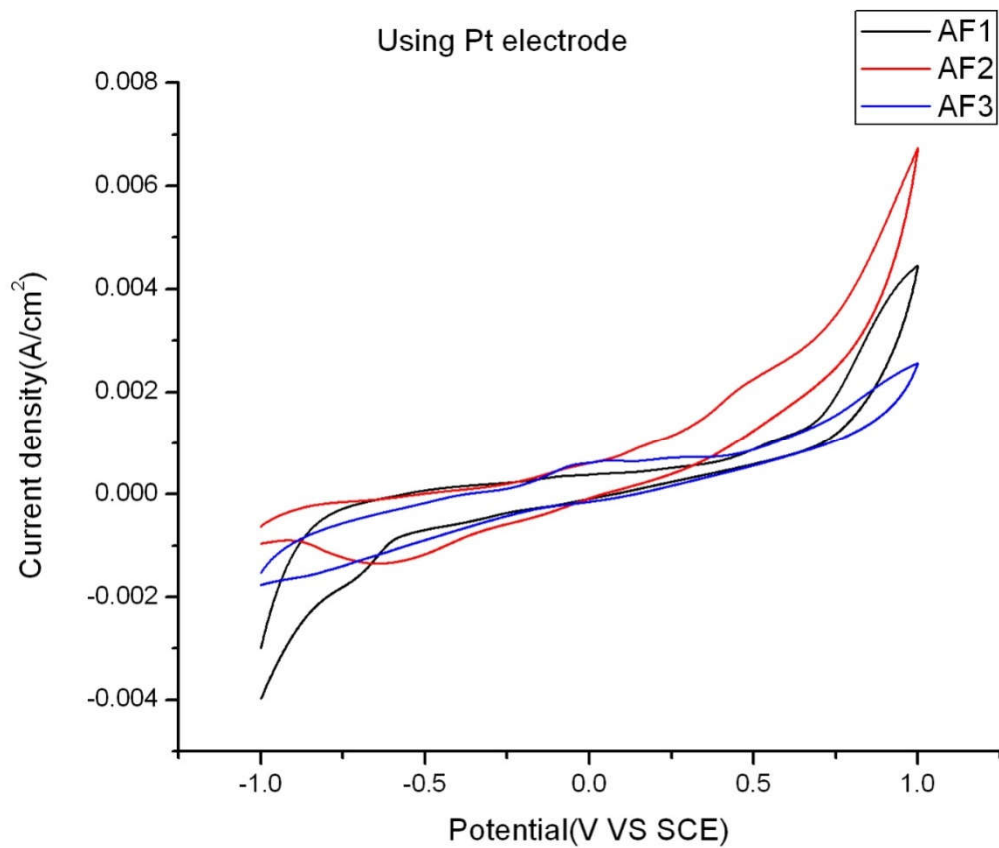


Figure no 4.1.5 Comparison of cyclic voltmeter of alcohol based biofuel with three different acid treatment using Pt electrode

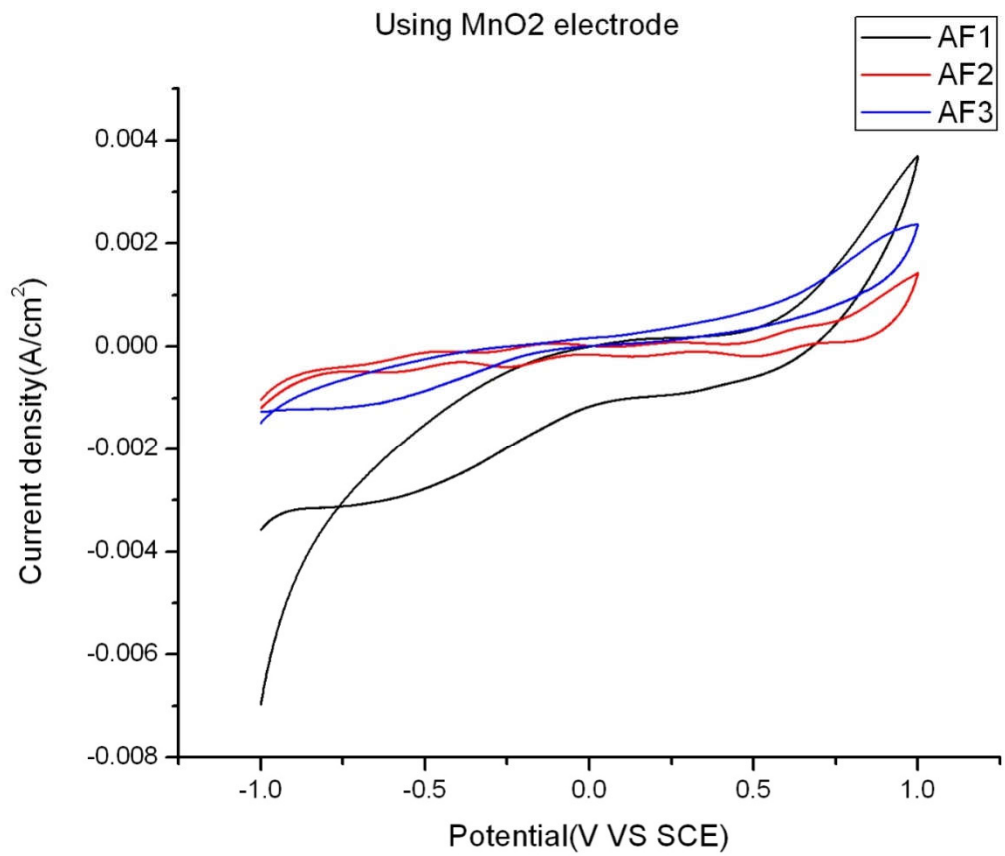


Figure no 4.1.6 Comparison of cyclic voltmeter of alcohol based biofuel with three different acid treatment using MnO₂ electrode

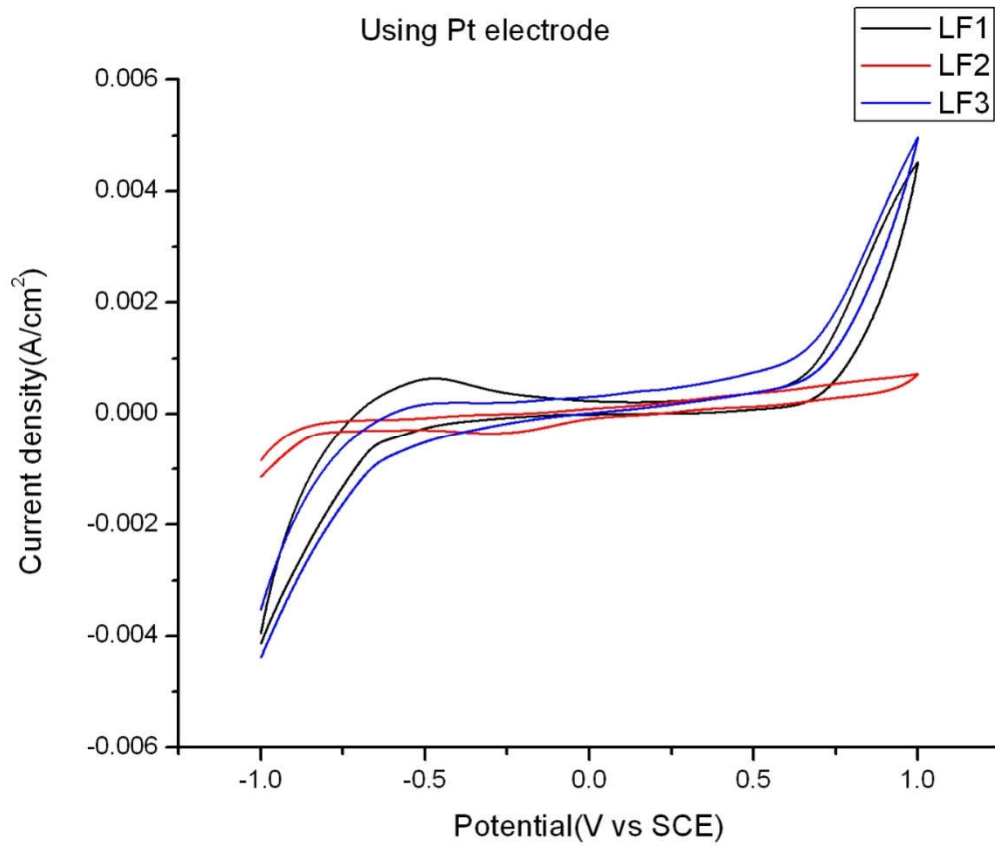


Figure no 4.1.7 Comparison of cyclic voltmeter of alcohol based biofuel with three different lime treatment using Pt electrode

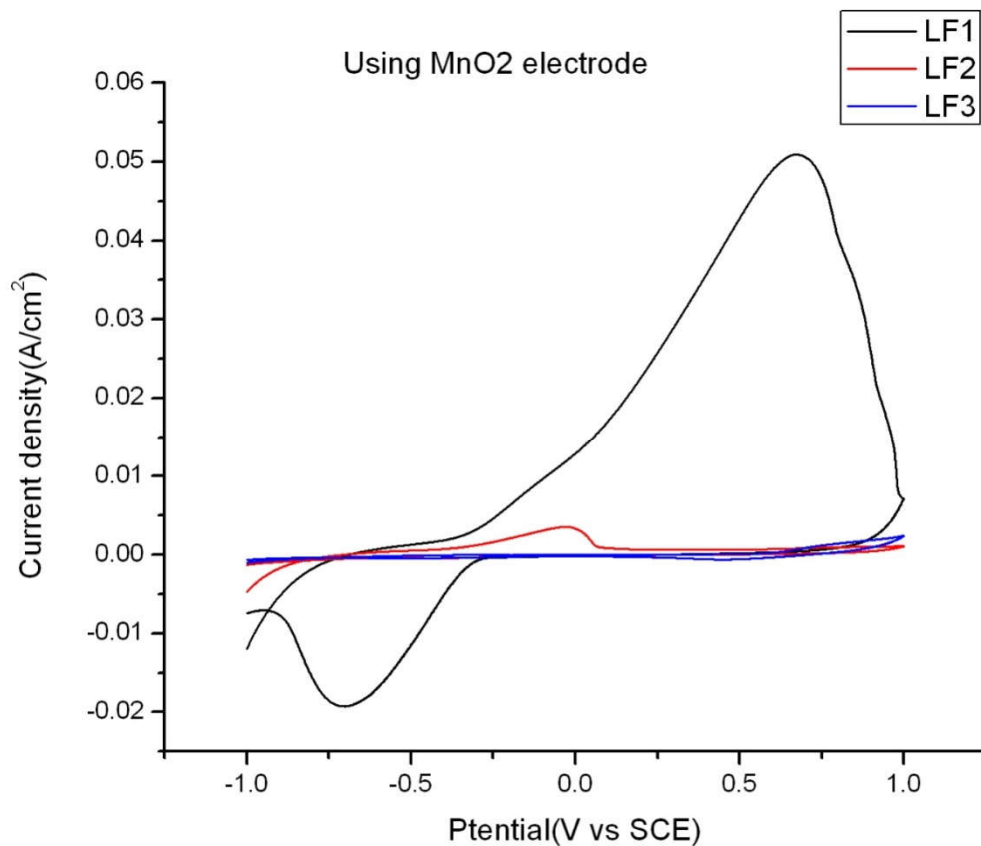


Figure no 4.1.8 Comparison of cyclic voltmeter of alcohol based biofuel with three different lime treatment using MnO₂ electrode

Table no 4.3 and 4.4 illustrate the various controlling parameter for production of bio alcohol with fermentation after enzymatic saccharification. The electrochemical oxygen of this bio alcohol has been study on Pt electrode (fig no 4.1.5) and MnO₂ electrode (fig no 4.1.6)

It is illustrate the good amount of energy and current obtained from the fuel. The treatment AE3 has given more current on electrochemical oxygen. It shows that the higher acid concentration depolymerisation of wood floor is higher gives the more fuel.

Figure no 4.1.7 and 4.1.8 illustrates cyclic voltammeter for electrochemical oxygen of bio alcohol with lime treatment on Pt and MnO₂ electrode. Here also see that the performance of MnO₂ electrode particularly with higher percentage (%) of Lime treatment is much better than the same on Pt. The energy contained energy and current are recomably high. Pt is very costly material and cannot be used in fuel cell as electrode for commercial purpose but MnO₂ is a chief material and the electrode has been fabricated by electrochemical deposition on 304 stainless steel.

POLARIZATION STUDY

Glucose based biofuel

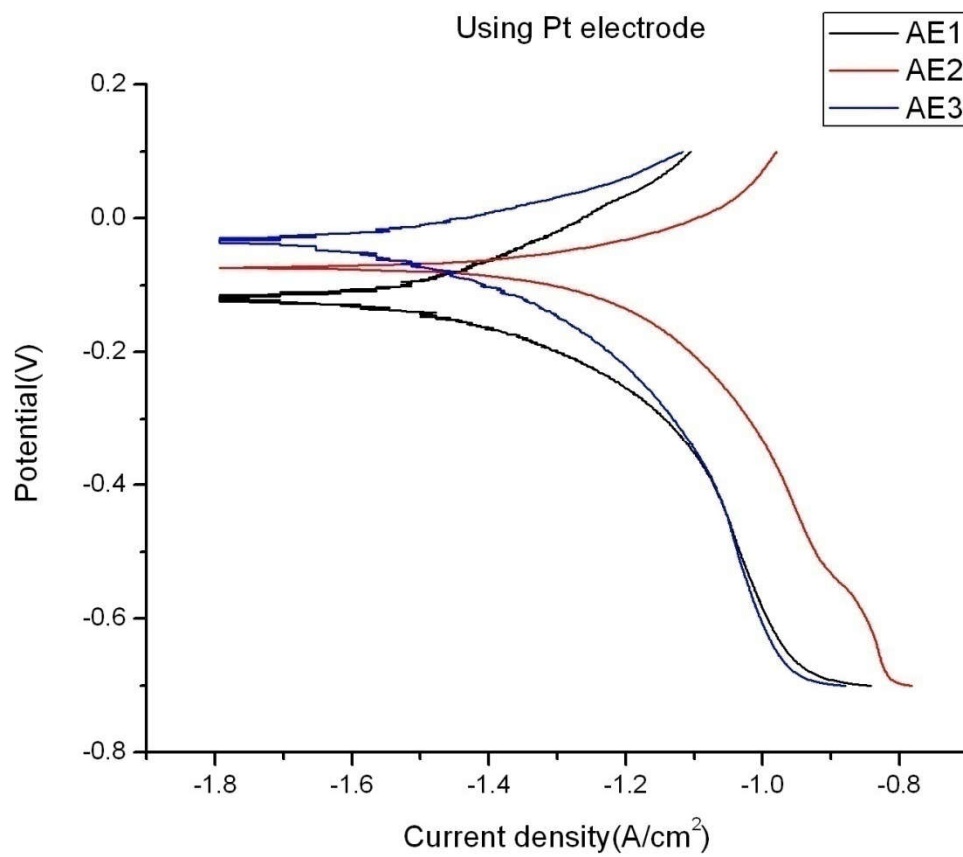


Figure no 4.2.1: Polarization diagram of glucose based biofuel with three different acid treatment using Pt electrode

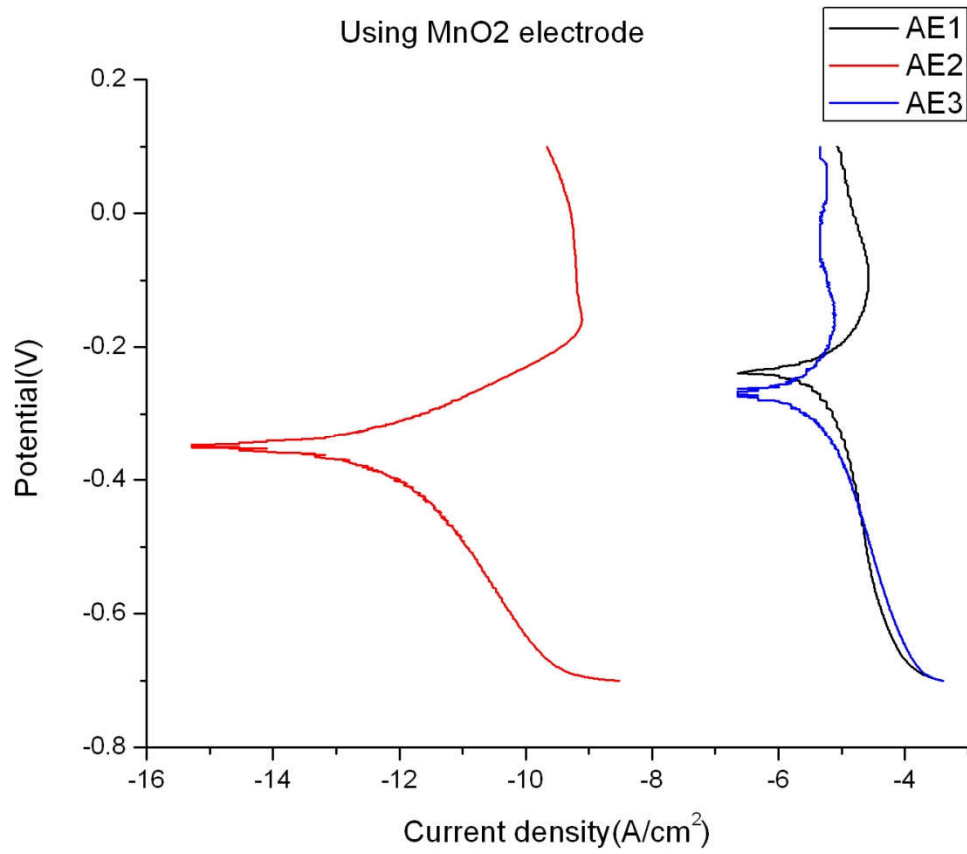


Figure no 4.2.2 Polarization diagram of glucose based biofuel with three different acid treatment using MnO₂ electrode

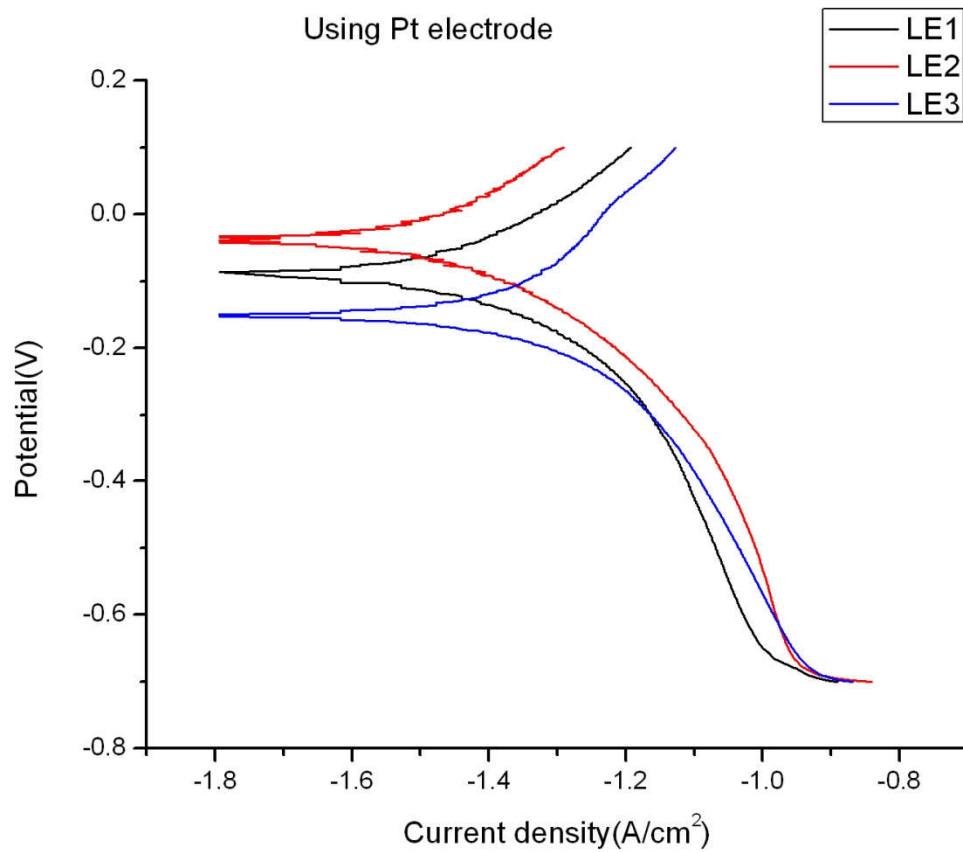


Figure no 4.2.3 Polarization diagram of glucose based biofuel with three different lime treatment using Pt electrode

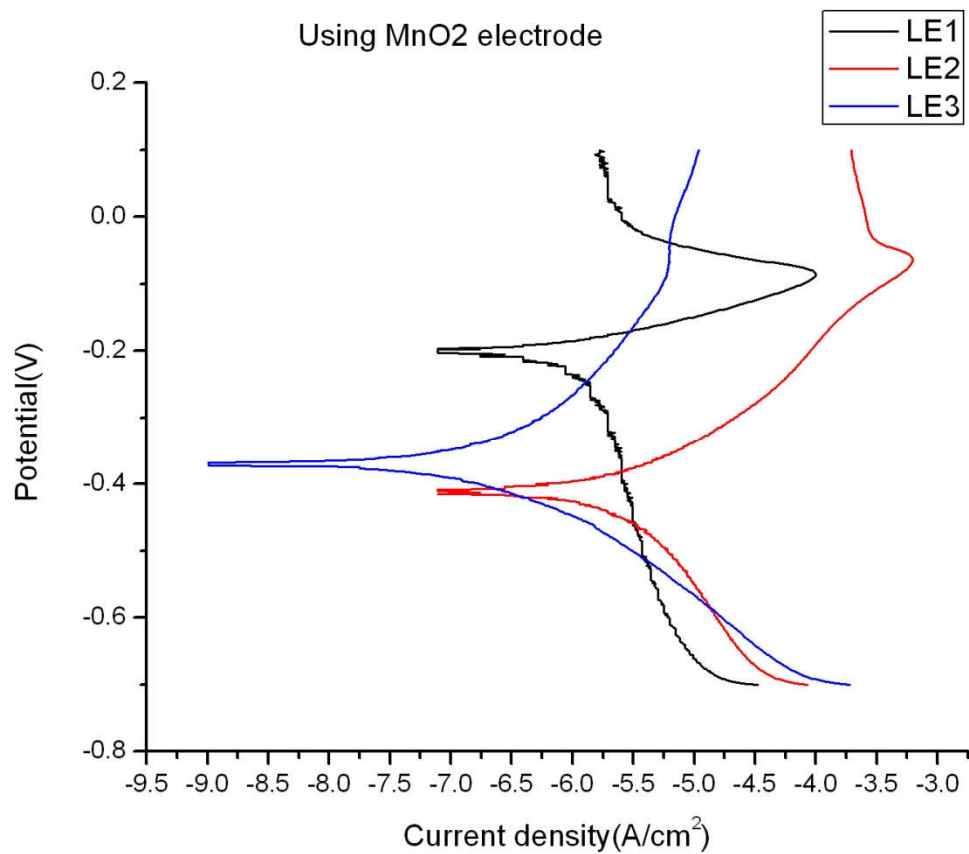


Figure no 4.2.4 Polarization diagram of glucose based biofuel with three different lime treatment using MnO₂ electrode

Alcohol based biofuel

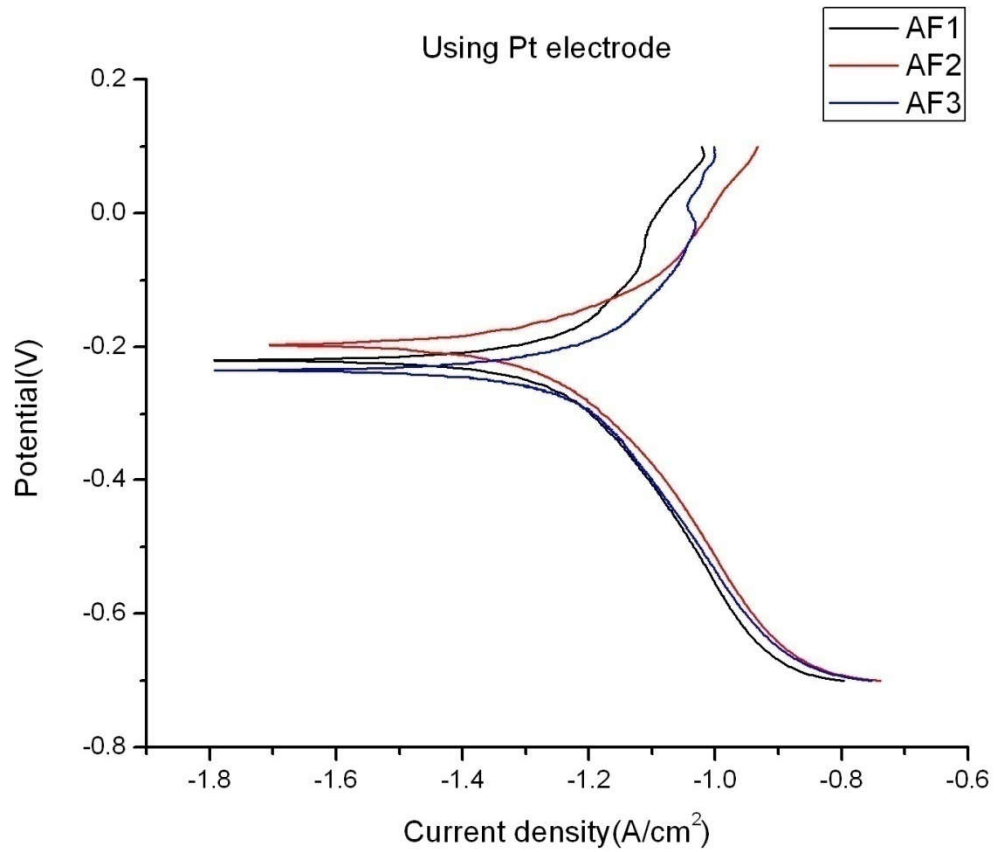


Figure no 4.2.5 Polarization diagram of alcohol based biofuel with three different acid treatment using Pt electrode

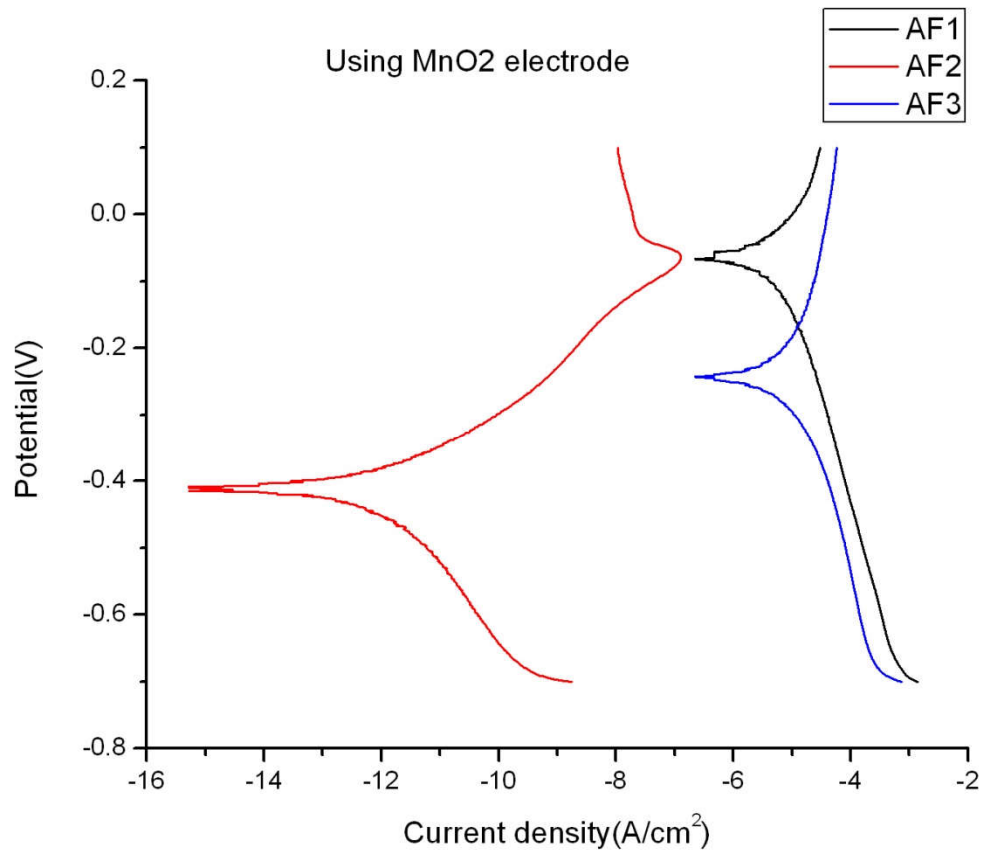


Figure no 4.2.65 Polarization diagram of alcohol based biofuel with three different acid treatment using MnO₂ electrode

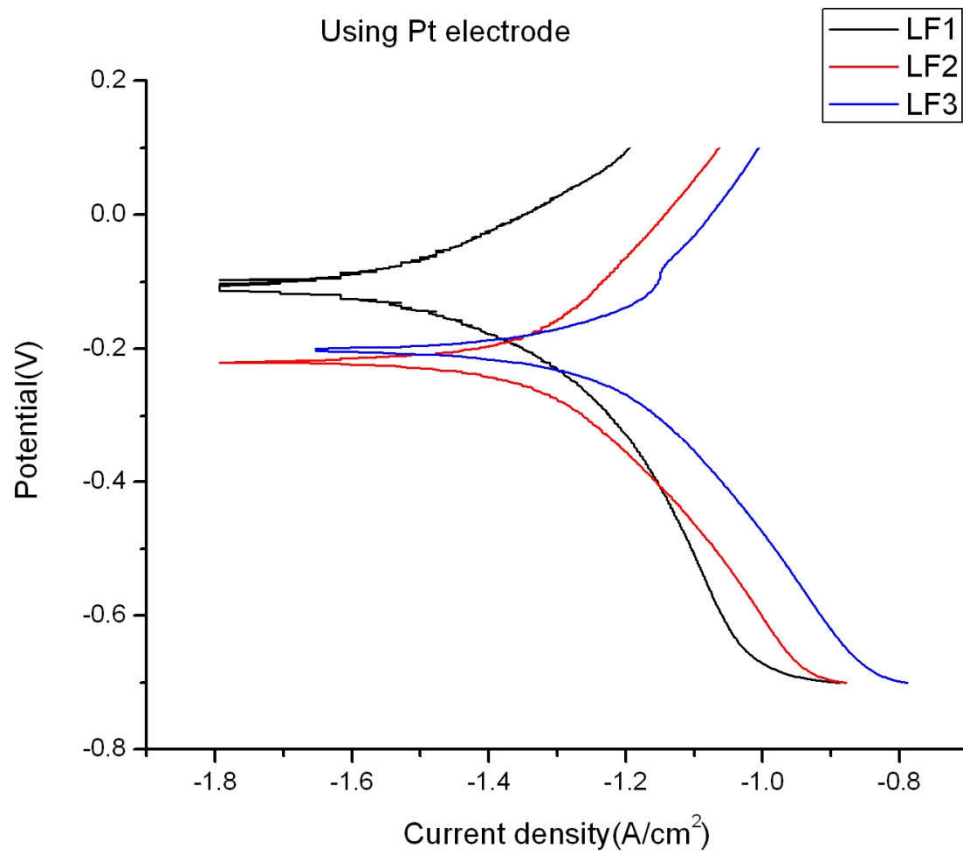


Figure no 4.2.75 Polarization diagram of alcohol based biofuel with three different lime treatment using Pt electrode

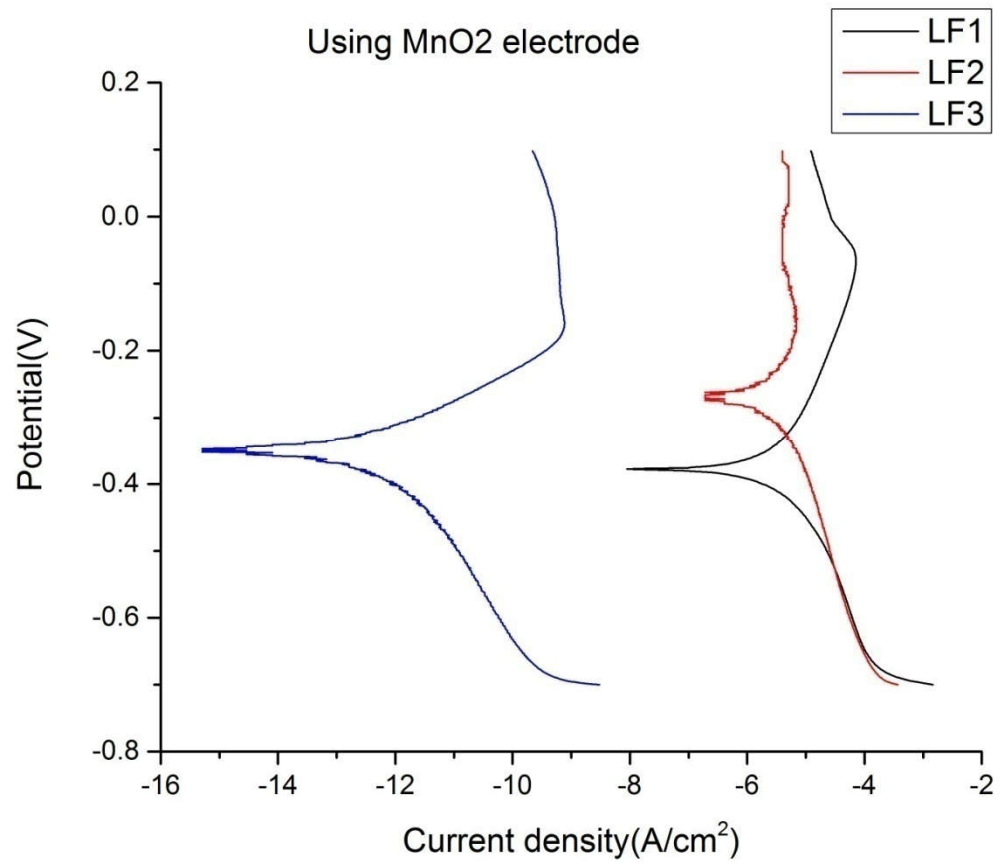


Figure no 4.2.85 Polarization diagram of alcohol based biofuel with three different lime treatment using MnO₂ electrode

Polarization study

Electrochemical oxygen on electrode polarizes the anode due to activation polarization and concentration polarization. Hence there is over voltage as given by the following equation.

$$\mathbf{E_{cell, net} = E_{cell} - (\eta_{Act} + \eta_{Conc} + \eta_R)}$$

Where η_{Act} = Activation

η_{conc} = Concentration

η_R = Electrolyte resistance

If the over voltage is more the cell potential in fuel cell is less and the current given by following equation is also less .

$$\mathbf{I = C_{cell}/R_L}$$

Thus, it is necessary to perform potentio dynamic of the electrode in the different biofuel produced as discussed above (table no. 4.1 to 4.4)

The potentio dynamic polarization on Pt and MnO₂ electrode are shown in figure 4.2.1 to 4.2.2 respectively in glucose based biofuel with acid treatment and lime treatment. If the curve shift to the right it means the polarization on the over voltage is less and the current is high and the electrode has high electro characteristic property for oxygen of the fuel. It is seen that while on Pt electrode there is not much reconcilable difference of the curve, on MnO₂ electrode there is huge shift in the curve to the right for AE3 and AE1 treatment. Pt electrode is less overvoltage than on MnO₂ electrode.

Figure no. 4.2.5 and 4.2.6 illustrate the polarization on Pt and MnO₂ respectively in bio alcohol with acid treatment. It is seen that with treatment AF1 and AF3 the curve shifted to the right on MnO₂ electrode. This means the over voltage is lower in this treatment but Pt electrode there is not much among the curve. The elector characteristics property obtained from polarization is illustrated in table no. 4.5 to 4.8.

Pt			MnO ₂	
Exp. No.	I _{Corr} (A/cm ²)	E _{corr} (Volt)	I _{Corr} (A/cm ²)	E _{corr} (Volt)
AE1	-1.3333	-0.12459	-5.4225	-0.2428
AE2	-1.2293	-0.08351	-12.72339	-0.35044
AE3	-1.42012	-0.032786	-5.6745	-0.2683

Table No. 4.5 Comparison of I_{corr} and E_{corr} using two electrode(Pt and MnO₂) of three different types of experiment with lime treatment of glucose based biofuel

Pt			MnO ₂	
Exp. No.	I _{Corr} (A/cm ²)	E _{corr} (Volt)	I _{Corr} (A/cm ²)	E _{corr} (Volt)
LE1	-1.4698	-0.0837	-5.8331	-0.2422
LE2	-1.52323	-0.035116	-5.79957	-0.41738
LE3	-1.4363	-0.14430	-6.9927	-0.3644

Table No. 4.6 Comparison of I_{corr} and E_{corr} using two electrode(Pt and MnO₂) of three different types of experiment with lime treatment of glucose based biofuel

Pt			MnO ₂	
Exp. No.	I _{Corr} (A/cm ²)	E _{corr} (Volt)	I _{Corr} (A/cm ²)	E _{corr} (Volt)
AF1	-1.2964	-0.21915	-5.4310	-0.0695
AF2	-1.32287	-0.20218	-12.855	-0.4104
AF3	-1.3200	-0.23509	-5.2415	-0.2407

Table No. 4.8 Comparison of I_{corr} and E_{corr} using two electrode(Pt and MnO₂) of three different types of experiment with acid treatment of alcohol based biofuel

Pt			MnO ₂	
Exp. No.	I _{Corr} (A/cm ²)	E _{corr} (Volt)	I _{Corr} (A/cm ²)	E _{corr} (Volt)
LF1	-1.49267	-0.104421	-5.7636	-0.3720
LF2	-1.40087	-0.21911	-5.6584	-0.26599
LF3	-1.3327	-0.20089	-11.5184	-0.3568

Comparison of I_{corr} and E_{corr} using two electrode(Pt and MnO₂) of three different types of experiment with lime treatment of alcohol based biofuel

4.2 SEM IMAGE OF MnO₂

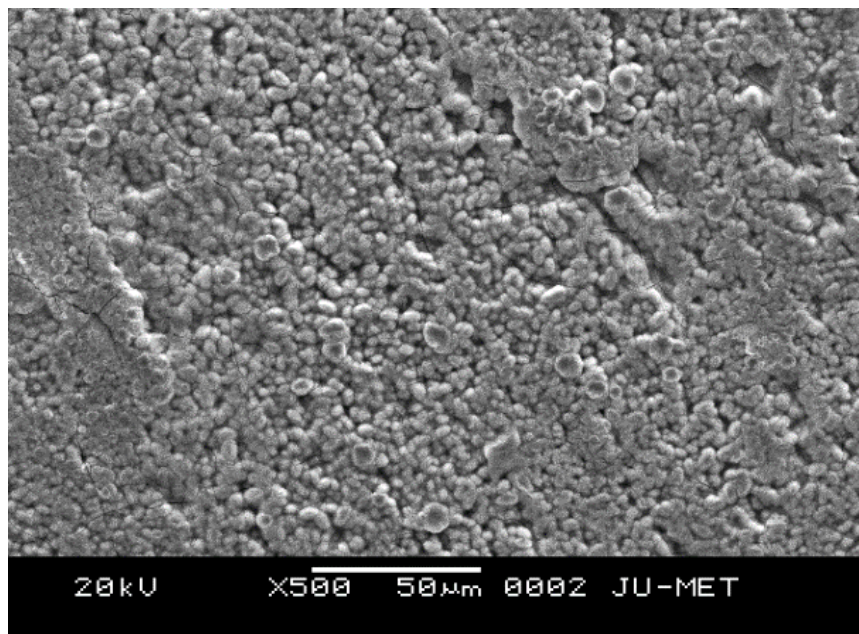
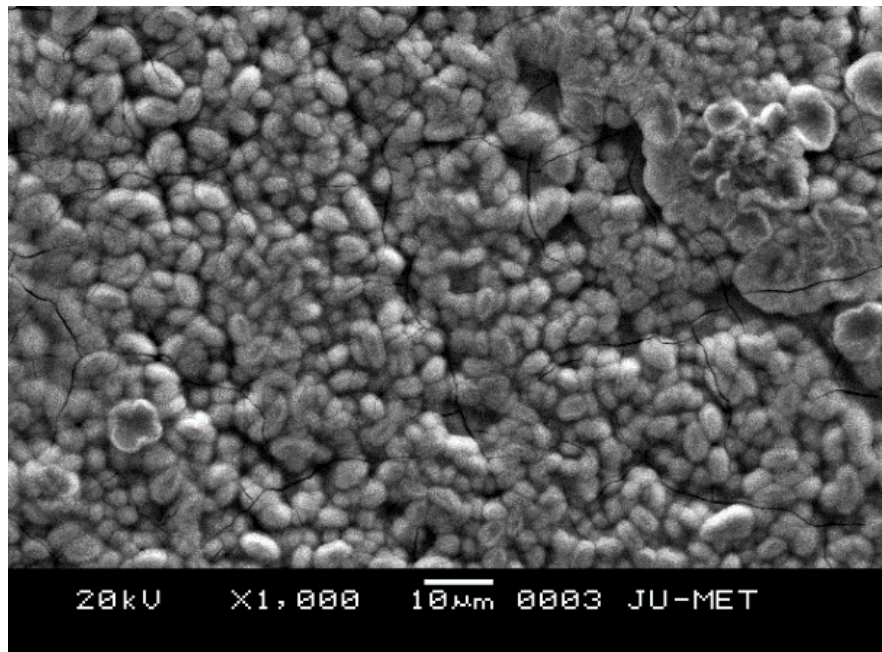


Figure no 4.3.1 SEM image of MnO₂ coating on 304 stainless steel plate

The study of morphology of MnO₂ electrode under SEM (scanning electron microscope) .Figure no 4.3.1 shows the SEM image of the MnO₂ electrode produce by electro deposition. The morphology of the surface clearly indicates number of fines globules distributed. There is chains in between globules these is enhance the effective area in 3D is several times more than the geometrical in2D. Hence more surface is available for electrochemical reaction of oxygen of biofuel on MNO₂ which gives an increase in current. These accounts for higher current obtain on MnO₂ surface than the Pt on electrochemical oxygen of glucose based and alcohol based biofuel.

CHAPTER NO: 5

CONCLUTION

CONCLUSION

From the foregoing result and discussion the following statement can be summarized.

1. Wood floor can be converted to biofuel either glucose or alcohol based by pre-treatment with acid or alkali and then enzymatic saccharification and fermentation.
2. It is seen that acid pre treatment is better than the lime pre treatment in term of percentage (%) of fuel extracted.
3. Higher is the Acid or Lime concentration more is the fuel conversion.
4. The electrochemical oxygen of fuel on MnO₂ and Pt electrode exhibit high current at a particular potential which varies from one treatment to another.
5. The energy contain obtained electrochemical oxygen of fuel this also high.
6. The performance of MnO₂ in respect of maximum current and energy since to better that for Pt electrode.
7. The scanning electron microscope image clearly reflect the effective 3D surface curve for electrochemical oxygen of bio fuel for MnO₂ electrode is much higher than geometrical 2D surface. This is the resign for good performance of MnO₂ electrode.

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