κ-Carrageenan and Aluminum Oxide as a Potential Replacement for Industry-Standard Materials in Proton Exchange Membrane Fuel Cell (PEMFC) Fabrication

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Abstract. Severe depletion of conventional sources of energy forced modern economies to actively participate in a global transition to renewable energy. With today’s modern technology, power, heat or mechanical energy can be produced by simply utilizing resources which can facilitate production of electricity. Energy converting devices such as fuel cells can perform and generate electricity using one-step electrochemical reactions. Fabrication of such technology uses materials which are of the highest quality and purity but are prohibitively expensive. To enable the Philippines to put up a fuel cell technology system to mitigate the dependence of the country on importation of energy sources as the demand continuously increase, the industry-based materials, Nafion® and cerium (IV) oxide, CeO₂, were replaced by κ-carrageenan and aluminum oxide, Al₂O₃ as ion-exchange membrane and radical scavenger, respectively. Fourier transform infrared spectrometer (FTIR) was used to verify graphene oxide (GO) formation, digital microscope (Mic-D) for surface morphology, and oxidation reduction potential (ORP) meter for measuring cell potential. The fabricated proton exchange membrane fuel cell (PEMFC) generated a maximum cell potential of 543.6 mV at an operating temperature of 27°C. Thus, the fabricated PEMFC from a cheap, renewable, and highly available material in the Philippines is a promising alternative to the expensive Nafion®-based fuel cells.

1. Introduction
Fuel cells are devices that convert chemical energy to electrical energy without the combustion of fossil fuels. It is a renewable source of energy that is composed of the anode and the cathode, which are the negative and the positive electrodes, respectively, together with a suitable electrochemical reaction as current source. In the anode, the reductant is oxidized, liberating an electron that travels down to the cathode. It is this electron transfer that results in the production of electric current [1]. Simply put, fuel cells are one-step energy converting devices that utilize electrochemical reactions [2]. The utilization of such a cell is dependent on the different parameters related to operating conditions and structures. These variables include the following: types of electrodes, types of reactants, and operating temperature [1]. In general, fuel cells are classified according to the type of electrolyte used to facilitate the reaction [3]. Based on this, Alkaline Fuel Cells (AFC), Direct Methanol Fuel Cells
(DMFC), Proton Exchange Membrane Fuel Cells (PEMFC), Phosphoric Acid Fuel Cells (PAFC), Molten Carbonate Fuel Cells (MCFC), and Solid Oxide Fuel Cells (SOFC) were devised.

PEMFC, also known as Polymer Electrolyte Fuel Cell (PEFC), is a low-temperature type of fuel cell which operates from 50-80°C that uses a solid electrolyte, usually polymer electrolyte membrane (PEM) to generate power ranging from a few Watts (W) to 100 kW [4]. Because this type of fuel cell is at the forefront of green energy [1], reproduction of such technology is extremely desirable. Fabrication of this type of fuel cell is quite simple but precision is needed for it to be successful. The fabrication process consists of these parts: film preparation, preparation of graphene oxide (GO), synthesis of aluminum oxide (Al₂O₃) cubes-GO composites, synthesis of Pt-GO-Al₂O₃ catalysts, preparation of the Membrane Electrode Assemblies (MEA), visualization of catalyst surface, and cell performance measurement.

Enabling the Philippines to put up a fuel cell technology system is one of the many urgent responses needed to mitigate the dependence of the country on importation of energy sources as the demand for it continuously increasing. However, fuel cell fabrication requires materials which are of the highest quality and purity causing it to become prohibitively expensive. Thus, this study aims to fabricate a potentially low-cost fuel cell using κ-carrageenan from seaweeds, a cheap, renewable, and highly available material in the Philippines as replacement for Nafion® as ion-exchange membrane. In addition, cerium (IV) oxide, CeO₂ is replaced by aluminum oxide, Al₂O₃ as radical scavenger. The fourier transform infrared spectrometer (FTIR), digital microscope (Mic-D), and oxidation reduction potential (ORP) meter are used to monitor oxidation of graphene to GO, to examine surface morphology, and to measure the cell potential, respectively.

2. Materials and Methods

2.1. Film Preparation
The κ-carrageenan films were prepared using gelation technique [5]. Briefly, 2 wt. % of Bengel K100 κ-carrageenan powder was dissolved in water with vigorous stirring at an elevated temperature of 80°C. After the powder dissolved completely, the solution was immediately cast. The gel was left to dry at room conditions. Enough aldehyde was added to just cover the κ-carrageenan film and this was then irradiated in an oven using microwave pulses for 30 seconds at 700 W.

2.2. Preparation of Graphene Oxide (GO)
The Hummer’s method [6] was performed to synthesize graphene oxide (GO). Initially, 2 grams of graphite and 2 grams of sodium nitrate, NaNO₃ were mixed in 50 mL of sulphuric acid, H₂SO₄ and kept in an ice bath with continuous stirring for 2 hours. Six (6) grams of potassium permanganate, KMnO₄ was added to the suspension and the reaction was maintained at a temperature lower than 15°C. The mixture was then stirred at 35°C for 2 days and produced a brownish paste. Dilution of the brownish paste with 100 mL water caused the temperature to rise to 98°C and produced a lighter brown color. Two hundred (200) mL water was added. Ten (10) mL of hydrogen peroxide, H₂O₂ was added to terminate the reaction which was confirmed by the appearance of yellow color. The mixture was washed and centrifuged with 10% hydrochloric acid, HCl and deionized water for several times to achieve neutral pH. Subsequently, the final product was dried and the GO was obtained as a powder.

2.3. Synthesis of Graphene Oxide-Aluminum Oxide (GO-Al₂O₃) Composites
One hundred (100) mg of GO was dissolved in 60 mL distilled water by sonication for 2 hours until a yellow-brown suspension was formed. One tenth (0.1) mmol of Al₂O₃ was added to the solution. The resulting mixture was vigorously stirred for 2 hours. The solution was transferred to a Teflon™-lined container. Ten (10) mL of toluene (C₆H₆), 1.5 mL oleic acid (C₁₈H₃₄O), and 0.1 mL ethylenediamine [C₂H₄(NH₂)₂] were added without stirring. The container was sealed and placed in an oven at 180°C for 24 hours. The black precipitate was washed with ethanol (C₂H₅OH) for several times.
2.4. Synthesis of Pt-GO-Al₂O₃ Catalysts
The potassium hexachloroplatinate (IV), K₂PtCl₆ with a platinum (Pt) content of 0.15 g was dispersed in 100 mL ethylene glycol (C₂H₆O₂) by sonication for 30 minutes. Thirty-five hundredths (0.35) g of GO-Al₂O₃ was added into the mixture. The pH was adjusted to 10 using 1.0 M NaOH/C₂H₆O₂ solution while stirring for another 30 minutes. After the dispersion process, the Pt ions were reduced to Pt⁰ by intermittent microwave-heating with pulses every 5 seconds for three times. After reduction, the pH of the suspension was adjusted to 1 using 0.1 M HCl to promote adsorption of Pt particles onto supports.

2.5. Preparation of the Membrane Electrode Assemblies (MEA)
The electrocatalyst powders were filtered, washed, and vacuum dried at 80°C for 10 hours. The resulting catalyst powder, 5 wt. % of κ-carrageenan, and isopropyl alcohol [(CH₃)₂CHOH] in a ratio of 1:6:10 was stirred vigorously. The slurry was screen-printed onto the κ-carrageenan film using two tenths (0.2) mg·cm⁻² for the anode and 0.4 mg·cm⁻² for the cathode, respectively. The loaded layers were dried at 60°C for 10 minutes and at 90°C in inert conditions for 3 minutes. The assembly was bonded together by hot press for 90 seconds.

2.6. Visualization of Catalyst Surface
Photomicrographs of the film surface were obtained using Olympus Mic-D Digital Microscope (Model No.: Mic-D001; ASIN: B0000U3CDC). The membrane electrode assembly was placed in a glass slide and positioned directly onto the movable stage. The magnification setting was at its maximum (500x) and the focus knob was adjusted to obtain a clear photomicrograph of the membrane electrode assembly.

2.7. Cell Performance
Cell potentials were recorded using a Hach HQ11D portable ORP meter lent by Cleanway Environmental Management Solutions, Inc. The potential recording was performed as follows: the ORP meter was calibrated using deionized water for several times to achieve the stabilized potential baseline with respect to normal conditions. The anode and the cathode side of the fuel cell were attached to the ORP meter using electrical clips. The hydrogen gas was supplied continuously to the system. The ORP reading was then recorded. It was then repeated for several times to obtain readings as necessary. All measurements were carried out in three replicate runs and the average values were reported.

3. Results and Discussion
The film that was composed of octanal-modified κ-carrageenan (see Figure 1a) was coated with Pt-GO-Al₂O₃ catalyst (see Figure 1b). This was sandwiched between gas diffusion layer (GDL) sheets and was clamped together using conducting plates. The fabricated PEM fuel cell is shown in Figure 1c.

![Figure 1](image_url)

**Figure 1.** (a) Treated κ-carrageenan film; (b) Synthesized Pt-GO-Al₂O₃ catalysts; (c) Fabricated PEMFC.
3.1. FTIR Analysis

This method was used to monitor the oxidation of graphene to graphene oxide (GO). Figure 2 shows the IR spectrum of the synthesized GO. The peak at 1,037 cm\(^{-1}\) indicated the presence of C–O bond which confirms the existence of oxide functional groups after the oxidation process. The C=C bonds still remain on the GO spectra which can be seen in peaks residing at 1,617 cm\(^{-1}\). The broad peak at 3,354 cm\(^{-1}\) was from the O–H stretch from water molecules absorbed by the GO. Since octanal has low water miscibility with water, it was used to decrease the water-holding capability of the κ-carrageenan film.

Figure 3 presents the IR spectrum of the octanal solvent. The peaks at 2,843 cm\(^{-1}\) and 1,707 cm\(^{-1}\) correspond to the C–H and C=O stretches. In the κ-carrageenan film spectrum, Figure 4, the peak 1,220 cm\(^{-1}\) corresponds to the S=O of the pendant group sulfates. Glycosidic linkages were indicated in the spectrum by the presence of a peak at 1,032 cm\(^{-1}\) ascribed to all types of carrageenan. D-galactose-4-sulfate and 3,6-anhydrogalactose-2-sulfate were also indicated by peaks 842 cm\(^{-1}\) and 92 cm\(^{-1}\), respectively, which are consistent with the results reported by Webber et al. (2012) [7].

On the other hand, Figure 5 shows the IR spectrum of κ-carrageenan film + octanal. The peak at 1,707 cm\(^{-1}\) disappeared from the spectrum. The loss of this peak suggests a reaction of the aldehyde and the hydroxyl group of the film. One aldehyde group may link the polymer chains by reacting with the hydroxyl groups of the polymer and produce a hemi-acetal or an acetal.

3.2. Mic-D Analysis

Figures 6a and 6b shows the photomicrographs of the anode and the cathode surfaces, respectively. From these photomicrographs, it can be seen that not the entire surface was completely coated by GO-Al\(_2\)O\(_3\). At the black portion of the micrographs no light passes through, so this is likely where the
catalyst and the catalyst supports reside, whereas in the light regions, light is transmitted, meaning, probably only the catalyst is present, i.e., the very fine Pt has gaps that allow light to pass through and itself reflects incident light. Note that the uncoated regions (light regions in the film) have no consistent shape.

![Mic-D photomicrograph of the (a) anode and (b) cathode.](image)

**Figure 6.** Mic-D photomicrograph of the (a) anode and (b) cathode.

### 3.3. Oxidation Reduction Potential (ORP) Analysis

Potential measurements under a constant temperature of 27°C and continuous fuel supply conditions were performed and represented in Figure 7. The fabricated fuel cell generated a maximum potential of 543.6 mV with fast initial current generation upon introduction of reductant gas. It can be observed that the longer time the fuel is supplied, the more fuel reaches the catalyst sites and so, more fuel reacts to generate current, thus continuously increasing the potential over time. The total run time for this fabricated fuel cell, up to the time of flooding, was about 25 minutes (~ 1,498 seconds).

![Cell potential characteristic curve of the fabricated PEMFC.](image)

**Figure 7.** Cell potential characteristic curve of the fabricated PEMFC.

Flooding is a phenomenon caused by excessive humidity generated by the cell reaction, i.e., water was observed coming out of the fuel cell assembly. The proton conductivity of the membrane deteriorated as the water molecules in the system accumulates resulting in changes in its physical properties. Because the membrane swelled, the pore size decreased to the point where the protons were not be able to pass through, resulting in cell potential drop. This occurrence, associated with
resistance to both the flow of ions in the electrolyte membrane and to the flow of electrons through the electrically conductive fuel cell components, was reported also by Wang et al. (2011) [8].

4. Conclusion

The fabricated proton exchange membrane (PEM) single fuel cell generated a maximum cell potential of 543.6 mV at 27°C that substantiates the feasibility of utilizing κ-carrageenan and aluminum oxide, Al₂O₃ as a potentially substitute for Nafion® as ion-exchange membrane and cerium (IV) oxide, CeO₂ as radical scavenger, respectively. Thus, eliminating the constraint of prohibitively expensive industry-based materials in the fabrication of fuel cells. Although the cell potential generated from the fabricated fuel cell is lower than the 1.23 V obtained using Nafion® [9], an advantage of the fabricated fuel cell that is in direct contrast to Nafion®-based fuel cells, is its almost instantaneous current generation. Commercial fuel cells are characterized by a long induction period before current generation, especially after storage [9]. Regardless of how the fuel is supplied, the cell potential increases over time until flooding occurred, wherein the cell potential dropped because the physical properties of the membrane were changed by the presence of excess water molecules. Thus, the fabricated PEMFC from a cheap, renewable, and highly available material in the Philippines is a promising alternative to the expensive Nafion®-based fuel cells.

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