Reduced Graphene Oxide/FeNiCoCu Catalyst Materials Production, Characterization for PEMFC; Its Electrochemical Modelling Studies, and Performance Comparison

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Abstract
Fuel cells are energy converters that use hydrogen-based fuels. They are noise-free and highly efficient. They have important advantages which include high tolerance to impurities in the fuel, using various fuel types directly or through additional fuel converting systems. Fuel cell components are interconnectors, gas diffusion layers, electrodes and membranes. “Membrane Electrode Assembly” (MEA) is the part that includes opposing electrodes (anode – cathode) and the membrane between them. Reaction kinetics are accelerated by catalyst materials embedded into the MEA, which are conventionally platinum and other noble metals. Production of noble metal is hard to conduct and their resources are constantly decreasing as their demand increases which results in rising prices. Furthermore, for the purpose of using less noble metal by increasing particles’ surface areas; they are produced in nanoscale but it is difficult to control the kinetic behavior of particles in nanoscale. Alternative catalyst material research will encourage widespread usage and increase availability of fuel cells. In this case FeNiCoCu nanoparticles are used as a catalyst material for fuel cells. Nonetheless, surface area is a critical parameter for catalysts. Properties of reduced graphene oxide are mostly revealed. Hence reduced graphene oxide supported FeNiCoCu catalyst material further expands the surface area in catalyst layers. In this study, FeNiCoCu particles were synthesized with ultrasonic spray pyrolysis method and supported with reduced graphene oxide; reaction kinetics and material characteristics were investigated and were used as initial parameters for electrochemical modeling studies. Results were compared with previous studies that included different catalyst materials.

1. Introduction
Fuel cells are electrochemical devices that use chemical energy to produce energy as electrical power. Ability to make this conversion in reverse makes these devices opportune for in-situ energy production. They don’t produce vibrations or sound unlike internal combustion engines and they emit water vapor as a by-product which makes these devices environment friendly. Fuel cells use either hydrogen or hydrogen-based fuels. They are considered to be used on various transportation fields such as trains, automobiles and ships. Even though they aren’t the ultimate solution to world’s energy storage problem, fuel cells are excellent alternatives when batteries or supercapacitors aren’t sufficient enough tools. Their advantages include highly efficient conversion rates, high power density, ability to use various fuel types and tolerance to impurities in the fuels [1-2]. Fuel cells include 2 primary reactions to operate; “Hydrogen Oxidation Reaction” (HOR) and “Oxygen Reduction Reaction” (ORR). Mostly ORR is the inhibiting step in fuel cell operation equations [3]. In order to obtain adequate performance levels, an electro catalyst material and/or layer is required which is contained inside both anode and cathode electrode layers. Pt and Pt-based noble materials are conventionally used catalyst materials but noble materials are rare and therefore expensive. In addition to the numerous security restrictions brought by hydrogen-based fuels, costly catalyst layer hinders the widespread usage of fuel cells. Development of new generation, accessible and better fuel cell electro catalyst materials are the main aim of this...
study. Properties of transition metal and graphene-based catalysts as alternatives have been reported [3, 4]. Figure 1 shows a membrane-electrode assembly with conventional catalyst loading.

Figure 1. Cross-section image (left) and schematic (right) of a PEMFC membrane-electrode assembly [2].

In this study, FeNiCoCu nanoparticles were synthesized with Ultrasonic Spray Pyrolysis and Hydrogen Reduction (USP-HR) method. USP-HR method was adopted in order to produce highest possible surface area while controlling the size distribution. To further increase the surface area and catalytic effect, nanoparticles were mixed with Reduced Graphene-Oxide (RGO). Catalytic effect was tested with dried catalyst mixture. These tests provided the initial values for electrochemical modelling studies. Simulations were conducted to compare catalytic performance of FeNiCoCu – RGO fuel cells to conventional Pt-based fuel cells.

2. Experimental
FeNiCoCu particles and RGO were produced separately. Final catalyst material was characterized with gas consumption tests. Characterization results were used for modelling studies.

2.1. Production of FeNiCoCu Nanoparticles
Nano particles were synthesized with Ultrasonic Spray Pyrolysis technique. A precursor solution with 0.2M concentration of nitrate salts was prepared. Precursor solution was mixed for 15 minutes at 500 rpm for homogeneous mixture. For aerosol generation 1.3 MHz frequency was used while the precursor solution’s temperature was controlled by a refrigerated circulating bath. Reduction zone was a quartz tube of 40 cm length and 3 cm diameter. Reduction temperature was 800 °C with 1 L/min H₂ flow. Particles were collected in ethanol and were dried afterwards.

2.2. Preparation of Catalyst Material
RGO (reduced graphene oxide) and FeNiCoCu particles were mixed at a 1:1. Both RGO and FeNiCoCu were dried and weighed equally. Powders were mixed mechanically for gas consumption tests.

2.3. Gas Consumption Tests
H₂ gas and air was passed from dried and bulk powder catalyst material in order to obtain initial parameters for electrochemical modelling studies. Figure 2 shows the schematic of gas flow test. H₂ consumption values were used for anode side, and air consumption values were used for cathode side. It was assumed that air held 21% oxygen.

2.4. Modelling Studies
Proton exchange membrane fuel cell (PEMFC) was electrochemically modelled with both conventional and prepared catalyst materials. Laboratory scale, single cell fuel cell was used for initial parameters of PEMFC with conventional catalyst material. Results from “Gas Consumption Tests” were used for initial parameters of PEMFC with FeNiCoCu – RGO catalyst material.

3. Results and Discussion
Catalyst material was characterized with various different methods. RGO and FeNiCoCu were characterized by XRD separately for phase analysis. Figure 3 shows the XRD pattern for RGO and alloy particles.

Figure 3. XRD analysis of a) FeNiCoCu b)RGO

As catalytic activity correlates proportionally with surface area, SEM images were used to determine particle size and shape of FeNiCoCu particles. SEM results of RGO and FeNiCoCu can be seen on Figure 4.
and EDS results on Table 1 showed elemental
distribution was homogeneous.

**Figure 4.** SEM results of FeNiCoCu and RGO particles
at, a) RGO x10,000 b) RGO x50,000 c) FeNiCoCu
x10,000 d) FeNiCoCu x 50,000 enlargements.

**Table 1.** EDS analysis results of FeNiCoCu particles

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<th>Ni</th>
<th>Co</th>
<th>Cu</th>
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Electrochemical simulation results revealed the catalytic
performance of FeNiCoCu – RGO mixture. Figure 5
shows the geometry of the model. Figure 6 shows the
comparison of fuel cell parameters between different
catalyst materials.

**Figure 5:** Fuel cell model geometry

**Figure 6.** Oxygen molar concentration (mol/m³)

4. Conclusion

Reduced Graphene-Oxide (RGO) phase was produced
with modified Hummers method and FeNiCoCu particles
were produced with USP – HR method. Characterization
studies were conducted with XRD, SEM – EDS analysis.
RGO and FeNiCoCu were mixed at same amounts to
obtain final catalyst material. Gas consumption tests
provided initial parameters for electrochemical studies.
Simulation showed FeNiCoCu – RGO is a promising
alternative as a catalyst material.

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