Assessing Carbon Dioxide Equivalent Emissions in the Preparation of the Platinum Nanophase Electro Catalyst Composite Electrode

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Abstract—The highly catalytic activity of Platinum Group Metals (PGMs) in the production of hydrogen by water electrolysis is achieved using a new approach by nanotechnology of reducing PGMs into nanometer size and integrating them in a nanophase composite electrode. Water electrolysis is the cleanest process of obtaining hydrogen. However, with the use of nanotechnology process, there is a need to reassess the process and determine degree of its environmental friendliness.

The analysis of likely environmental impacts with regard to the manufacturing process of the platinum nano-composite electrode and of its component materials was the focus of this paper. Life Cycle Inventory Assessment and Carbon Dioxide Equivalent calculation for each component of the electrode were established. Umberto for carbon footprint software was used to assist to develop flow-charts and to determine carbon dioxide equivalent emissions for each component of the electrode. The results of the analysis showed that there are likely direct emissions involved when heating, carrying out calcination and drying materials. Palliative recommendations were suggested in accordance with the types of emissions identified.

Keywords— Nanophase composite electrode, PGMs, Electrolysis of water, LCIA, Carbon Dioxide Equivalent Emissions

I. INTRODUCTION, OBJECTIVE AND METHODS

An electrode made of nanophase composite material can use noble metals, predominantly platinum group metals (PGMs), for high electro catalytic electrolytic activities.

The application of expensive noble metals incorporated into membrane electrodes for the environmental friendly systems PEM fuel cell and SPE electrolyser provides the highest efficiencies. Much effort in terms of research has been undertaken to bring down to least possible the noble metals content in the membrane electrodes to reduce capital costs. This is possible by the use of nanotechnology in which chemicals are more or less involved. Chemicals are generally source of emissions.

To argue that renewable energy systems can be considered as clean technology calls for the achievement of the ecology leg aims of sustainability. An environmental assessment over synthesizing nanophase composite electrode is therefore proved pertinent.

A Solid Proton Exchange (SPE) electrolyser as well as an Electrolysis cell equipped with nanophase composite electrodes satisfy to environmental sustainability requirements either at zero or to insignificantly low GHG emissions when producing hydrogen by water electrolysis. Electrolysis is a non-polluting process. In addition to the effectiveness advantage that may offer platinum nanophase composite electrode, the need to assess to the manufacturing process and the analysis of emissions identification by components, estimation of energy consumption, and determination of the overall equivalent carbon dioxide emissions are necessary to clear up the process environmentally sound. The analysis was achieved using Life Cycle Inventory Assessment (LCIA) of the Life Cycle Assessment (LCA) (ISO 14040 standard) [1]. Life Cycle Inventory Assessment for a product consists of developing an analytical process tree in which all processes are examined from raw materials extraction, input materials through processing operations, to final products, waste recycle, disposal treatments, and emissions are mapped out and connected, and mass and energy balances are closed.

Umberto for Carbon Footprint (UFC) software version package served to develop the LCIA and do calculation of the carbon equivalent dioxide of materials, identified as carbon footprint. UFC is a graphical modelling tool able to develop product’s life cycle analysis drawn on a mapping network model interface. UFC has an in-built database comprising data of raw and elementary processed materials gathered from the Publicly Available Specification 2050 (PAS 2050), Greenhouse Gas (GHG) Protocol Product Accounting & Reporting Standard and ISO 14067. It includes more than 4000 materials with global warming potential (GWP) values from the eco-invent database.
II. PREPARATION OF THE PLATINUM NANOPHASE COMPOSITE ELECTRODE

The preparation of the platinum nanophase composite electrode is critical for high catalytic activity to produce hydrogen by water electrolysis efficiently. The expectation for such electrodes is an effective yielding amounts of hydrogen. Therefore, high current densities are to be generated but using low energy input and electrodes to work in a low concentration electrolyte, operating at low temperatures [2].

The preparation of Platinum (Pt.) nanophase composite electrode has four (4) phases which elaborately provided 4 life cycle inventory assessments. These are LCIs for HMS, HMS-Pt., Pt./C, and the Pt. nanophase composite electrode.

Hexagonal Mesoporous Silica (HMS) is a matrix, the kind needed to develop a nanoscale structure material [3]. HMS is of great interest in the area of catalysis owing to its thicker framework wall and its response as a catalyst, showing performance by its thermal stability and wormhole framework structure [4]. HMS is not commercially available and the challenge would be to produce it at both laboratory and industry scale. Laboratory scale HMS has been developed as shown in Figure 1[2]. The development of this figure was done through our own analysis and assessment of the published data in an UMBERTO for carbon footprint software [5] environment.

There have been some indication that chloroplatinic acid hexahydrate (H$_2$PtCl$_6$.6H$_2$O) can serve as a source of platinum [2]. H$_2$PtCl$_6$.6H$_2$O could therefore be used successfully to prepare HMS-Pt material by incipient wetness impregnation of H$_2$PtCl$_6$.6H$_2$O acid upon the mesoporous HMS matrix [2]. This is indicated in Figure 2 based on our assessment and analysis of data using UMBERTO. The Platinum salts are reduced to form nanophase particles on HMS using a solution of methanol/formaldehyde and by carbonisation with a low cost liquefied petroleum gas [2].

HMS-Pt is then soaked into a sodium hydroxide (NaOH) solution to remove HMS matrix by stirring. The resulting nanophase platinum composite material can then be treated with ultra-pure water and dried in oven at 100°C [2].

The Platinum nanophase powder is treated to improve its nano-physical properties with XRD, TEM and BET methods. It is then dispersed and magnetically stirred in a solution of ultra-pure water, isopropanol and binder/proton Nafion to form a catalytic ink [2].

An analogue order mesoporous carbon nanotube material that is carbon-supported platinum nanophase electrocatalyst (Pt/C) can be prepared with expectation to serve as matrix support of order mesoporous to enhance the catalytic reactivity of the platinum catalytic ink which was coated upon (Fig. 3) [6].

Pt/C nanophase can be prepared through an impregnation reduction technique by suspending a treated carbon black in the glycol/isopropanol solvent with chloroplatinic acid hexahydrate (H$_2$PtCl$_6$.6H$_2$O) as metal precursor and sulphuric acid (H$_2$SO$_4$) as pH-regulator. Formaldehyde reduction is then done to ensure the deposition of Platinum (Pt) onto the carbon black support material [6]. The data from the preparation process was collected, assessed and analyzed using UMBERTO as shown in Figure 3.

In final, platinum nanophase composite electrode material can be formed by carbonization of reduced/unreduced HMS-Pt
using a low commercial cost LPG with a heating rate of 1.67°C/min, from 50 up to 800°C. HMS matrix is then removed from the cooled HMS-Pt with NaOH by stirring. Subsequently, the platinum nanophase resulting powder can be treated with ultra-pure water and dried in an oven at 100°C and magnetically stirred and dispersed in Nafion solution prepared for obtaining a catalytic ink.

The catalytic ink can be applied by coating upon the carbon-supported platinum substrate (Pt/C) as shown in Figure 4 [2].

III. ELECTRO ACTIVITY OF THE PLATINUM NANOPHASE COMPOSITE ELECTRODE

It has been demonstrated that electro catalysts performed at 0°C and 40% KOH does not provide high electro activity. Furthermore, it was also demonstrated that below an applied potential of 2V, no activation was noted for the conductive substrate Pt/C. However, an effective result is obtained at 60°C electrolyte with a better screened electroactivity of about 8.9JmA-1cm-2. The Pt nanophase composite electrode attained current densities of 0.6Acm−2 at an applied potential of −2V performing even better than the commercial Johnson Matthey Pt/C catalyst achieving only 0.317Acm−2 current density under same conditions applied [2].

The output of the balance sheet comprised HMS (a white solid) as the final product and some direct emissions (Table1) detailed as follows:
1) Deionized water used for washing the solid in the process T4 (Figure 1) is taken as wastewater and emission, unless recycled;
2) Ethanol (ETOH) airborne emission when drying and heating of HMS in the process T6 (Figure 1). Paper is intended for a conference, please contact your conference editor concerning acceptable word processor formats for your particular conference.
500 grammes of the collected ETOH in the process T5 when extracting the yellow solid from Soxhlet Extractor was considered good material since it was not seen as waste or emission.

B. HMS Carbon Footprint Summary

Table 2 resulted from the carbon footprint calculation by Umberto after obtaining the HMS input/output balance sheet. The carbon footprint for the preparation of 9.60g of the produced HMS amounted to 3.13Kg CO2eq. Table 3 gives more details of carbon footprint based individual materials.

C. HMS Carbon Footprint Details

The overall carbon footprint for preparing HMS was 3.24Kg CO2-eq. This means that the Carbon footprint from raw chemicals as well as from the sources of energy mix used are accountable to the final product HMS. The highest contribution of about 3.14Kg CO2-eq (96.75%) came from the use of energy, and notably electricity, from polluting no renewable resources of energy.
D. HMS-Pt Life Cycle Inventory Balance Sheet Results

The output balance sheet contained HMS-Pt material as the final product and assumed that some processes probably contributed to direct emissions during transformation operations such as when heating HMS-Pt (Figure 2, T8), drying it in hot air (Figure 2, T4), and at room temperature (Figure 2, T6), and when filtering and rinsing HMS-Pt with deionized water (Figure 2, T7).

E. HMS-Pt Carbon Footprint Summary

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In the preparation of HMS-Pt direct emissions were observed at relatively low values. These were mostly chemicals, of which methanol contributed 0.01% and formaldehyde 0.07%. 99.48% of the calculated carbon footprint was from the use of electricity produced from non-renewable energy mix, which emission is taken as being indirect. Table 4 resulted from the carbon footprint calculation by Umberto after obtaining the HMS-Pt input/output balance sheet. The carbon footprint was equivalent to 3.90Kg CO₂eq after the preparation 20.50g of HMS-Pt.

F. Pt/C Carbon Footprint Summary

Pt/C is a gas diffusion support structure of porous micro-texture. This structure served as support to delicate ultra-fine platinum particle structures built from the HMS matrix. Pt/C nanophase can be prepared through an impregnation-reduction technique of suspending a treated carbon black (Cabot Vulcan® XC-72) in a solvent like glycol/isopropanol with a metal precursor such as chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O) and a pH-regulator either sulphuric acid (H₂SO₄) or sodium hydroxide (NaOH).

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No evident record was reported in the preparation of Pt/C (Williams et al., 2009). However in the preparation of Pt/C were from the carbon footprints of individual chemicals used and which were indirect to the preparation of Pt/C.

G. Nanophase Catalyst Composite Electrode Carbon Footprint Summary

The composite electrode balance sheet comprised the Pt nanophase composite electrode as the final product and some likely direct emissions which can be detailed as follow:

1) LPG can emit sulphur oxides (SOₓ), carbon monoxide (CO), nitrogen oxides (NOₓ) and particulate matters at high temperatures (Edward et al., 1999); this probably reflects the carbonization of HMS-Pt by LPG at 800°C (Figure 4 in T1), unless precautions are taken.
2) Sodium dioxide (NaOH) was used as a template for the removal of HMS from the HMS-Pt (Figure 4, T2). Unless recycled, NaOH can be considered as an emission when removing HMS template. The debris of the HMS material removed can be considered as an emission unless recycled (Figure 4 in T2).

V. Recapitulation Of The Carbon Footprint Values In The Process Of Preparing Platinum Nanophase Composite Electrode

The LCIA and carbon footprint calculation of the composite electrode was essentially assisted by the Umberto for carbon footprint software which helped to build an inventory analysis and provided a useful database of materials with respective carbon footprint. Direct emissions were likely involved when heating, calcinating, drying materials. Other direct emissions given in the literature were considered [4] and [2].

VI. Conclusion

The new approach in the use of PGMs for highly catalytic activities for the production of hydrogen by water electrolysis and the reduction in the loading of expensive PGMs into
composite electrodes can be achieved using nanotechnology. Water electrolysis, using electrodes, is known to be an environmental friendly process. Meanwhile the preparation of the platinum nanophase composite electrode is not neutral in terms of carbon dioxide emissions. Life cycle inventory assessment and carbon footprint calculation were used to determine the overall equivalent carbon dioxide to producing such an electrode. The preparation of 119.23g platinum nanophase composite electrode counted approximately 8.78 kg CO2-eq.

In actual fact nearly all the equivalent carbon dioxide calculated by component was from due to the use of energy; though providing from energy mix source. Chemicals were the main direct emitting agents when used for synthesizing raw materials.

Airborne emissions and emissions to soil, which can be handled, were also identified.

The following palliative measures on energy used for each and every process involved would be:
A. The quantification of exact energy by achieving the development of standards in energy supply for precise processes under clear-cut conditions.
B. To look at friendly energy resources.

The two above palliative measures involved, are of major contribution at the industrial scale manufacturing of the platinum nanophase composite electrode. This approach may clarify the path towards sustainable development of efficiently and effectively produced hydrogen by water electrolysis.

Into the bargain, ways are to be found to minimize toxic contamination from the use of raw chemicals for environmental impacts of the processes used be optimized.

REFERENCES