Carbon Footprint Analysis in the Preparation of the Platinum Nanophase Electro Catalyst Composite Electrode

Junior Mabiza, and Charles Mbohwa

Abstract—A new approach in the use of PGMs for the highly catalytic activity in the production of hydrogen by water electrolysis, is to reduce PGMs into nanometer size (nanophase), then integrate them into electrodes. Water electrolysis is an environmental friendly process of producing hydrogen.

This study was for the cognition of likely impacts to environment with regard to the manufacturing process of the composite electrode. The Life Cycle Inventory Assessment method and the carbon footprint calculation in the preparation of the composite electrode were 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 footprints. Direct emissions were likely involved when heating, calcinating, drying materials. Palliative recommendations were suggested in accordance with the types of emissions identified.

Keywords—Platinum nanophase electrocatalyst composite electrodes, Electrolysis of water, LCIA, Carbon footprint

I. INTRODUCTION, OBJECTIVE AND METHODS

NANOPHASE electrode material for high electro catalytic electrolytic activities can be made of noble metals, which are predominantly platinum group metals (PGMs).

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. Arguing that the adoption of renewable energy systems 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 to be pertinent.

Junior Mabiza is with the University Of Johannesburg, P. O. Box 524, Auckland Park Kingsway Campus, Johannesburg (phone:+27788796283; e-mail: jmabiza2008@hotmail.fr).

Charles Mbohwa is with the University of Johannesburg, P. O. Box 524, Auckland Park Kingsway Campus, Johannesburg South Africa (e-mail: cmbohwa@uj.ac.za).

SPE electrolyzer as well as Electrolysis cell equipped with nanophase composite electrodes satisfies environmental sustainability requirements either at zero or insignificantly low GHG emission for the production of hydrogen by water electrolysis, which is a non-polluting process. It is therefore important to identify emissions, to estimate energy consumption, and to determine the overall carbon equivalent of chemicals used during the manufacturing process of nanophase electrodes with a view to finding the optimum environmentally sound and efficient process. This was approached by Life Cycle Assessment Inventory (ISO 14040 standard) [1], which allowed the calculation of the overall carbon footprint.

II. PREPARATION OF THE PLATINUM NANOPHASE COMPOSITE ELECTRODE

The preparation of the platinum nanophase composite electrode is critical for high catalytic activity, in producing the hydrogen by water electrolysis efficiently. In order to achieve this, high current densities would have to be created using low energy input. The electrodes would have to work effectively using low concentration electrolytes operating at low temperatures [2].

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

Hexagonal Mesoporous Silica (HMS) is a matrix of the kind needed to develop a nanoscale structure material [3].HMS is of great interest in the area of catalysis owing it 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.
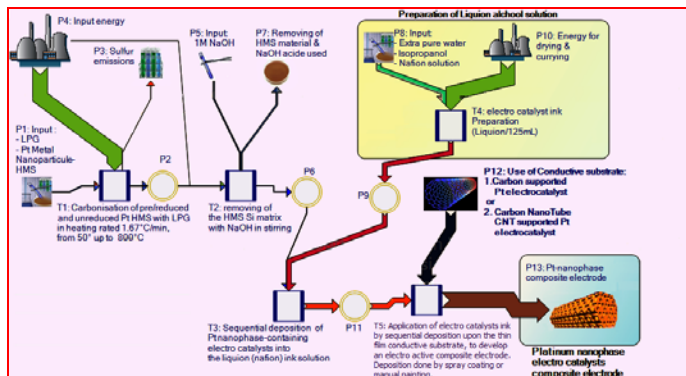
There have been some indication that chloroplatinic acid hexahydrate ($H_2PtCl_6.6H_2O$) can serve as a source of platinum. [2] This information was successfully used to prepare HMS-Pt by incipient wetness impregnation upon the mesoporous HMS matrix [2]. This is indicated in Figure 2 based on our assessment 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 carbonization with a low cost liquefied petroleum gas [2].

Fig. 1 The flow-material in the preparation of HMS material. (Developed using Umberto software)

Fig. 2 Flow-materials in the preparation of HMS-Pt. (Developed using Umberto software)

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 ($H_2PtCl_6.6H_2O$) as metal precursor and sulphuric acid (H_2SO_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.

Fig. 3: Flow materials in the preparation of Pt/C. (Developed using Umberto software)

Finally, 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].

Fig. 4 Flow materials in the preparation of the Pt nanophase composite electrode. (Developed using Umberto software)

IV. LIFE CYCLE INVENTORY ASSESSMENT AND CARBON FOOTPRINT CALCULATIONS

A. HMS Life Cycle Inventory Balance Sheet Results

TABLE I
HMS INPUT/OUTPUT BALANCE SHEET

HMS balance sheet was obtained through Umberto after the development of the flow material analysis in Figure 1. It summarizes all input and output materials and shows processes or transitions in which materials were involved through HMS preparation.

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 II
HMS CARBON FOOTPRINT SUMMARY

Table II 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

TABLE III
HMS CARBON FOOTPRINT: TOTAL DETAILS

The overall carbon footprint for preparing HMS was 3.24Kg CO_2-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

TABLE IV
HMS-PT CARBON FOOTPRINT SUMMARY

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 CO_2eq 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 ($H_2PtCl_6 \cdot 6H_2O$) and a pH-regulator either sulphuric acid (H_2SO_4) or sodium hydroxide (NaOH).

TABLE V
PT/C CARBON FOOTPRINT SUMMARY

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 (SO_X), carbon monoxide (CO), nitrogen oxides (NO_X) 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).

TABLE VI
PT NANOPHASE COMPOSITE ELECTRODE: CARBON FOOTPRINT SUMMARY

V. RECAPITULATION OF THE CARBON FOOTPRINT VALUES IN THE PROCESS OF PREPARING PLATINUM NANOPHASE COMPOSITE ELECTRODE
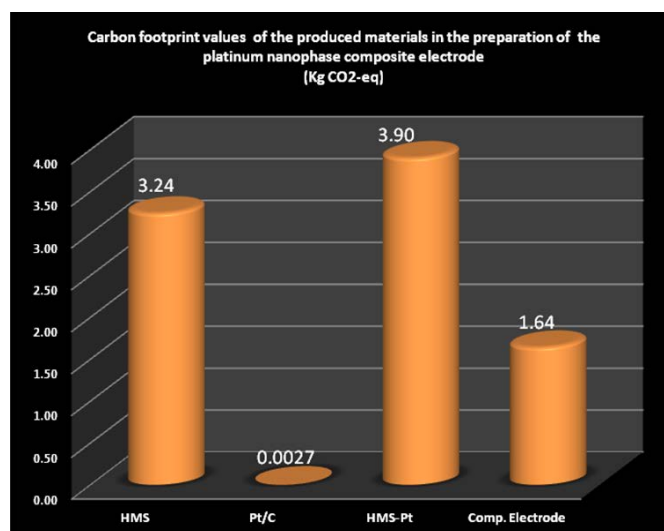

Fig. 5 Carbon footprint values of the produced materials in the preparation of the platinum nanophase composite electrode

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

A new approach in the use of PGMs for the highly catalytic activity in the production of hydrogen by water electrolysis, is to reduce PGMs into nanometre size (nanophase), then integrate them into electrodes. Water electrolysis is an environmental friendly process.

The preparation of the platinum nanophase composite electrode is not neutral to emissions at all. A life cycle inventory and carbon footprint analysis attempted to identify the overall carbon footprint in producing such electrodes. This provided, for the preparation of 119.23g platinum nanophase

composite electrode, approximately 8.78 kg CO_2-eq.

Nearly all carbon footprint measured came from significant amounts of energy mix used; though chemicals emitted as well. The following palliative measures on energy used for each and every process involved would be:

1) To quantify exact the energy by achieving standard data of the energy consumption
2) To look at friendly energy resources

The two above palliative measures involved, can help at industrial scale manufacturing. This approach may clarify the path towards sustainable development of efficiently produced hydrogen by water electrolysis.

Additionally, ways need to be found to minimize toxic contamination from use of raw chemicals if the environmental impact of the above processes is to be optimized.

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