Optimisation of Electrochemical Treatment of Artificial Wastewater using Cyclic Voltammetry

Anirudh B. T. Nelabhotla and Carlos Dinamarca

***Abstract*—Solar PV and wind turbine technologies are the prime sources of renewable energy and have rapidly increased their share in the total electricity production in the recent years. However, these technologies are highly dependent on nature and makes them an unreliable source of energy from an end-point perspective. Power to Gas (PtG) technology resolves this issue and provides an opportunity to convert these intermittent sources of energy into a more reliable one. With the processes of electrochemistry combined with methanogenesis PtG technology is able to provide a more reliable source of energy in the form gases (hydrogen or methane), that can be both stored and transported. This article discusses various electrochemical parameters such as voltage, current, electrode material, pH and temperature using cyclic voltammetry technique in order to select the best electrode material. Three electrode materials (platinized titanium mesh, carbon felt and graphite rod) are compared with each other for their electrochemical performances at 4 different pH and 6 different temperatures. The results show that carbon felt electrode material is the most efficient and inexpensive material for further research in the field of bioelectrochemical wastewater treatment.**

***Index Terms*—Cyclic voltammetry, hydrogen, microbial electrochemical cell, methane, wastewater.**

I. Introduction

There has been a rapid increase in the world renewable energy share, triggered in part by the staggering amount of research and engineering development in the field of sustainable energy supply. Especially in the renewable power sector, the non-hydro renewable electricity has increased by 17.3% in just 1 year (2015 to 2016). Solar PV and Wind power are the leaders in renewable power generation showing 32.9% and 12.7% increases in their respective capacities during the same year [1]. The increase in renewable electricity in some of the European countries have been such, that they have exceeded the demand of the electricity during certain days of the year. This is mainly due to the fluctuating nature of solar and wind power production systems as they are dependent on the dynamics of nature and remain irregular sources of renewable power [2]. In 2016, an estimated amount of about 30-60 GW of residual power was generated due to this intermittency in power production [3].

However, the world is still highly dependent on fossil fuels which have not seen any decline in their consumption over the years and thereby showing no decline in global CO_2 emissions. The IEA report states that approximately 32 Gt of CO_2 has been emitted for each of the 3 consecutive years from 2014 to 2016 [4]. Therefore, many researchers have shown interest in technologies which are able to harness the residual power to provide a more reliable and practical energy source and simultaneously be able to capture the industrial carbon emissions [5].

Power to Gas (PtG) technology is one such approach that has recently come into focus with the increase in available residual renewable power [3], [6]–[10]. PtG technology converts the excess renewable power into energy rich gases such as hydrogen and methane that can be integrated into the existing gas grids [2], [8], [11]–[13]. Electrochemical and bioelectrochemical treatment of wastewater are able to produce hydrogen [14], [15] and methane [16]–[18] respectively. Hydrogen can also be produced through bioelectrochemical methods but methane is often produced as a by-product and is preferred over hydrogen for other practical issues such as storage and transport [19]–[24].In this research article we explore non-precious and inexpensive electrode materials for the electrochemical treatment of artificial wastewater over various parameters in a single chamber electrochemical cell. The aim of the study was to optimise the working parameters and select the best electrode material combination for bioelectrochemical treatment of wastewater that is able to form biofilms and produce methane. The theoretical standard potentials required for electrolysis of water and bioelectrochemical treatment of wastewater can be defined with the following equations:

$$2H^+ + 2e^- \rightarrow H_2 \qquad E^\circ = -0.414 \text{ V}$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \qquad E^\circ = -0.244 \text{ V}$$

II. Materials and Methods

A. Artificial Wastewater (AWW) Preparation

An 135 mL reactor bottle was used as the electrochemical cell and filled with 120 mL of artificial wastewater made of [25] K_2HPO_4 $3H_2O$ 3.0 g/L, KH_2PO_4 11.8 g/L, $NaHCO_3$ 6.0 g/L, NaCl 1.0 g/L, NH_4Cl 1.0 g/L, $CaCl_2$ 0.2 g/L, $MgSO_4$ $\cdot 7H_2O$ 0.15 g/L, 10 mL/L of trace metal solution [26], and 10 mL/L of vitamin solution [27]. The pH of the solution was approximately 7 and the pH was changed using KOH pellets.

B. Electrode Preparation

Three different electrodes viz Platinum coated titanium mesh (Pt; 20 mm × 20 mm × 3 mm; Ti Shop, London, UK), Carbon felt (Fe; 20 mm × 20 mm × 3 mm; Alfa Aesar, Thermo

Manuscript received March 5, 2018; June 23, 2018. This work was supported in part by the Norwegian Research Council and University College of Southeast Norway.

The authors are with the Faculty of Technology, Natural and Maritime Sciences, University College of Southeast Norway, Porsgrunn, 3918, Norway (e-mail: anirudh.nelabhotla@usn.no, carlos.dinamarca@usn.no).

Fisher GmbH, 76057, Karlsruhe, Germany) and Graphite rod (Gr; 152 mm × 6.15 mm; Alfa Aesar, Thermo Fisher GmbH, 76057, Karlsruhe, Germany) were soaked in 1 M HCl for 24 hours followed by 1 M NaOH for 24 hours so as to remove all the contaminants [28]. An Ag/AgCl reference electrode with a standard potential of +0.199 mV vs SHE (Amel S.r.l., Milano, Italy) was used for the cyclic voltammetry experiments. All the voltages mentioned in the article are vs Ag/AgCl reference electrode.

C. Cyclic Voltammetry (CV)

The electrochemical cell was fitted with two electrodes at a time as Cathode-Anode: Pt-Pt, Pt-Fe and Pt-Gr along with the reference electrode. The electrode connections were made using Gamry Interface 1000 B Potentiostat (Gamry Instruments, Warminster, PA, USA). The cyclic voltammetry was run on these electrode pairs at 6 different temperatures viz. 30, 35, 40, 45, 50 and 55 ℃ and 4 different pH viz. 7, 7.5, 8 and 8.5. The CV ranges (the negative sign defines cathode and doesn't affect the magnitude of the voltage) for the different electrode combination were selected based on the electrochemical overload on the reactor and are tabulated (Table I). A scanning rate of 100 mV/s was applied for all CV experiments and were run in triplicates.

TABLE I: CV RANGES FOR DIFFERENT ELECTRODE COMBINATIONS

Electrode Combinations	CV range (V)
Pt-Pt	-1.000 to 1.000
Pt-Fe	-0.700 to 1.000
Pt-Gr	-0.700 to 1.000

III. RESULTS

A Cyclic voltammetry experiment is carried over a range of voltages to determine the voltage at which a particular electrochemical reaction occurs. The peak current of the CV curve and the corresponding voltage represent hydrogen production from artificial wastewater. The peak current and the corresponding voltages for all the temperatures and pH have been represented in the following Fig. 1-4. By comparing all the curves at different pH, it can observed, as general trend, that the peak currents decrease and voltages increase in their magnitude with the increase in pH (with a few exceptions). This could be due to the decrease in proton concentration, which is the reactant for the electrochemical reaction. Similarly, a general trend can be drawn on the effects of changing temperature, where the peak currents show an incline in their graph with the increase in temperature. This could be mainly due to the increase in ion movement within the electrolyte that increases the diffusion towards electrode and thereby the rate of reaction corresponding to the current generated. On the other hand, the voltages do not show a visible trend in their changes with increase in temperature.

Comparing the individual graphs and the electrode combinations: In Figure 1, i.e. the AWW at pH 7, the highest peak current of about 36.6 mA is observed for Pt-Fe at a voltage of -0.453 V and 45 ℃, however, it can be observed that at 50 ℃ a lesser peak current of about 35.9 mA occurs at a lesser voltage of -0.440 V. In Figure 2, even at a pH of 7.5 the Pt-Fe electrode combination was able to generate the highest peak current of about 36.3 mA at corresponding voltage of 0.514 V and a relatively high temperature of about 55 ℃. The effect of temperature on voltage is still to be investigated as there seems to be no particular pattern unlike current as mentioned previously. In figures 3 and 4 we can observe that the peak currents never cross 35 mA and the corresponding magnitudes of voltages are always above -0.450 V and -0.500 V respectively. These results suggest that the conditions set for the reactor are clearly unfavorable for the electrochemical reaction to be carried out.

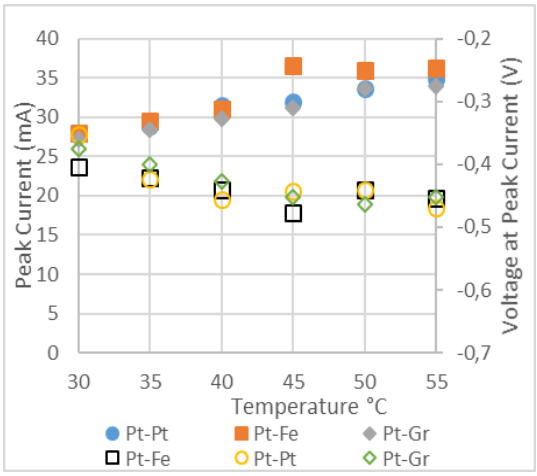

Fig. 1. Peak current (solid fills) and voltage (no fill and secondary axis) at peak current at different for CV of AWW at pH 7.

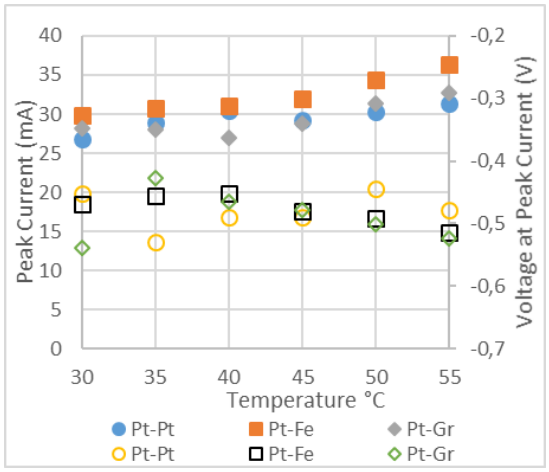

Fig. 2. Peak current (solid fills) and voltage (no fill and secondary axis) at peak current at different for CV of AWW at pH 7.5

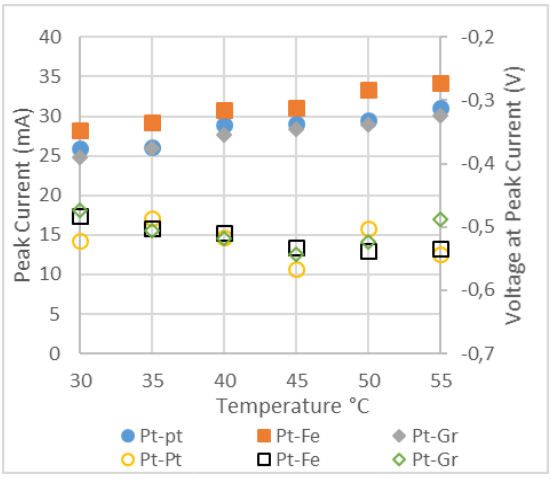

Fig. 3. Peak current (solid fills) and voltage (no fill and secondary axis) at peak current at different for CV of AWW at pH 8.

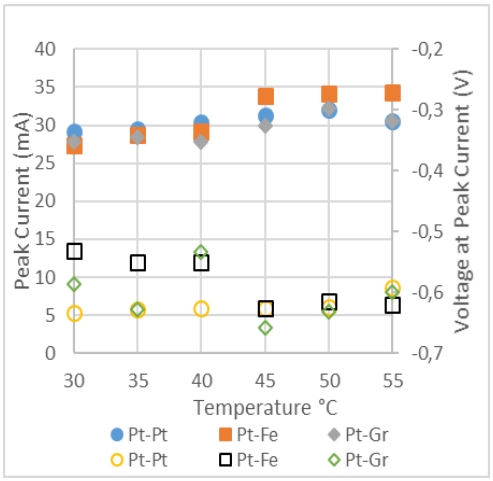

Fig. 4. Peak current (solid fills) and voltage (no fill and secondary axis) at peak current at different for CV of AWW at pH 8.5.

On observing all the figures it can stated that the electrode combination of Pt-Fe has been performing better than other electrode combinations in a consistent manner resulting in higher peak currents. Although the corresponding voltages do not reflect similar level of consistency they have been relatively low. Followed by the carbon felt electrode, the graphite electrode has performed comparable to the platinised platinum electrode. All the graphs evidently show most overlaps of peak current have occurred between Pt-Gr and Pt-Pt. Previous reports have suggested the use of carbon felt electrode as a bioanode and turned into biocathode for wastewater treatment in 2 chamber electrochemical cell [29]. Other researchers were able to use carbon felt as a biocathode for the production of acetate [30]. Similar reports on graphite rod have shown graphite as a cathode for methane production via electrochemical methanogenesis [31], [32].

IV. Conclusion

From the above results it can be said that the carbon felt electrode material at a temperature of 45 ℃ and a pH of 7 make up an optimized electrochemical reaction. The carbon felt electrode has "high surface area and porosity that is able to provide abundant redox reactions sites, excellent electrolytic efficiency and mechanical stability" [33]. It is very commonly used electrode material as it provides good electrical conductivity at a relatively low cost. Due to the above mentioned properties the authors have now started developing biofilm on the carbon felt material to operate a Single Chambered Microbial Electrochemical Cell (SCMEC) for wastewater treatment that can be integrated with existing Anaerobic Digestion plants.

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Anirudh Bhanu Teja Nelabhotla was born in India, in February 1992. He obtained his bachelors degree in biological sciences from Birla Institute of Technology and Science, Pilani, India. He then graduated from Newcastle University, UK with a masters degree in clean technoology. Currently, he is pursuing the PhD at the University College Southeast Norway (USN) on electrochemical unit integration with biogas production processes. His research interest lie in the field of chemical engineering combined with biological sciences with applications in wastewater treatment.

Carlos Dinamarca has a PhD in environmental biotechnology and is associate professor at the Department of Energy, Process and Environmental Technology USN, Porsgrunn. He has more than 20 years' experience in the fields of water chemistry and environmental technology both in industry and scientific research. His main research activity is in the field of anaerobic processes, were he has several publications. He is interested in syntrophic anaerobic phenomena, autotrophic metabolism and fermentation linked to practical applications.