Full communication

Electrochemistry for biofuels waste valorization: Vinasse as a reducing agent for Pt/C and its application to the electrolysis of glycerin and vinasse

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A B S T R A C T

Waste vinasse has been used, for the first time, as a reducing agent to prepare a 20 wt% Pt/C electrocatalyst. After alkalization and subsequent filtration, abundant cations such as Ca, Mg and Fe were effectively removed, precipitating as hydroxides and insoluble phosphates. Pt chemical reduction was carried out under reflux in the presence of Vulcan XC-72R carbon by the action of reductive species such as sugars and phenols present. Reduction was confirmed by thermal analysis and X-ray diffractograms displaying the typical Pt fcc structure formed by nanocrystals. In the transmission images, an irregular dispersion of the Pt nanoparticles was observed on the carbon support, with the presence of large agglomerations with a cotton-like structure. This structure was found to be very active for glycerol electrolysis in an alkaline membrane electrolysis cell, comparable to commercial materials. Finally, results for electrolysis of the vinasse were also presented, demonstrating the possibility of valorizing this residue by the production of hydrogen.

1. Introduction

Worldwide environmental concerns about the consequences of climate change are growing due to the increasingly evident effects on global weather. One proposal for diminishing these impacts is by reducing our dependence on fossil fuels. For this, renewable energy sources are successfully being explored, especially solar and wind energy. Nevertheless, one of the drawbacks of these sources is the mismatch between offer and demand. Energy vectors such as hydrogen can fill this gap, via generation in electrolyzers powered by surplus electricity from renewable energies. At peak demand, hydrogen can be used in fuel cells to produce electricity that would give support to the electrical network [1].

Hydrogen can be produced by different routes, among which electrolysis is of interest because, among other reasons, high purity H_2 is obtained [2]. In particular, electrolysis (or electroreforming) of organic compounds has emerged as an alternative due to the reduced energy requirements compared to water electrolysis [3]. This technology is more attractive if renewable fuels can be used, e.g., bioethanol [4] or glycerol [5]. Recent approaches have proposed the direct valorization of biomass wastes through the generation of hydrogen, from lignin [6,7], or other forms of native biomass [8,9]. Most of these electrolyzers are based on the application of the polymeric electrolyte membrane skeleton due to its compactness, the possibility of obtaining higher current densities, its higher gas purity and safer operation [10].

The complexity of the electrochemical reactions involved in these systems requires use of an electrocatalyst. This is conventionally formed by widely dispersed noble metal nanoparticles on a high surface area carbon support. Among the spectrum of noble metals, platinum-based (or pure Pt) materials are recognized as the most active [11]. Conventional preparation methods are based on chemical reduction by the action of chemicals such as formic acid, formaldehyde, sodium borohydride, hydrazine or polyols [12]. Some of these compounds are not environmentally innocuous. This has stimulated a growing interest in the development of green, eco-friendly and sustainable methods for the synthesis of Pt nanoparticles, including the utilization of plant extracts, algae, microorganisms, fungi, wood materials, among others [13]. Little effort has been devoted to the utilization of wastes as reducing agents. To the best of our knowledge, Coccia et al. [14] employed lignin to produce Pd and Pt nanoparticles. Baruwati and Varma obtained Au, Ag, Pd and Pt nanoparticles from grape pomace extract [15]. The reductive activity of these "eco-friendly" reducing agents is due to the presence of proteins, amines, amino acids, phenols, sugars, ketones, aldehydes, carboxylic acids and polyphenols [13].

Sugarcane vinasse may be a candidate as a reducing agent for a green and sustainable method for preparing Pt/C. Vinasse is the waste
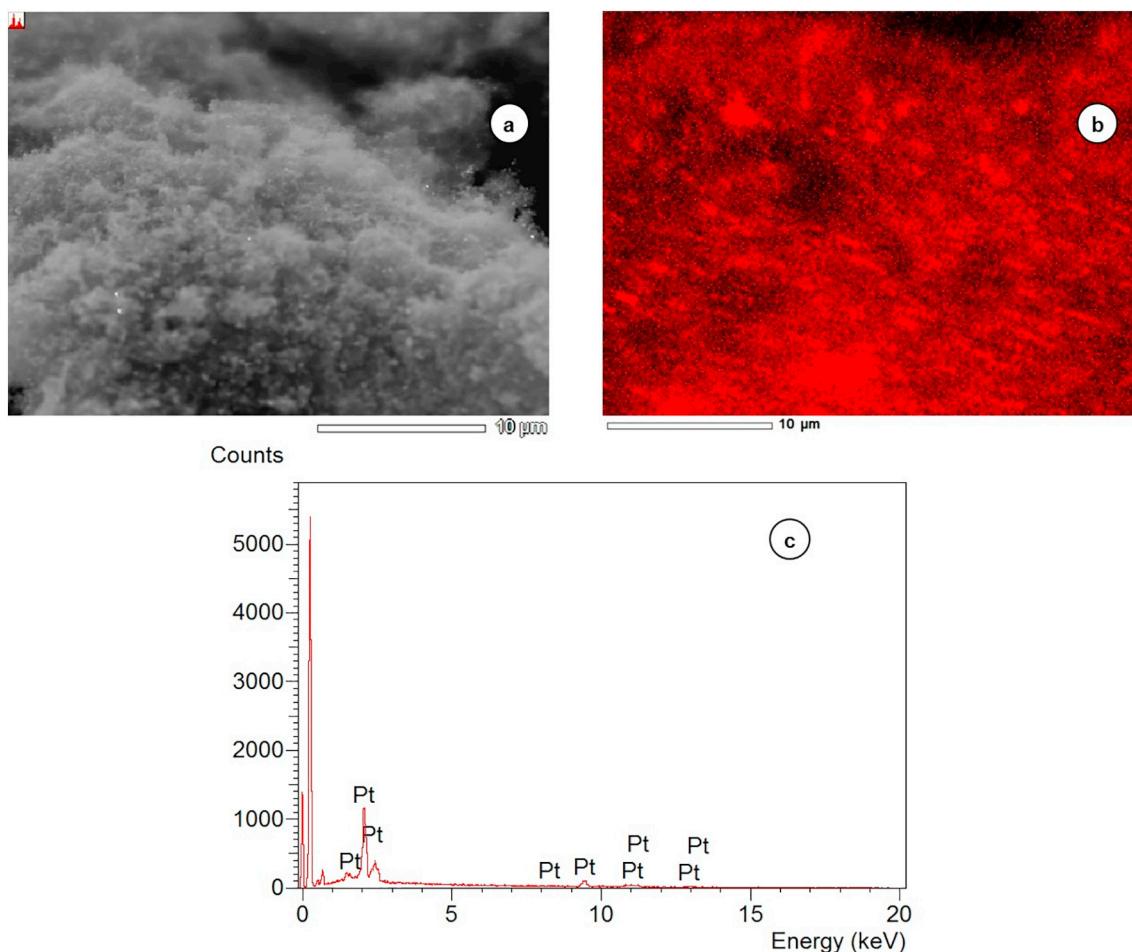
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Fig. 1. (a) SEM image of the electrocatalyst, (b) Pt EDX mapping and (c) the EDX spectrum of the vinasse-prepared 20 wt% Pt/C.

produced by the fermentation process in the sugarcane industry, and contains phenols, sugars, alcohols and short-chain organic acids. For each liter of ethanol produced, 13.7 L of vinasse are obtained and applied in soil fertirrigation [16]. However, the high organic and inorganic contents have raised concerns about the conservation of soils and aquifers, motivating the search for alternative applications. Thus, one of the aims of this study is, indeed, the utilization, for the first time, of waste vinasse for preparing Pt/C. After a pretreatment to reduce inorganic interferents, the prepared Pt/C was characterized physicochemically and applied, as the second objective of the study, in glycerol electrolysis. Glycerol is a byproduct of the generation of biodiesel, and is becoming increasingly valorized due to the significant rise in biodiesel production [17]. One possible means of glycerol valorization is electrochemical reforming to produce hydrogen, which can then be used for the hydrogenation of biodiesel [5]. Finally, the third goal of the study is to demonstrate the possibility of using the vinasse as a fuel in the electrolyzer.

2. Materials and methods

Sugarcane vinasse was kindly donated by the ethanol manufacturing plant Jalles Machado (city of Goianésia, Goiás, Brazil). Before using it as a reducing agent, a pretreatment consisting of alkalization and subsequent filtration was applied in order to remove the inorganic cations and anions as precipitates. The vinasse-prepared 20 wt% Pt on carbon black (Vulcan XC-72R, Cabot Corp.) was synthesized by chemical reduction with the supernatant. To prepare 250 mg of electrocatalyst, 200 mg of carbon black was dispersed in 150 mL of vinasse with the aid of ultrasound. Afterwards, the amount of platinum precursor

($H_2PtCl_6\cdot6H_2O$, Sigma Aldrich) required to deposit 50 mg of metal was also added. The reaction mixture was vigorously stirred and maintained under reflux conditions with the aid of a heating mantle for 4 h. Subsequently, the reaction medium was left to cool naturally and settle in order to facilitate filtration, carried out using filter paper (polyamide, 0.2 μm pore size, Sartorius). The obtained powder was thoroughly washed with distilled water and then with boiling ethanol in order to wash away any remaining organic and inorganic compounds. Finally, the catalyst was dried in an oven at 90 °C overnight, weighed and stored in closed amber glass vials until further use. Details of the characterization techniques are given in the Supplementary Information (SI).

The anode for the glycerol and vinasse electrolysis experiment was prepared from the vinasse-prepared and commercial 20 wt% Pt/C electrocatalyst. A catalytic slurry was prepared by mixing the required catalyst mass, a 10 wt% Nafion® (IonPower, USA) emulsion normalized with respect to the amount of carbon, and a mixture of 2-propanol (99%, Vetec, Brazil) and water as the solvent. The thick ink was applied directly by a paintbrush onto a carbon cloth diffusion layer (Zoltek, USA). The deposited metal loading was 2 mg cm^{-2}. In the case of the cathode, the procedure and materials were similar, with the exception of the metal loading (0.5 mg cm^{-2}) and the use of the commercial electrocatalyst, 20 wt% Pt/C (NovoCell). The electrodes were dried in an oven for 1 h at 80 °C. The active area of the electrodes was 4 cm^2. The alkaline membrane was a PBI film [Danish Power Systems (DPS, Denmark)] immersed for one week in 4 mol L^{-1} KOH (40 μm dry basis).

Single-cell electrolysis tests were carried out in an alkaline membrane electrolysis cell, AMEC. Fuel and comburent were supplied by peristaltic pumps (Exatta, Brazil), which allowed for precise regulation of the flow rate (1 mL min^{-1} for both streams). The anolyte was
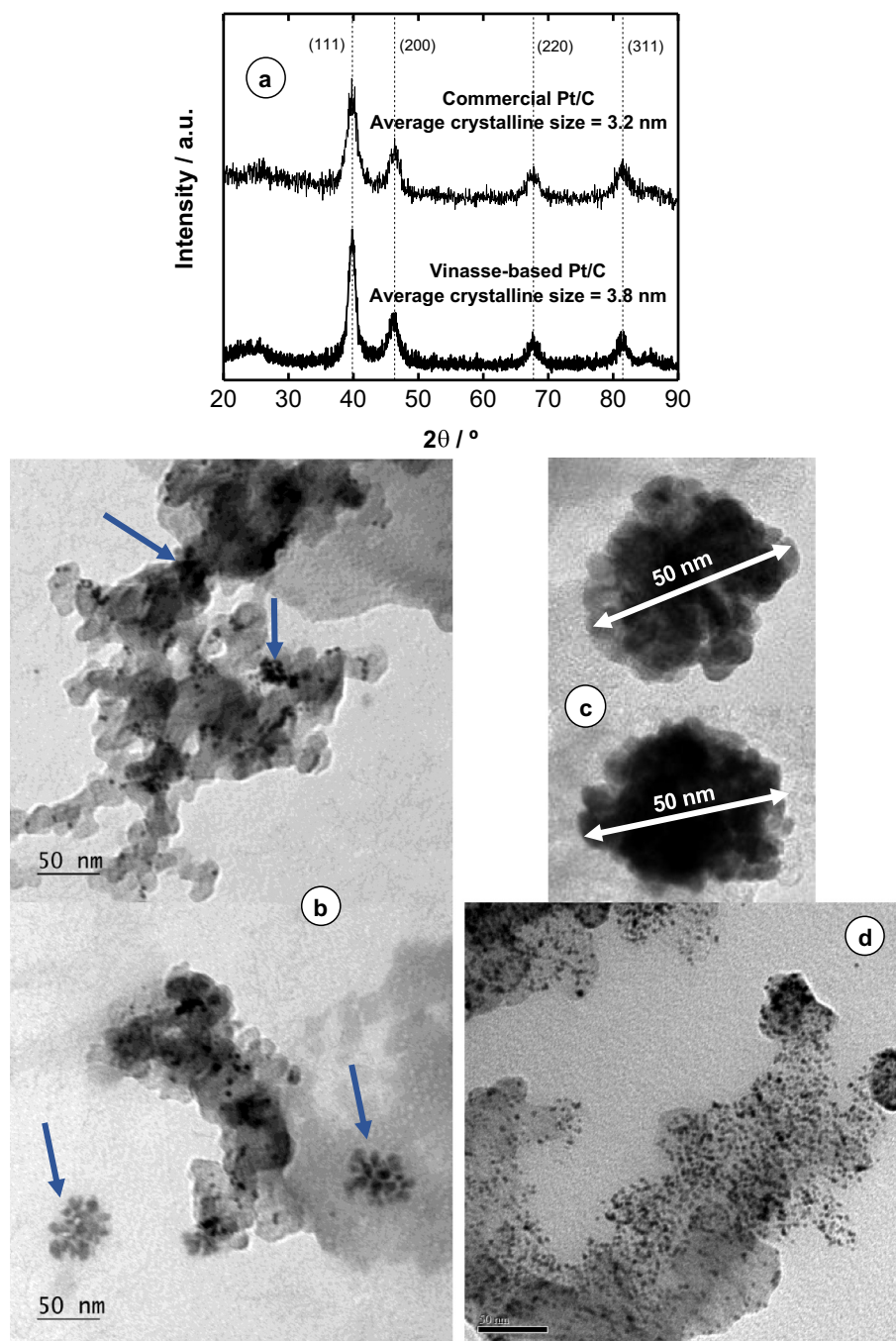
Fig. 2. (a) XRD patterns of vinasse-prepared and commercial Pt/C, (b) TEM images of the vinasse-prepared Pt/C, (c) closer micrography of the cotton-like Pt agglomerates formed in the vinasse-prepared Pt/C and (d) TEM images of the commercial Pt/C.

$1\,mol\,L^{-1}$ glycerol and $4\,mol\,L^{-1}$ KOH, while the catholyte was $2\,mol\,L^{-1}$ KOH, corresponding to the values optimized in a previous study [5]. Polarization curves were recorded with the aid of an AU-TOLAB PGSTAT 302 N potentiostat/galvanostat (Metrohm Autolab BV, The Netherlands) in linear sweep voltammetry mode, from 0.0 to 1.0 V at a scan rate of $0.2\,mV\,s^{-1}$. The glycerol used in the AMEC was derived from biodiesel synthesis, purified as described elsewhere [18]. More details of the experimental setup can be found elsewhere [5].

3. Results and discussion

Table S1 and Fig. S1 compare the parameters and the physical aspects of the raw and treated vinasse. After the alkalization and filtration

steps, a notable decrease in the values of some of the cations and anions present in the vinasse was observed, especially orthophosphate, calcium, magnesium and iron. Based on the appearance of flocs, we speculated that insoluble hydroxides and phosphates had formed. The removal of inorganic species was confirmed by the elemental analysis of the solid flocs, shown in Table S2. The filtered basified vinasse was then used as a solvent and reducing agent for preparing the Pt/C electrocatalyst. To confirm the deposition and absence of inorganic impurities on the vinasse-prepared Pt/C, Fig. 1 shows the corresponding EDX spectrum of the prepared material, as well as the mapping of Pt on one selected surface over several points selected for EDX analysis. As can be observed, only Pt and C were detected in the EDX analysis, confirming the absence of inorganic impurities. Fig. 1b shows that Pt was relatively
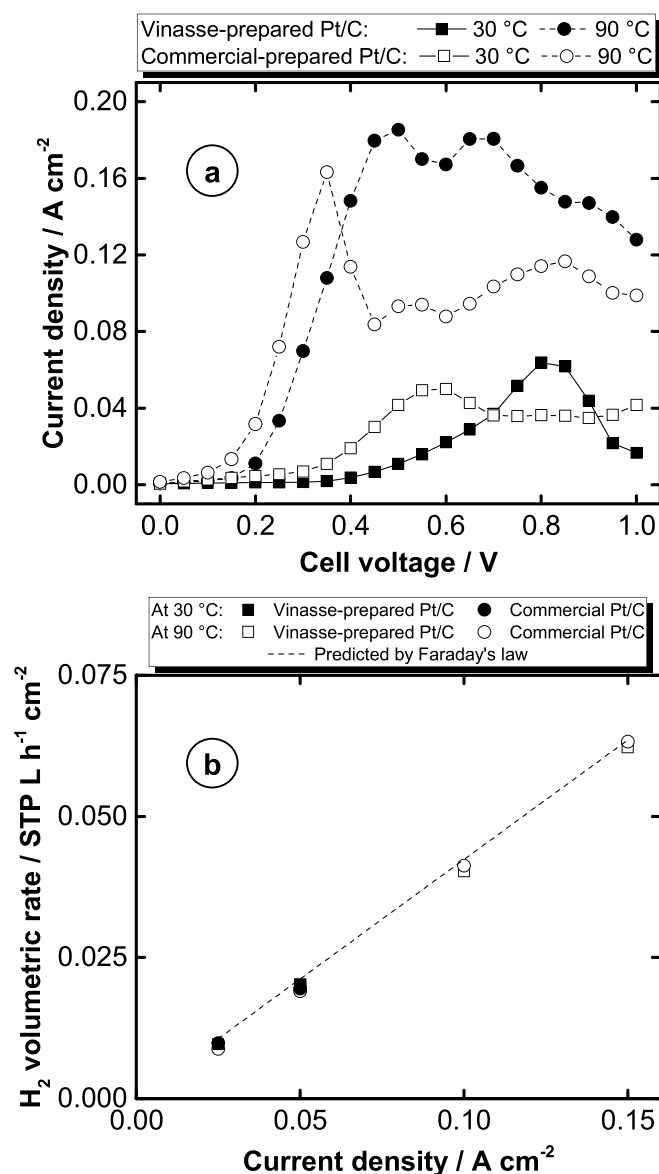
Fig. 3. (a) Polarization curves of purified waste glycerol in the AMEC at different temperatures and (b) hydrogen volumetric rate produced in the electrolysis.

No peaks corresponding to other crystalline facets were found. By application of Scherrer's equation, an average crystal size of 3.8 nm was found, slightly larger than that in commercial Pt/C (3.2 nm), evidencing the formation of crystallites in the nanometric range. Fig. 2b and c display transmission electron micrographs of the vinasse-prepared Pt/C electrocatalyst. The TEM images show a heterogenous particle size distribution, from small nanoparticles to large agglomerations (see arrows in Fig. 2b). Interestingly, the large agglomerations of nanocrystals acquired the form of a *cotton-like* structure formed by small nanocrystals with abundant Pt (111) facets (Fig. 2c and high resolution TEM micrograph in Fig. S3). This nanostructure is completely different to the homogeneous Pt nanoparticles deposited on carbon seen for commercial Pt/C (Fig. 2d). The observed irregular particle size distribution of the vinasse-prepared Pt/C might be explained by the different reducing agents present. While simple sugars could promote the formation of smaller particles, large phenol molecules, with several "reducing active sites" in their structure, might favor the agglomeration of Pt nanoparticles. Moreover, phenols might also provide a template structure for the cotton-like architecture.

In order to study the electrochemical activity of the Pt/C derived from vinasse and test its suitability for hydrogen production from purified waste glycerol, Fig. 3a shows polarization curves obtained at different temperatures for the vinasse-prepared and commercial (reference) Pt/C in the AMEC (blank voltammograms are described and discussed in the SI, Fig. S4). A smaller onset potential is displayed by the commercial electrocatalyst. The smaller and more dispersed Pt nanoparticles of the commercial Pt/C are expected to interact more actively with the carbon support, the source of oxygenated species whose role is crucial in glycerol electrooxidation [20]. Another possible explanation may lie in the apparent abundance of Pt (111) domains in the vinasse-prepared Pt/C, which are known to possess a higher onset potential for the formation of Pt-OH$_{ads}$ species [21]. In terms of maximum current, the vinasse-prepared Pt/C showed remarkable performance in glycerol electrolysis, attaining higher maximum currents. Based on surface area availability (Table S3), commercial Pt/C should have outperformed vinasse-prepared Pt/C. In order to explain this result, it is necessary to take into account the importance of effective mass transport of glycerol towards active sites and the release of oxidized products in attaining maximum performance [22]. In the case of the commercial Pt/C, a fraction of small nanoparticles was expected to be in the small pores of the carbon support. Impaired mass transport could result in the rapid deactivation/blocking of Pt active sites, thereby reducing the utilization of the Pt surface. In the case of the vinasse-prepared Pt/C, the existence of a considerable proportion of larger particles may have reduced the amount of Pt particles occluded in the nanopores of the carbon structure, resulting in a more favorable catalyst architecture for mass transport. This type of particle nanostructure has already demonstrated enhanced intrinsic mass transport [23], and, more interestingly, activity for glycerol electrooxidation [24]. Such mass transfer limitations are responsible for the limitations in the current density, followed by a decrease in this parameter. This decrease could be attributed to the poisoning of the catalytic sites by covering with OH$_{ads}$ species and the buildup of strongly adsorbed oxidation products [25]. Fig. 3b displays the volumetric production rates of hydrogen in the glycerol AMEC. As can be observed, the experimental rates fitted well to those predicted by Faraday's law, confirming the feasibility of the system even when vinasse-prepared Pt/C catalyst was used. The results presented here show, for the first time, the possibility
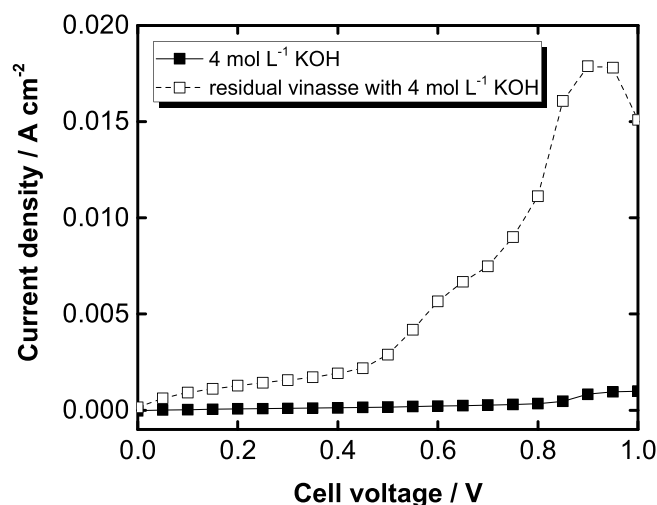
well distributed on the carbon surface. Moreover, a Pt mass percentage of 20 wt% was confirmed. Further confirmation of the 20 wt% metallic loading was provided by thermal analysis (Fig. S2). To investigate the species responsible for the reductive capacity of vinasse, Table 1 shows the total polyphenol and reductive sugar concentrations. As can be observed, reducing sugars and phenols are consumed during the Pt reduction process, confirming their role as reducing agents (both species are known for their antioxidant power [19]). Complete removal of reducing sugars was achieved, whereas the amount of polyphenols was reduced to 66%.

Fig. 2a displays the diffractogram of the vinasse-prepared and commercial Pt/C. Typical metallic fcc Pt diffraction peaks are observed.

Table 1
Total polyphenols and reducing sugar contents before and after the preparation of 250 mg of 20 wt% vinasse-prepared Pt/C (GAE: gallic acid equivalent).

	Basified vinasse – before preparation of Pt/C	Basified vinasse – after preparation of Pt/C
Total phenols content/mg GAE L^{-1}	259.3	156.7
Total reducing sugars/equivalent mg glucose L^{-1}	77.7	Not detected

Fig. 4. Electrolysis curves in the AMEC for $4\,mol\,L^{-1}$ KOH and residual vinasse in $4\,mol\,L^{-1}$ KOH at 90 °C with the vinasse-prepared Pt/C electrocatalyst.

of coupling the valorization of the two main by-products of the biofuel industry, i.e. vinasse from the production of ethanol from sugarcane and glycerol from the production of biodiesel. This hydrogen could be used in situ to hydrogenate biodiesel in order to help to solve one of the main limitations of biodiesel, its stability to oxidation [26].

A final test was carried out in order to verify the possibility of using the alkaline vinasse as a fuel in an electrolysis device with the vinasse-prepared Pt/C as anodic catalyst. The results are presented in Fig. 4. Despite the relatively poor performance observed for the oxidation of a more complex substrate such as vinasse, the results show that this residue might potentially be used for in situ generation of hydrogen at sugarcane facilities. The utilization of this commodity could lead to energy gains in the sugarcane industry, as already demonstrated by Silveira et al. [27].

4. Conclusions

Residual vinasse from the sugarcane industry can be used as a reducing agent for the preparation of a Pt/C electrocatalyst, due to the action of reducing compounds such as sugars and phenols. Successful deposition of Pt particles on the carbon support with the formation of nanosized Pt crystals was achieved. However, some nanocrystals agglomerated, forming large cotton-like Pt particles. Despite this, vinasse-prepared Pt/C, when tested in a single-cell AMEC, demonstrated excellent performance compared to commercial Pt/C for waste glycerol electrolysis, producing hydrogen. Finally, the vinasse-prepared Pt/C was found to be active for the electrolysis of the vinasse. Thus, this study combines the utilization of a valueless vinasse residue for the preparation of Pt/C with the valorization of glycerol, a by-product of the biodiesel industry, as well as vinasse, through the generation of H_2 by electrochemical reforming.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.elecom.2019.03.012.

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