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Conversion of nitrogen to ammonia using a Cu/C electrocatalyst in a polymeric electrolyte reactor

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ABSTRACT

The electrochemical conversion of N_2 to NH_3 using a polymeric electrolyte reactor is a promising method to accelerate the green production of hydrogen carriers. On this basis, we report the efficiency of ammonia production by the nitrogen reduction reaction using a Cu/C catalyst in a polymeric electrolyte membrane reactor. The Cu/C catalyst was prepared by the $NaBH_4$ reduction method and characterized by X-ray diffraction, transmission electron microscopy, cyclic voltammetry, and conversion experiments performed in a polymer electrolyte membrane fuel cell type reactor. The X-ray diffraction results showed the presence of CuO_2 and carbon phases, while the TEM images showed a high agglomeration of copper nanoparticles on carbon. The onset potential of nitrogen reduction was near to the Cu (I) to Cu^0 reduction peak. Mass spectroscopy was used to observe the production of N_2H_2 and NH_3 and the consumption of N_2. Maximum ammonia production was detected at 0.0 V with a NH_3 yield rate of 38.4 μg h^{-1} cm^{-2} and a faradaic efficiency of 42.57 %.

1. Introduction

Due to the increasing interest in routes to decarbonization, researchers have recently turned their attention to the use of ammonia in fuel cells [1], highlighting the fact that this gas is an abundant source of protons but does not release carbon into the atmosphere. If research initiatives in commercial direct ammonia fuel cells are successful, the demand for ammonia will increase. This gas is currently predominantly produced by thermal processes [2], with large amounts of energy being dispersed without useful work.

Electrochemical reactions dissipate less energy, because the process occurs through electron–nucleus interactions. In this regard, there are groups studying the electrochemistry of the nitrogen reduction reaction (NRR), with two main aims: (i) the production of an important input for industry and a potential fuel of the future; and (ii) the storage of hydrogen in a molecule that can be easily diluted in water and transported in a safer and cheaper way than hydrogen itself [3,4].

The first studies on the NRR were based on catalysts such as Pt, Au, Ag, Ru, and several other transition metals [5]. Copper has been studied due to its low cost and excellent catalytic performance in applications such as oxygen and CO_2 reduction, where the oxides can adsorb hydrogen molecules, thus facilitating the hydrogenation of these species [6,7]. The NRR activity of Cu, however, is low, so various strategies have been employed to boost its catalytic activity, including the use of electron-deficient Cu nanoparticles [5] and electrodeposited dendritic Cu [8].

The synthesis of ammonia by conventional electrochemical methods has the disadvantage of generating a product contaminated with the electrolyte needed for the electrochemical circuit. In addition, the low solubility of nitrogen in aqueous media requires a purification step and the onset potential of nitrogen reduction is very close to the onset of hydrogen evolution, making it difficult for N_2 to access the catalytic sites on the electrode [8]. The advantages of using a proton exchange fuel cell architecture suitable for the electrochemical reaction of gaseous reactants (H_2 and O_2) for ammonia production, compared to conventional methods, are that it facilitates access to the electrode catalytic sites, and produces ammonia with no electrolyte contamination. The anode oxidizes H_2, providing protons, while the NRR occurs at the cathode, generating ammonia as the output [9]. This work presents a study of this type of reaction, with the conversion of N_2 and H_2 into ammonia under ambient temperature and pressure conditions in a fuel cell polymeric electrolyte reactor using a Cu/C catalyst for the NRR.

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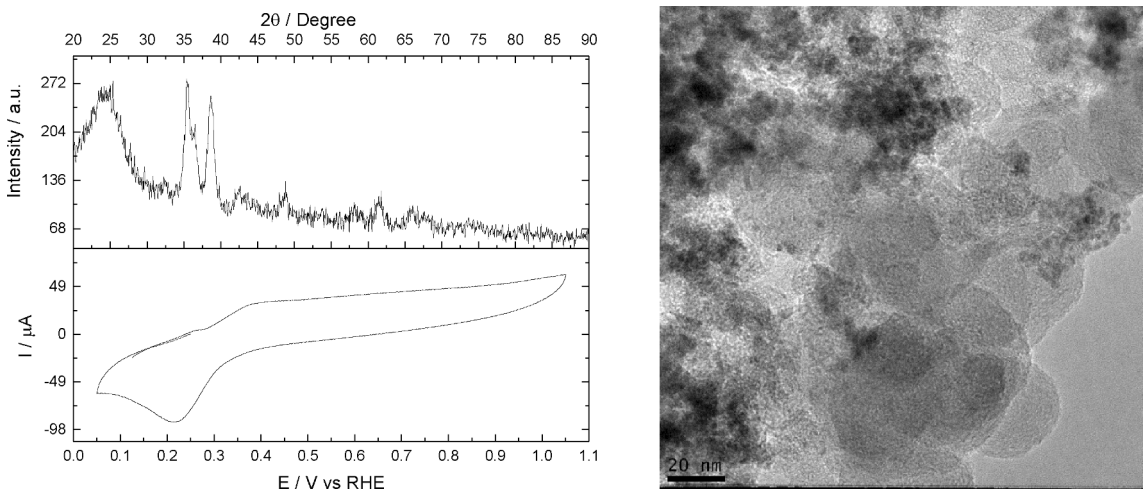

Fig. 1. (a) X-ray diffractogram of Cu/C at 2° min^{-1} (2θ = 20° to 90°). (b) Cyclic voltammetry of Cu/C in 0.1 mol/L H_2SO_4; (c) TEM image of the Cu/C catalyst prepared by the $NaBH_4$ reduction process.

2. Experimental

Copper supported on carbon was prepared in a ratio of 20 % (m/m) of the metallic load at the Carbon Vulcan XC72 electrocatalyst by the reduction of $CuCl_2{\cdot}2H_2O$ (Aldrich) salt using $NaBH_4$. In this method, the carbon was dispersed in a solution containing the Cu salt. This solution was sonicated for 10 min, and then $NaBH_4$ in alkaline solution (ratio 5:1 $NaBH_4$: metal ions in NaOH 1 mol/L) was added to the catalyst vessel. After 1 h under stirring the suspension was filtered, washed with ultrapure water, and dried at 70 °C for 2 h [10].

The electrocatalyst was characterized by X-ray diffraction performed on a Rigaku Miniflex II with CuKα radiation source in a 2θ scan range from 20° to 90° at 2° min^{-1}. The electron microscopy images were obtained using a transmission electron microscope (TEM) model JEM-2100 operated at 200 keV. The voltammetry studies were carried out in an Autolab PGSTAT 30 potentiostat/galvanostat in 0.5 mol/L H_2SO_4 in a conventional electrochemical cell.

Glassy carbon (GC) was used as a support for the working electrodes with a geometric area of 0.071 cm^2. A Pt sheet was used as the counter electrode and a reversible hydrogen electrode as the reference. The working electrodes were constructed by dispersing 8 mg of electrocatalyst in 1 mL water and 20 μl of Nafion® solution (5 %), sonicated for 15 min. Aliquots of 20 μl of the dispersion were pipetted onto the glassy carbon support surface and dried. Throughout the experiments, the solution was constantly saturated with N_2 (gas).

The conversion experiments were performed in a polymer electrolyte membrane reactor fuel cell (PER-FC), with a cathode composed of a diffuse layer and a catalytic layer of 1 mg copper cm^{-2}, applied by painting a mixture of the catalyst, Nafion solution (5 %) and isopropyl alcohol. The anode was prepared using a similar procedure, replacing Cu/C by Pt/C (Basf ®). The linear sweep voltammetry and chronoamperometry experiments were performed using an Autolab PGSTAT 302 N potentiostat with a current booster. The unit cell with stainless steel plates for serpentine fuel delivered electrical work as a reactor. The dry N_2 flow at the cathode was 50 mL min^{-1} at 25 °C while at the anode the flow delivery was 50 mL min^{-1} of H_2 humidified in a bottle heated to a temperature of 85 °C on the anode.

The polymeric electrolyte reactor experiments were assisted by online differential mass spectroscopy (DMS) coupled to the reactor's cathodic outlet, as described in previously published work [11]. The products of the cathodic reaction were also collected for 300 s in vials with 1 mL of water at increments of 200 mV. HPLC (YL9100) with a UV/vis detector at a wavelength of 420 nm was employed to analyze the products, in a 0.5 mL min^{-1} flux of water (95 %) and acetonitrile (5 %) isocratic run in a C18 column (Phenomenex Luna 5 μm, 250 × 4.6 mm). The calibration curve followed the equation: Intensity = 0.019 + 0.012 [ammonia].

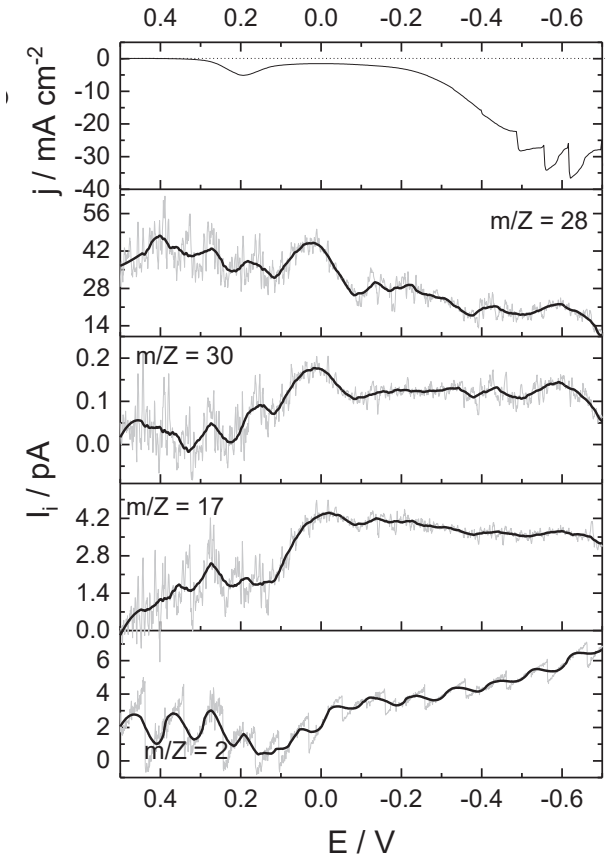

Fig. 2. Electrochemical N_2 reduction reaction at the Cu/C cathode at room temperature in the PER-FC with $\nu = 1$ mV s^{-1}, and the ionic currents measured for *m/z* 28, 30, 17 and 2 (the black lines show a 2-order polynomial regression).

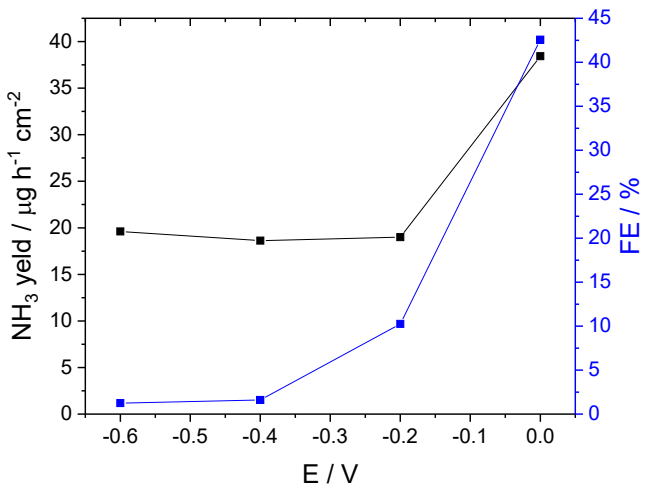

Fig. 3. NH_3 formation rate and faradaic efficiency (FE) at different potentials on Cu/C.

3. Results and discussion

Fig. 1 shows the physical characterization of Cu/C material. The X-ray diffraction study (a) revealed the presence of peaks at ~ 35°, 46° and 63°, corresponding to the (1 1 1), (2 0 2) and (1 1 3) planes of CuO (JCPDS # 45–0937). The reflections of CuO_2 (JCPDS # 05–0667) were also observed at ~ 36° (1 1 1), ~39° (2 0 0) and ~ 62° (2 2 0). The carbon support (JCPDS # 50–926) was identified by the peak at ~ 25° (0 0 2). In the cyclic voltammograms (b) an oxidation peak was observed at 0.35 V and a reduction peak at 0.22 V, related to the redox pair Cu^0/Cu^+ as reported by Amayreh et al. [12]. The TEM micrograph (c) show the high agglomeration of copper nanoparticles on carbon, in agreement with the results of the Cu/C preparation method reported by Lima et al. [13] and Godoi et al. [10].

Fig. 2 shows the *j/V* curves for the polymer electrolyte reactor fuel cell (PER-FC) during the nitrogen reduction reaction. It can be seen that the current at more positive potentials is approximately 0 mA cm^{-2}, and as the measurement goes on to more negative potentials, a reduction peak was observed at ~ 0.2 V, probably associated with the reduction of copper, as observed in the cyclic voltammetry (Fig. 1b). This peak is not associated with the nitrogen reduction process as shown by the unaltered trends observed in the ionic currents detected by DMS.

However, this reductive process seems to hide the onset potential of nitrogen reduction in this reactor, since it can be set at ~ 0.1 V, due to the large variations in I_i associated with the m/z values 17, 28 and 30, corresponding respectively to NH_3, N_2 and N_2H_2. In the literature the N_2 reduction onset potential reported in different media is about −0.2 V and 0.1 V [4,14]. For $m/z = 28$, there is a decrease in current with decreasing potential, indicating the consumption of nitrogen, while for $m/z = 17$ and 30 there is an increase in I_i, with maximum NH_3 and N_2H_2 production observed at close to ~ -0.05 V.

In the literature [4] the formation of N_2H_2 is reported as a step in the reduction of N_2 to ammonia, as less energy is required for its formation. However, when observing the I_i for H_2 ($m/z = 2$), it was noted that this follows the $|j|$ of the *j/V* curve, indicating that the excess of protons delivered in the cathodic catalytic layer probably favors the formation of N_2H_2.

The dependence of ammonia production on potential is shown in Fig. 3. At −0.4 V the NH_3 yield rate and FE values were close to those reported by Lin et al. [5], and obtained by linear sweep voltammetry measurements using electron-deficient Cu nanoparticles. The highest ammonia production occurred at 0.0 V with a NH_3 yield rate of 38.4 μg h^{-1} cm^{-2} and a faradaic efficiency (FE) of 42.57 %. These values are considerably higher than the highest values of NH_3 yield rate and FE reported by Lin et al. [5], 17.2 μg h^{-1} cm^{-2} and 6.56 %, respectively, demonstrating the effectiveness of the use of Cu nanoparticles as the NRR catalyst in a PER-FC. At more negative potentials, the ammonia production decreased considerably, with a NH_3 yield rate around ~ 18 μg h^{-1} cm^{-2}, confirming the results of DMS measurements.

It is also noted that the faradaic efficiency drops as the potential decreases, probably linked to the incomplete reduction of nitrogen and the recombination of protons to form H_2. This experimental setup produces faradaic efficiency and NH_3 yield rates comparable to the best results in the literature obtained using other kinds of reactors [4,14]. This setup circumvents the limitations of aqueous electrolytes, including low gas solubility, product contamination, and flow operation, reducing the negative effect of hydrogen evolution.

4. Conclusion

The nitrogen reduction reaction over carbon-supported Cu nanoparticles in a polymeric electrolyte reactor type fuel cell at ambient conditions produced a very high NH_3 yield rate and FE. The highest values of the NH_3 yield rate and FE were observed at 0.0 V, 38.4 μg h^{-1} cm^{-2} and 42.57 %, respectively, and are comparable to the best results reported in other kinds of reactors, and higher than those obtained using electron-deficient Cu nanoparticles, attesting to the effectiveness of the PER-FC architecture combined with Cu nanoparticles. The faradaic efficiency decreased at more negative potentials due to the incomplete reduction of nitrogen to N_2H_2 and the recombination to H_2 of protons transported by the Nafion membrane to the cathode chamber.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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