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# Assesing mass and charge balance over time in urea electrooxidation reaction over modified electrodes with Fourier Transform Spectroscopy

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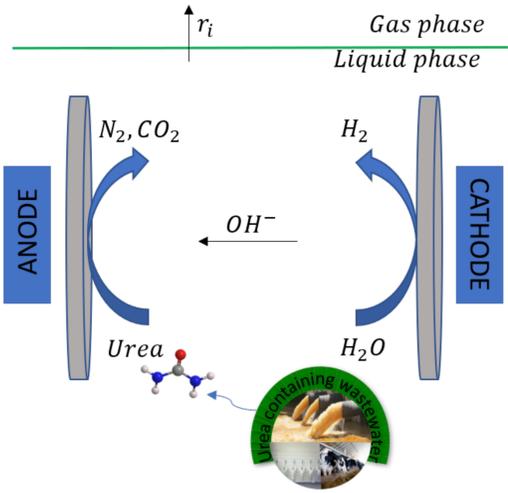
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## Graphical Abstract

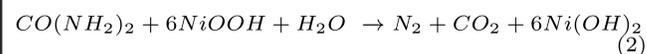


## Introduction

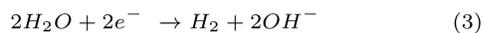
- Hydrogen ( $H_2$ ) is a key energy vector for clean mobility and industry decarbonization.
- Urea-containing wastewater electrolysis for  $H_2$  production requires less energy than water electrolysis.
- In this work, liquid and gas phase were monitored during urea long-term electrolysis in order to assess mass and charge balance.
- An electrochemical H-type cell divided by a proton exchange membrane was used to unveil the effect of the evolution of  $OH^-$  ions on urea electrooxidation.

## Reactions

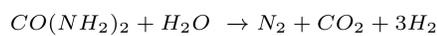
At the anode:



At the cathode:



Overall:



## Methodology

- Liquid phase was monitored using Fourier Transform Spectroscopy.
- The gas phase concentration was monitored using Gas Chromatography connected directly to the reactor.
- The gas rate production was measured indirectly using the rate of change of pressure in the reactor.

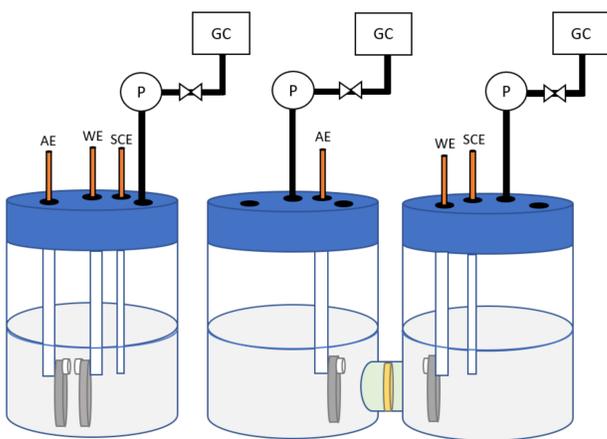


Figure 1: Schematic representation of the set up used for long-term electrolysis experiments.

$$r_i = \frac{V}{RT} \frac{dP_i}{dt}; \quad r_i^{th} = \frac{dQ/dt}{zF}; \quad \eta_i = r_i / r_i^{th}$$

## References

B. K. Boggs, R. L. King, and G. G. Botte, "Urea electrolysis: Direct hydrogen production from urine," Chem. Commun., no. 32, pp. 4859–4861, 2009, doi: 10.1039/b905974a.

## Acknowledgements

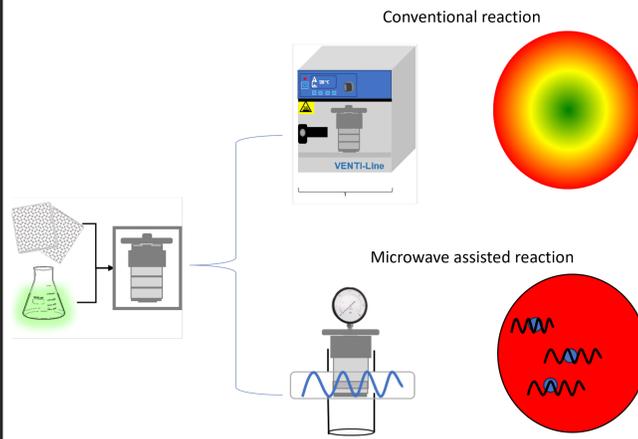
We thank Ministry of High Education and Technology of Dominican Republic (MESCYT) for the financial support.

## Hydrothermal synthesis

Different  $Ni_{0.8}M_{0.2}$  bimetallic electrodes were synthesized by conventional hydrothermal reaction and microwave-assisted hydrothermal reaction.

Synthesis conditions:

- For conventional heating: 120 °C, 10 h.
- For microwave heating: 120 °C, 1 h.



## Characterisation

In Fig. 2 a and b are the SEM images of a pristine nickel foam surface and a modified surface of  $Ni_{0.8}Co_{0.2}$  by microwave radiation, respectively. In general, the microwave synthesized electrodes have shown an increased Double layer capacitance (Cdl) (and therefore of ECSA) with respect to the electrodes synthesized by conventional heating (Fig.1 d). All modified electrodes show good wettability unlike the highly hydrophobic nickel foam surface (Fig. 1 c).

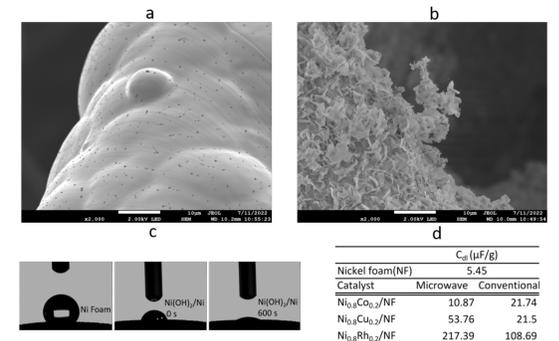


Figure 2: a),b) SEM images of a pristine and a modified electrode, c) droplet test of a pristine nickel foam and  $Ni(OH)_2/NF$ . d) double layer capacitance of synthesised electrodes.

## Conclusions 1

- Microwave assisted hydrothermal reactions is around 10x faster than conventional heating.
- The reaction medium and nanoparticles distribution is more homogeneous when performed using microwave heating.
- Higher double layer capacitance (hence, ECSA) was observed for electrodes synthesised by microwave radiation.

## Evolution of the gas and liquid phase during urea electrolysis

In Fig.3 FTIR spectra provide a visual representation of the liquid phase ( $C_{urea}=0.3M$  in KOH 1 M electrolyte) at different times during electrolysis at 1500 mV vs RHE on a nickel foam electrode. In general, the spectra show a noticeable change in chemical composition. For the non-separated compartments in Fig. 3, an unexpected  $OH^-$  affected peak reduction is observed, probably due to the formation of  $Ni(OH)_2$  at the anode, which has an effect on the efficiency. For the divided reactor experiment, the  $OH^-$  affected peak decrease sharply during the reaction, after 48h this peak is not longer detected, at which point the reaction has stopped.

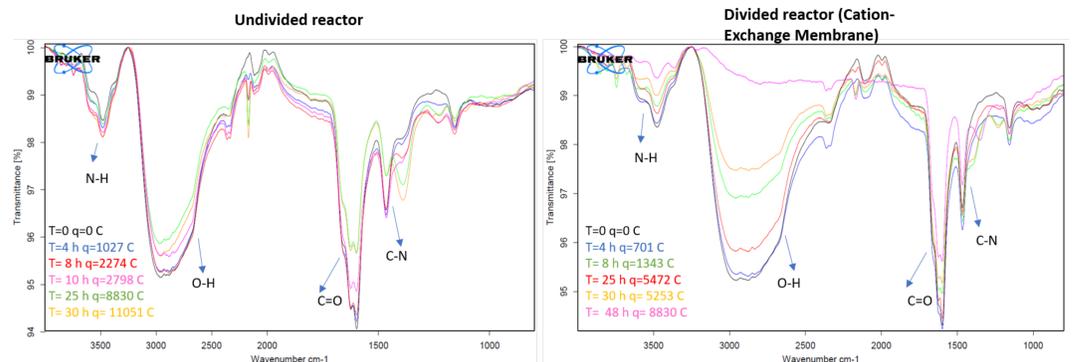


Figure 3: FTIR spectra of the liquid phase during urea electrolysis.

Figure 4 shows the gas rate during urea electrolysis. In contrast to other articles  $CO$  and  $CO_2$  were detected during urea electrolysis.  $CO$  rate was higher than  $CO_2$  in the gas phase, however, is well know that  $CO_2$  reacts in  $KOH$  solution forming  $K_2CO_3$ . The ratio  $r_{H_2}/r_{N_2}$  decreased with time, probably due to secondary reactions that arise as the urea concentration decreases in the liquid phase.

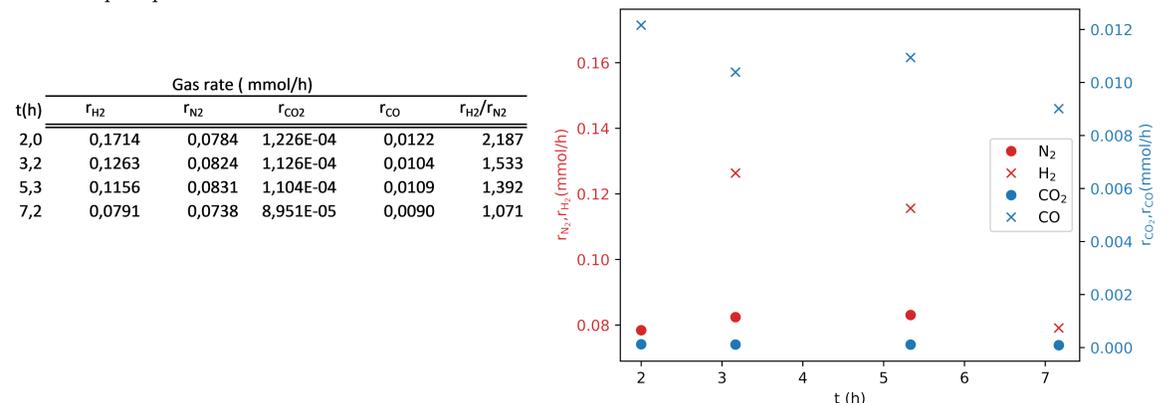


Figure 4: Gas rate during urea electrolysis.

## Conclusions 2

- The gas phase during the electrolysis of a urea solution is mainly composed of  $H_2$ ,  $N_2$ ,  $CO$ ,  $CO_2$ . The concentration of hydrogen was found to be about 50%, this value is 10% lower than expected according to the stoichiometry of the reaction.
- The evolution of the liquid phase was followed by FTIR. Both in a divided-reactor and in the undivided-reactor, a reduction of the  $OH^-$  affected peak area was observed, affecting the reaction rate and conversion.

## Perspectives

- Modified electrodes, which have a larger ECSA, will be used for UOR in order to enhance the rate of the reaction and efficiency.