Modelling and stochastic optimization of a three-compartment electrochemical reactor for CO2 electroreduction to formic acid using neural networks

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Abstract

Among different configurations, the three-compartment electrochemical reactor has demonstrated promising results for the CO2 reduction towards formic acid. To facilitate the technology’s scale-up, it is essential to assess the system’s performance and identify the most crucial operational variables. Modelling the system also provides valuable insights into tailoring process variables to achieve formic acid that meets specific requirements. In this context, a case study is proposed to address the non-linear optimization problem of installing the CO2 electroreduction process in a cement industry, aiming to minimize overall cost. Furthermore, various scenarios are considered to evaluate the economic viability of implementing this CO2 electroreduction technology.

**Keywords**: CO2 electroreduction, three-compartment electrochemical reactor, neural network, empirical modelling, non-linear optimization.

* 1. Introduction

Some of the main challenges facing society are related to climate change and global warming. The anthropogenic emission of CO2 is a precursor to these phenomena. Various strategies, such as the use of renewable energy sources or improving energy efficiency, are proposed to mitigate these CO2 emissions. In this sense, CO2 electroreduction (ERCO2) to value-added products emerges as one of the most promising CO2 utilization processes from both economic and environmental perspectives (He et al., 2023). This technology transforms the CO2 molecule into other chemical products (e.g., formic acid, methanol, ethylene) in an electrocatalytic process by applying an external voltage. Additionally, it allows for the storage of energy from renewable sources in the form of chemical bonds (Ozden et al., 2022).

In recent years, several research efforts have focused on developing efficient CO2 electrolyzers for ERCO2, primarily addressing reactor configuration, catalyst selection (Díaz-Sainz et al., 2023), process variable evaluation (Díaz-Sainz et al., 2021), and electrode fabrication (Abarca et al., 2023). Three-compartment configurations have shown promising results in ERCO2 to formic acid (Yang et al., 2020). These devices offer advantages over conventional one or two-compartment reactors, such as high Faradic Efficiencies toward formic acid, long-term stability, and direct formic acid production (Fernández-Caso et al., 2023). Furthermore, lab-scale commercial devices are available to study the process performance, facilitating the determination of suitable conditions for process scale-up and enabling the development of predictive models that can be useful tools in designing larger-scale electrolyzers.

The cement industry is one of the so-called hard-to-abate sectors, where CO2 emissions cannot be avoided by conventional strategies, and CCUSs (Carbon Capture Utilization and Storage) are proposed. ERCO2 to formic acid gains special relevance, as this chemical product is typically used for wastewater effluent treatment as a pH-neutralizing reactant. Formic acid production can be tailored by adjusting ERCO2 operational variables to meet industry requirements; hence, optimization work is needed to minimize the overall process cost.

This work aims to develop a predictive model using an artificial neural network (ANN)-based methodology capable of determining optimal conditions for obtaining formic acid with specific specifications via CO2 electroreduction. Besides, this model is implemented in a case study of the cement industry to optimize the process according to industrial requirements.

* 1. Methodology
		1. Experimental set-up

A commercial lab-scale three-compartment electrochemical reactor (Dioxide Materials) is employed to evaluate the influence of different process variables. Specifically, a 33-centered experimental design is proposed, analyzing three operational variables; i) CO2 inlet flow rate, ii) humidity of the CO2 feed, and iii) the current density applied to the system. Other influencing variables, such as the central compartment inlet water flow rate or anolyte inlet flow rate, are assessed using literature data (Yang et al., 2020). Each experimental point is duplicated to enhance the data quality, ensuring robust inputs to the ANN.

* + 1. Model development

A neural-network-based model is created using Neural Designer (Artificial Intelligence Techniques, Ltd) to construct the numerical expressions based on the data input collected during the experimental work with the commercial reactor. The input variables and their levels are presented in Table 1:

Table 1. Variables and different levels of the input variables to the ANN model.

|  |  |  |  |
| --- | --- | --- | --- |
| **Variable** | **+** | **-** | **O** |
| Central water flowrate (ml min-1) | X1 | 0.17  | 0.065  | 0.12  |
| Current density (mA cm-2) | X2 | 200  | 45  | 90 |
| Cathode water feed (g h-1) | X3 | 3  | 0.5  | 1.5 |
| CO2 flowrate (l min-1) | X4 | 0.06  | 0.02 | 0.04 |

As target variables, formic acid concentration and energy consumption (CE) (Eq. 1) are considered.

|  |  |
| --- | --- |
| $$Energy Consumption \left(\frac{kWh}{kmol}\right)=\frac{Q∙V}{C\_{Formate}}$$ | (1) |

Where Q is the total charge supplied to the electrochemical cell (A), V is the absolute cell potential (V), and CFormate is the molar flowrate of formate in the output stream of the electrochemical reactor (mol s-1). The model is normalized to the geometric area of the electrochemical reactor to allow the system performance analysis at different scales.

* + 1. Case study

The optimization problem of the system variables is proposed using a cement industry as a case study. A cement plant, located in Cantabria (Spain), with an overall 63.7 l min-1 CO2 emission, is chosen to propose the installation of an ERCO2 system to mitigate CO2 emissions and recycle CO2 into formic acid, which is required in the plant as a pH-neutralizing reactant. The overall cost is established as the objective function (OF) to minimize, considering the CAPEX and OPEX of the system.

|  |  |
| --- | --- |
| $$OF=CAPEX+OPEX$$ | (2) |
| $$CAPEX=Area∙RC/5$$ | (3) |
| $$OPEX=TEC∙EP-TCO\_{2}∙\left(ETS-CC\right)+(FAD-FA)∙FAP$$ | (4) |

In these equations, *Area* is the reactor geometric area (m2), *RC* stands for the reactor cost (27000 € m-2, based on the previous acquisition costs of electrochemical reactors for CO2 electroreduction), *TEC* denotes the total energy consumption (kWh), *EP* is the electricity price (0.105 € kWh-1), *TCO2* corresponds to the CO2 transformed (t), *ETS* signifies the CO2 emission right cost (81.65 € t CO2-1), CC is the capture cost (€ t CO2-1), *FAD* represents the demanded formic acid (t), *FA* indicates the produced formic acid (t), and *FAP* represents the formic acid market price (4100 € t-1). *CAPEX* evaluates the cost of constructing the scaled CO2 electrolyzer, annualized over five years. *OPEX* considers the cost of the electricity needed in the ERCO2 process, savings related to the non-utilization of CO2 emissions rights, CO2 capture cost, and savings on the demand for formic acid from external sources.

This optimization problem is constrained by requirements for product quality, plant characteristics, and limitations in model construction (Table 2). This results in a constrained non-linear optimization minimization problem (MINLP) addressed using the General Algebraic Modelling System (GAMS, GAMS Development Corporation, Washington, DC, USA). A reduced gradient algorithm is applied to solve the MINLP problem, utilizing the CONOPT solver to obtain the optimal solution.

Table 2. Constrained variables for the optimization problem

|  |  |  |  |
| --- | --- | --- | --- |
| **Variable** | Constrain | Up | Low |
| Central water flowrate (l min-1 m-2) | Model | 0.34  | 0.13  |
| Current density (mA cm-2) | Model | 200  | 45  |
| Cathode water feed (g h-1) | Model | 3  | 0.5  |
| CO2 flowrate (l min-1) | Plant | 63.7  | - |
| Formic acid concentration (g l-1) | Quality | 120 | 80 |

Moreover, different sensitivity analyses are conducted to evaluate the impact of parameters such as electricity price, emission right cost, or formic acid price on the economic feasibility of the ERCO2 installation.

* 1. Results
		1. Model deployment

The predictive model is constructed using machine learning, where data obtained from the experimental work is utilized to build the ANN architecture. As depicted in Figure 1.a, the ANN consists of several interconnected neurons: i) the scaling layer adjusts inputs to a proper range, ii) the perceptron layer combines and weights the input dataset, transforming it through an activation function into an output, iii) the unscaling layer restores the output to its original units, and iv) the bounding layers restrict the output value. The selection and optimization of neurons are carried out through an iterative process, aiming to achieve the best possible fit to the provided data for building the ANN. The resulting model includes four neurons in the scaling layer (one for each input variable), two perceptron layers with linear and hyperbolic tangent activation functions, and two neurons for both unscaling and bounding layers. The model deployment demonstrates a high level of adjustment, fitting the experimental data with an R2 of 0.991.



Figure 1. a) ANN architecture for the predictive model, b) Gradient Boosting variable importance coefficient chart, and c) variable correlation matrix

Besides, the significance of the input values concerning each output is assessed through a gradient-boosting approach (Figure 1.b), to examine potential non-linearities in the system. For both output variables, the applied current density (X2) exhibits the highest impact, with a coefficient exceeding 0.8. Regarding the correlation among different variables (Figure 1.c), it is evident that the correlation values are below 0.4, indicating weak relationships between the different variables. Notably, the most robust correlation is observed between the current density (X2) and the CO2 flowrate (X1), showing an inverse effect of -0.363.

Furthermore, the development of the ANN enables the derivation of an empirical mathematical model that relates the input and output variables. The mathematical expressions defining the architecture of the ANN are manually extracted and implemented as the model equations in the optimization problem presented below.

* + 1. Case study

The optimization problem, centered on the cement industry, considers an annual demand of 100 t of formic acid. Furthermore, the chosen CO2 capture technology for the initial case study is MEA (Monoethanolamine) absorption, recognized as one of the most advanced and competitive systems, with an estimated capture cost of 63 € t CO2-1 (Wang et al., 2017).

In this context, the outcomes reveal that the objective function (overall cost) has a negative value of -76476 € y-1, meaning significant savings with the implementation of the ERCO2 installation. The CAPEX is estimated at 36228 € y-1, while the OPEX is -112704 € y-1. The positive economic balance is primarily due to OPEX, where savings related to the costs of emission rights make this technology economically viable. The optimal reactor geometric area is determined at 6.71 m2, producing 9.67 t of formic acid per year, with a concentration of 106.62 g l-1, meeting the required product quality. Furthermore, the operational variables of the three-compartment electrochemical cell are established, with a CO2 flowrate of 60.3 l min-1, a current density of 200 mA cm-2, a water content in the CO2 feed stream of 0.5 g l-1, and a water central flow of 0.172 l min-1 m-2.

Besides, the influence of external factors on the objective function, such as the electricity price, emission rights price, or formic acid market price, is assessed through different sensitivity analyses, as shown in Figure 2. As observed, variations in electricity prices do not significantly affect the overall cost of the process. This can be attributed to the higher relevance of CO2 emission and capture and formic acid costs. Regarding the CO2 emission right cost, economic viability is dependent on its price. In cases where the ETS price is lower than the capture cost per ton of CO2, the cost becomes positive, indicating that the savings related to a lower CO2 emission cost do not compensate. However, forecasts for the ETS market in Europe suggest an increase in emission costs, making the ERCO2 installation more lucrative in the coming years. Finally, for the formic acid price, the effect is inverse, as the price increases, the cost rises. This is related to the fact that only 10 % of the total demand for formic acid from the cement plant is covered by the ERCO2 process; therefore, the market must be tapped for the rest of the demand, and the cost is strongly affected by price variations.



Figure 2. Sensitivity analyses for variations in the electricity, emission right, and formic acid prices.

* 1. Conclusions

The investigation of the three-compartment electrochemical reactor for ERCO2 involves the analysis and modelling of various operational variables. This leads to the development of an empirical model based on ANN. It is noteworthy from this variable that the current density applied is the most influential variable affecting performance. This model represents valuable insights for future technology implementation and scale-up.

Within this context, a case study delves into the deployment of an ERCO2 reactor in the cement industry. The optimization of main operation variables and the reactor’s geometric area is carried out to align with the requirements of the industrial plant requirements. The results of non-linear optimization results indicate a 6.71 m2 reactor with the capability to produce 9.67 t of formic acid per year.

Moreover, the economic feasibility of the ERCO2 process is assessed under various scenarios. This involves evaluating the influence of the electricity price, CO2 emission cost, and fluctuations in formic acid prices. Significantly, the CO2 emission cost emerges as the most crucial factor. In accordance with this finding and anticipating the projected rise in emission rights costs, the ERCO2 process's long-term economic viability is ensured in this case study.

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