Digitalization and Control of an Experimental Electrochemical Reactor

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Abstract

Climate change and global warming have an increasing impact on our daily lives, thus attracting increasing attention from researchers. Among various economically-viable methods to alleviate global warming trends, the electrochemical approach provides the possibility of reducing CO_2 gas to valuable chemical products. This article provides an overview of our recent work on digitalizing an experimental electrochemical reactor for CO_2 reduction at UCLA and developing a process control scheme for this reactor using machine learning modeling tools. Our work starts with training a neural network model with years of historical experimental data to investigate the underlying physical and chemical phenomena of the reactor. After having a high-level overview of the correlations between input and output variables, a single-input single-output control scheme is developed based on the integration of classical control with support vector regression methods. Lastly, the closed-loop control scheme is implemented in LabVIEW and the experimental setup is integrated with the Smart Manufacturing Innovation Platform.

Keywords

Electrochemical Reactors; CO_2 Reduction; Machine Learning Modeling; Process Control; Smart Manufacturing.

Introduction

Since the first warning of global warming in the 19th century delivered by the Swedish scientist Svante Arrhenius, we have witnessed the fastest increment of average temperature in the past 50 years. Large amounts of carbon dioxide (CO_2), one of the main chemical components that warm our planet, are continuously being released into the atmosphere as a result of human activities. To address this climate crisis, scientists and engineers from various domain areas have proposed the replacement of fossil fuels with clean or nuclear sources of energy, in parallel to the development of CO_2 capture technologies. CO_2 capture is an energy intensive process that requires more energy to remove carbon from more diluted sources such as air. In addition to physical methods for CO_2 capture, chemical approaches provide a way to convert captured CO_2 into valuable chemical products. When put together, carbon capture and conversion technologies can enable the recycling of CO_2 from the atmosphere and become carbon neutral if powered with energy harvested from renewable, carbon-neutral sources. In the last decade, the electricity-driven CO_2 reduction reaction has attracted increasing attention from researchers for its promise not only to transform CO_2 into useful fuels and chemicals, but also as a mean to store excess renewable electricity at global scales (Morales-Guio et al., 2018).

CO_2 reduction refers to a chemical process that transfers electrons and protons to the carbon atom to reduce its oxidation state, which weakens the molecular stability and increases the reactivity of carbon atoms in CO_2 molecules for further chemical reactions. The key technical challenge in implementing this reaction is to overcome the high energy barrier for the activation of CO_2. The three main strategies for CO_2 activation and reduction are of a thermochemical, photochemical, and electrochemical nature (Lu and Jiao, 2016). Thermochemical CO_2 reduction already operates at global scales. The main challenge to this process is that it requires the generation of hydrogen gas as reducing agent in a separate, energy intensive step. The production of hydrogen at industrial scales typically involves the reforming of hydrocarbons and the further emissions of CO_2 (Centi et al., 2013; Wang et al., 2011). In contrast, photochemical CO_2 reduction can directly transform CO_2 and water into fuels and chemicals in one device using sunlight. To date, however, these technologies have been limited to low solar-to-chemical conversion efficiencies due to the complex kinetics for light absorption, charge separation and charge transfer occurring at solid-liquid heterojunctions (Kumar et al., 2012). Electrochemical methods for CO_2 reduction, on the other hand, circumvent many of the challenges associated with thermochemical and photochemical methods. CO_2 electrochemical reactors, for example, can be coupled to any source of electricity, not only solar, and can be used for the direct transfer of electrons and protons to CO_2 molecules at ambient temperatures and at high rates (Lu and Jiao, 2016). Despite the theoretical advantage of the electrochemical approach for CO_2 reduction, the reaction mechanisms are still

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not fully understood. Indeed, the complexity of the transport-reaction processes involved makes this transformation one of the greatest challenges in the fields of catalysis and energy (Jin et al., 2021). The high complexity of the electrochemical CO_2 reduction reaction offers a unique test ground for advanced machine learning (ML) technologies. The higher the complexity of a transport-reaction process, the larger the dataset needed to decouple and understand the underlying physico-chemical processes and the larger the computational power needed.

Attributed to the substantial increase of computational power, cloud or local data storage, and open source machine learning libraries, machine learning methods have found broad applications in science and engineering. Theoretically, based on the universal approximation theorem of neural networks (Wang, 2017), ANN models can provide a unique and accurate approximation for any nonlinear input-output relations existing in the recorded dataset. Therefore, in electrochemical science research, the ML neural network method can be considered as a data-driven approach that indeed has the potential to facilitate the processes of understanding the underlying mechanisms and efficiently substitute first principle-based equations (Mistry et al., 2021). For example, an ANN model was developed to fit and compare the nonlinear adsorbate-substrate interaction between CO_2 and different types of catalyst for CO_2 electrochemical reduction (Ma et al., 2015). In Huang et al. (2018), a ML method was used to capture the structure-activity relationship between the absorption energies and the nanoparticle structure of the copper catalyst. Ulissi et al. (2017) adopted a ML method in their study to explore the mechanism of a complex surface reaction. These recent investigations demonstrated the applications of ML methods to provide computational insights into the fundamental and microscopic understanding of chemical and electrochemical reactions.

Besides the application in theoretical research areas, efforts are made to implement ML technologies in industrial manufacturing tasks, including but not limited to process control, real-time optimization, supply chain management, anomaly detection and monitoring carbon footprint (Bertolini et al., 2021; Wenzel et al., 2019). Unlike the objectives of most scientific research projects that aim to map static input-output relations, ML tasks for industry and process control involve making intelligent decisions for continuously operating processes based on real-time dynamic information. This application takes advantage of the ability of the ML model to process time series data to approximate the instantaneous operation status or to predict future process behavior, which is also known as time series forecasting (Bontempi et al., 2012). Specifically, in Wu et al. (2019), a method was proposed to approximate the output behavior using a recurrent neural network model (RNN) trained with historical time series data. Furthermore, a model predictive control (MPC) algorithm based on the RNN model was developed and evaluated through a large-scale chemical process simulation (Wu et al., 2019, 2021).

With the exponential growth of industrial data and ML/AI applications, a new era of industrial revolution has been initiated, and we are approaching the next generation of manufacturing processes, namely, Industry 4.0 or Smart Manufacturing. Novel smart technologies give rise to this revolution, such as the Internet of Things (IoT), cloud and edge computing, industrial AI, and digital twins, are mainly exploited by large-scale data analysts and require intensive computational support, which implies that manufacturing is shifting to a data-driven era (Tao et al., 2019; Zhong et al., 2017). In other words, the key step to achieving smart manufacturing is how to comprehensively collect useful data, and extract maximum information hidden in the dataset for the benefit of daily operations. Recent research has proposed strategies to implement smart manufacturing to various process systems. Ren et al. (2021) discussed a data workflow for the implementation of smart manufacturing to additive manufacturing without intensive computational resources. Qi and Tao (2018) reviewed and compared the roles of big data and digital twins in smart manufacturing and proposed future directions to improve the application of these two technologies. However, implementing advanced ML to fully process industrial data requires strong computational power, which is not always available in manufacturing industries, especially in small and middle companies.

To this end, a government-funded non-profit organization, the Clean Energy Smart Manufacturing Innovation Institute (CESMII), is leading the development of a Smart Manufacturing Innovation Platform (SMIP), which aims to provide technical support and services to manufacturing enterprises to facilitate the application of smart manufacturing. Specifically, the SMIP provides an online database with pipelines for data transmission to store user data. Furthermore, packages and toolboxes for developing data-driven models (e.g., ML/ANN model, data extraction algorithm) are available on the SMIP via Docker container virtual environment technology that can also be used to access advanced ML model training, process control, and optimization algorithms. Additionally, manufacturing equipment, such as reactors, controllers and sensors can be connected to the online server to be automated or monitored remotely (Çıtmacı et al., 2022).

This manuscript provides an overview of our work. Inspired by the aforementioned research achievements of adopting ML methods to address scientific and engineering challenges, we utilized an ANN model to study the underlying physical and chemical rules of the electrochemical reactor and used the ANN model prediction to enhance the empirical-principles equation of this reactor. Subsequently, a single-input single-output (SISO) process control scheme was developed based on the feedback information provided by a support vector regression-based (SVR) estimator and gas chromatography (GC) measurements. Subsequently, closed-loop control experiments were performed to evaluate the performance of the control scheme. To embed the control scheme into the reactor, LabVIEW software is utilized to establish an operating system for the digital control of each experimental equipment. Lastly, the developed system is synchronized to the SMIP server for further investigation of the aforementioned cloud-based technologies.

Experimental Electrochemical Reactor

The electrochemical reactor used in this study is designed to reduce CO_2 gas to hydrocarbon and oxygenate products, including liquid and gas fuels, reagents and other valuable chemicals that are consumed in our daily lives. The setup of the reactor is shown in Figure 1, and it has two chambers separated by an ion-exchange membrane. Each chamber contains one of the electrodes, where the cathode is the working electrode, and it is submerged in a bicarbonate buffer solution. During operation, the CO_2 gas is fed into the buffer solution and subsequently transported to the surface of the working electrode, where the CO_2 will be reduced by electrons and protons from water. The working electrode is a solid cylinder made of copper, the best-known metal for reducing CO_2 to hydrocarbons and oxygenates, to maximize the reactor performance and energy usage (Vasileff et al., 2018). In this setup, the working electrode rotates at a fixed speed throughout the experiment to create a consistent mass transfer profile in the solution, which has a critical impact on product selectivity (Jang et al., 2022). Finally, gas chromatography (GC) is used to analyze the composition of gas outcomes and quantify the productivity of gas phase products (hydrogen, carbon monoxide, methane, and ethylene) within every sampling period (i.e., 20 minutes for our experiments). Liquid-phase products are collected and quantified off-line at the end of the experiment utilizing nuclear magnetic resonance (NMR).

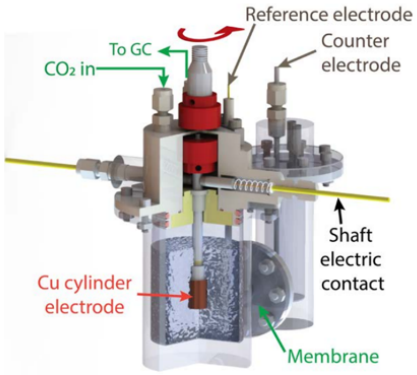

Figure 1: Schematic of UCLA's electrochemical reactor.

Machine Learning-based Modeling

Developing a mathematical model to describe the underlying physical and chemical phenomena of a reaction process is the first step in the implementation of any novel reactor in industry. However, the mechanism for the electrochemical reduction of CO_2 remains unknown due to the complexity of the reaction. Moreover, experimental uncertainties such as sensor detection limits and human errors introduce additional variance to the observation, making the modeling task more challenging. Attributed to the stochastic nature of the artificial neural network (ANN) and its demonstrated ability to capture highly nonlinear relations, a data-driven model can be constructed to account for the input-output relationship of this electrochemical reactor and account for the experimental data variance. In our work Luo et al. (2022), a feedforward neural network (FNN) model with two hidden layers was found to be capable of capturing the designated input-output relations of the electrochemical reactor. The mathematical expression of this FNN model can be described as follows:

$$\mathbf{Y} = F_{NN}(X) = \begin{cases} h_j^{[1]} & = \sigma^{[1]}(\sum_{i=1}^{p} \omega_{ji}^{[1]} x_i + b^{[1]}) \\ h_j^{[2]} & = \sigma^{[2]}(\sum_{i=1}^{p} \omega_{ji}^{[2]} h_i^{[1]} + b^{[2]}) \\ y_j & = \sigma^{[l]}(\sum_{i=1}^{p} \omega_{ji}^{[l]} h_i^{[l]} + b^{[l]}) \end{cases} \quad (1)$$

where $\mathbf{X} = [x_1, x_2] \in \mathbf{R}^2$ is the input of the FNN model with respect to the surface potential and the rotation speed of the working electrode. $\mathbf{Y} = [\hat{y}_1, \ldots, \hat{y}_{14}] \in \mathbf{R}^{14}$ is the output vector of the FNN model, which contains the production rate of 13 reduction products from the electrochemical reaction and the selectivity of the oxygenates. $\omega_{ji}^{[k]}$, i and $j = 1, \ldots, p$, $k = 1, \ldots, l$, represent the weights that connect the i^{th} input from the previous layer to the j^{th} neuron in the k^{th} layer, where l is the number of layers. $p = 64$ represents the number of logistic units in each layer. $b^{[k]}$ and $\sigma^{[k]}(\cdot)$ denote the bias and activation function used in the k^{th} layer. The Rectified Linear Unit (ReLu) and Softplus function, $S(x) = log(1 + e^x)$, are the activation functions for the hidden and output layers respectively to capture the nonlinear behavior observed in experiments.

To further account for the variance of data, the methodology of maximum likelihood estimation (MLE) is adopted in the loss function of FNN training to obtain the optimum weight matrix for the FNN model that would maximize the likelihood of output prediction by considering the experimental outcome in a probabilistic manner. Specifically, to simplify the computation, each output is assumed to be independent, so the likelihood function ($\mathcal{L}(\cdot)$) of the FNN predictions is approximated as the joint probability distribution of the experimental data, which can be written as follows:

$$\mathcal{L}(\mathbf{X}; \mathbf{W}) = \prod_{k=1}^{n \times m} f_{\mathbf{Y}}(y_k) \quad (2)$$

where $\mathbf{W}$, m, n, are the weight matrix of the FNN model, the number of input conditions applied in the experiments, and the number of FNN outputs, respectively. $f_{\mathbf{Y}}(y_k)$ stands for the probability density functions of the k^{th} result. Furthermore, by assuming that all results of the experiment are following the Gaussian distribution and are independent of each other, the optimal weight matrix (W^*) can be computed by maximizing the logarithm of the joint likelihood function that can be simplified into the following equation:

$$\mathbf{W}^* = \arg\min_{\mathbf{W}} \left(\sum_{i=1}^{m} \sum_{j=1}^{n} \left| \frac{y_{i,j} - \hat{y}_{i,j}(\mathbf{X}, \mathbf{W})}{\sigma_{i,j}} \right|^2 \right) \quad (3)$$

Thus, the loss function used to train the FNN model is shown as the following expression:

$$Loss = \frac{1}{m} \frac{1}{n} \sum_{i=1}^{m} \sum_{j=1}^{n} \frac{1}{v_{i,j}^2} \left| y_{i,j} - \hat{y}_{i,j} \right|^2 \quad (4)$$

where v is the coefficient of variance of each data point defined as the ratio of standard deviation and the respective output mean to normalize variability of different magnitudes. Therefore, the FNN model integrated with the MLE method is trained to maximize both the prediction accuracy and the output likelihood function.

Process Measurements and Characterization

Another major objective of this study is to investigate the methodology to implement real-time control in a novel experimental electrochemical reactor based on the data-driven models built with ML. Ideally, an advanced feedback control scheme should be able to achieve any desired and feasible setpoint by manipulating the control variables. However, in the current stage of the study, the amount of controllable variables is not sufficient to fully control all valuable product concentrations produced by the reactor. Therefore, this work aims to demonstrate the potential ML approach to develop a complete control scheme by establishing a single-input single-output (SISO) feedback control system, which has applied potential as the single input variable.

Due to the discussed limitation of the reactor, liquid phase products can only be analyzed once the operation is over, making them infeasible for real-time control. On the other hand, four gas-phase products (i.e., hydrogen (H_2), carbon monoxide (CO), methane (CH_4) and ethylene (C_2H_4)) can be collected and analyzed by the GC during the experiment and therefore they are candidate outputs for the control system. The relevant reactions for generating these gas products are shown as follows:

$$2CO_2 + 8H_2O + 12e^- \rightarrow C_2H_4 + 12OH^- \tag{5a}$$

$$CO_2 + 6H_2O + 8e^- \rightarrow CH_4 + 8OH^- \tag{5b}$$

$$CO_2 + H_2O + 2e^- \rightarrow CO + 2OH^- \tag{5c}$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{5d}$$

Among all gas products, ethylene productivity shows the strongest correlation with the surface potential and it also has significant value in the marketplace Jang et al. (2022). Therefore, C_2H_4 concentration is chosen as the single output state of the process in this study. During the operation, ethylene productivity is monitored by injecting the gas outlet stream into the GC, which first separates the injected molecules with different elution times and then analyzes the gas components using the built-in thermal conductivity detector (TCD) and flame ionization detector (FID). However, the GC requires a certain time period to obtain the result of each analysis and needs to be cooled down before taking the next round of samples. This raises a limitation of 20.33 minutes of sampling period to our feedback control scheme.

The performance of an electrochemical reactor is very sensitive to varying conditions. This results in a significant operation variance, even if the experimental system is prepared with the same procedures and the input conditions are held constant. In addition to that, it has been observed that after a certain threshold is reached, the production rate of ethylene remains constant with increasing surface potential. The applied potential beyond this threshold is intrinsically used for producing more methane. This phenomenon is explained as the product selectivity shifting to methane based on the theory that ethylene and methane share the same intermediate during the reaction (Hori et al., 1997). Besides the limitation of the sampling period, the copper catalyst appears to continuously deactivate as the reaction proceeds, which is another major challenge and uncertainty to implement the feedback control of this electrochemical reactor. This degradation is caused by multiple factors such as impurity absorption, surface restructuring, and reactive sites being blocked by unreactive species. Therefore, the reactor performance varies as the experiment proceeds, which requires the feedback controller to be adaptive to the continuous degradation.

Real-time Optimization

We proceed with a discussion on process optimization to determine energy optimal set-points for use in the process control system discussed in the next section. Specifically, we consider the following real-time optimization problem.

$$\mathcal{J} = \underset{\hat{x}\in\mathbf{D}}{\arg\max}\ R(\hat{x},V) - C(I,V) \tag{6a}$$

$$s.t. \quad F_{nn}(V,r) \approx x \tag{6b}$$

$$C(V,I) = c_e \times E(V,I) \tag{6c}$$

$$R(\hat{x},V) = \sum_{i=1}^{m} c_i \times \hat{x}_i \tag{6d}$$

$$-1.5 \leq V \leq -1.27 \tag{6e}$$

where V, r are the surface potential and the rotation speed of the working electrode. Function $R(\cdot)$ and $C(\cdot)$, $E(\cdot)$ are the revenue, cost and energy consumption of operating the electrochemical reactor that I, c_e and c_i denote the current density on the working surface and market price for electricity and the i^{th} product. In this case, the MLE-FNN model is used to predict the production rate of each product ($\hat{x}_i$) under different input combinations, and based on this, an open source optimization software is implemented to search for the optimal set point to be provided to the control scheme.

Feedback Control Scheme

In this study, the productivity of ethylene is quantified by its concentration in the product gas stream. The gas flow rate is fixed and the concentration can be obtained from the GC measurement. Although an FNN model has been developed to predict the production rate of each product species, it is trained on the steady-state data collected at the end of the experiments; thus, it cannot reflect instantaneous productivity. Recent research results have demonstrated the methodology of using a deep learning model (e.g., LSTM) to capture the time series dynamics of chemical engineering processes (Wu et al., 2019). However, neural network models generally require a large-scale dataset to develop, which is not available for most experimental research cases involving chromatographic measurement methods.

Considering the above limitations, a classic ML algorithm, support vector regression (SVR), is utilized to estimate the real-time ethylene productivity. SVR optimizes the generalization error bound by defining a support vector and penalizes data outside the support vector bound (Basak et al., 2007). The SVR algorithm can be visualized as in Figure 2 and expressed in the following mathematical form for linear

regression problems:

$$\min \ \frac{1}{2}\|w^2\| + C\sum_{i=1}^{l}(\xi_i + \xi_i^*)$$
$$st. \left\{ \begin{array}{l} y_i - \langle w,x\rangle - b \le \varepsilon + \xi_i \\ \langle w,x\rangle + b - y_i \le \varepsilon + \xi_i{}^* \\ \xi_i, \xi_i^* \ge 0 \end{array} \right\} \quad (7)$$

where ξ, ξ^* are named slack variables, $\langle \cdot\ ,\ \cdot \rangle$ means inner product operation, C refers to the tolerance limit for divergences, w and b are the weight matrix and bias, respectively, and y_i denotes the i^{th} data reference. In addition to that, polynomial kernels can be applied to the algorithm to perform polynomial regression. In our work, the 5^{th} order polynomial kernel is adopted to develop the ML-based estimator to provide continuous feedback information.

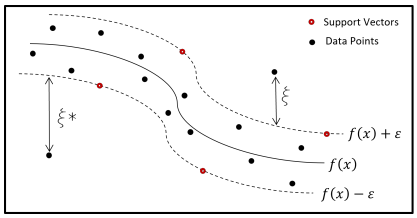

Figure 2: Support vector regression components. $f(x)$ is the proposed hyperplane, ε is the support vector margin, ξ and ξ^* are the distances to data points beyond the support vectors.

A proportional-integral control (PI) is used to perform real-time feedback control for the proposed SISO system. The control objective of our experiment is to maintain the optimum set point by adjusting the potential applied to the reactor. Specifically, the PI controller is alternating the applied potential based on the feedback information from the GC and ML-based estimator.

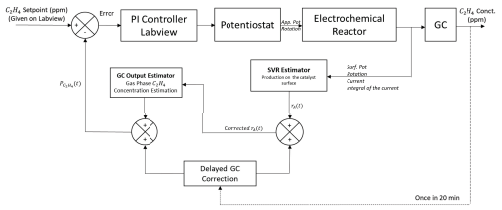

Figure 3: Closed-loop control scheme.

The developed control scheme is shown in Figure 3. Experimental devices in this study are connected to and monitored by LabVIEW. During the closed-loop operation, after receiving the setpoint from RTO, the PI controller will calculate the optimum control signal and send it to the potentiostat to adjust the surface potential. The SVR model estimates the output C_2H_4 concentration of the process every second since a GC reading is available only every 20 minutes. Even though an SVR model is trained with a sufficient amount of experiment data to give a reliable prediction of the real-time productivity of ethylene, it cannot fully capture the stochastic nature of this reaction. Therefore, it is essential to have a correction step to calibrate the SVR predictions when a new GC measurement is available and that accounts for the GC analysis delay. Thus, a correction algorithm is developed based on an empirical-principle-based theory to adjust the SVR model using delayed information (Çıtmacı et al., 2022).

Future Research Directions

Multivariable Control. With a better understanding of the electrochemical reactor, additional control variables can be adopted to implement a multivariate process control system to regulate the concentrations of multiple products. Another important candidate control variable is the rotation speed of the working electrode, which can adjust the mass transfer profile within the reacting chamber. In addition, key output variables, like CO product concentration, are observed to have a high correlation with the rotation speed. In this context, a more advanced control strategy will be studied to achieve this goal.

Real-time Machine Learning Modeling. With the development of computing and data science technologies, the ML approach becomes popular in broad research areas including chemical engineering and process control. The data shift problem, defined as the data distribution changed from the training set, is a major hold-back for implementing ML technologies in the industry. The data shift in the industry can be caused by many reasons, such as aging equipment or inherent process changings. The catalyst degradation is a scenario of a data shifting problem. To this end, real-time ML methodologies are being studied.

Smart Manufacturing Innovation Platform & Edge Computing. The experimental setup used in this research was digitalized by using the Smart Manufacturing Innovation Platform (SMIP) built by the CESMII. SMIP aims to increase operation data usage efficiency and introduce state-of-the-art ML and artificial intelligence (AI) technologies to the manufacturing industry. On the other hand, the implementation of ML/AI is much more computationally intensive than the conventional process. Although building a centralized data server to provide powerful cloud computing services is one approach to deal with computational power limitations in the manufacturing industry. However, this might not be the most effective solution since it will be limited by the local internet service. The edge computing concept, which means using local computation tools closer to the data source to perform preliminary calculations, is then proposed to improve the workflow. Therefore, one future task is to deploy effective functions and toolboxes on the SMIP to provide a convenient and reliable cloud-edge computing methodology.

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