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Decision tree analysis for efficient CO_2 utilization in electrochemical systems

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ABSTRACT

In this work, a database of 471 experimental data points excerpted from 34 different publications on electrocatalytic reduction of CO_2 was formed. Firstly, the database was examined by exploratory data analysis using box and whiskers plots. Then, decision tree analysis was applied to determine the significance of the variables and to reveal the conditions leading to higher faradaic efficiency, production rate and product selectivity. It was found that Cu content smaller than 71% resulted high faradaic efficiencies depending on the amount of Sn, catholyte type, applied potential and pH of electrolyte. In this case, applied potential and Cu content were found to have the highest significance among all the input variables. On the other hand, the most generalizable combination of variables leading to high level of rate occurred when the Cu content being less than 13%, using a membrane other than Selemion AMV, employing a backing layer such as TGP-H-60 and keeping the applied potential between −1.5 and −2.6 V; for which the applied potential and CO_2 flow rate were determined as the highest significant variables. Finally, the most generalizable path for the case of selectivity was obtained with Sn content higher than 15% and Cu content less than 52%, which leaded to formic acid production having the highest production rates. It was then concluded that, exploratory data analysis and decision trees can provide useful information to determine the conditions leading to higher CO_2− electroreduction performance that may guide the future studies in this area.

1. Introduction

In most industrial processes, large amounts of flue gases are emitted to the atmosphere from power plants, process furnaces in large refineries, petrochemical and chemical plants or incinerators due to the combustion of fossil fuels. The most abundant gas following nitrogen (N_2) in the outlet of these systems is carbon dioxide (CO_2), which corresponds to approximately 10 vol. % of the flue gas. Historically, it can be observed that CO_2 emissions have increased exponentially since 1950's, and the emissions are expected to rise by two folds by 2025 [1]; however, the contribution of CO_2 emissions to global warming impose a great environmental risk.

One possible solution to convert CO_2 emissions to valuable products could be the utilization of electrocatalytic routes towards hydrocarbons or carbon monoxide (CO) [2] by mimicking photosynthesis [3,4]. Although CO_2-electroreduction to such products is a promising route, industrial scale up still needs to overcome many technical issues [5]. In addition, it is very well known that electroreduction routes strongly depend on electrode design, electrolyte and operating potential during electrolysis [2,6–24]. These technical issues and the global concerns about the increase of CO_2 level in the atmosphere attracts an increasing attention in scientific community, as indicated by Fig.1, which shows the number of articles published through years including "CO_2 reduction" in their titles under the "Web of Science Core Collection". In the years between 1990 and 2018 (till the date of the search), 3121 articles have been published, and as further indicated by the figure, there has been a significant increase in the annual number of publications since the year 2010. The increase is even more significant especially for the last three years.

In the scientific literature, it is seen that one of the most important factors for the valorization of CO_2 is the electrode design; and for a better electrode design, especially it is very important to design catalysts that have high selectivity, low overpotential and longer stability in aqueous electrolytes [23]. Many research studies prove that transition metals like copper (Cu), nickel (Ni), gold (Au), indium (In) etc., transition metal alloys, mixed oxides [6] and many modified transition metal surfaces with different nanostructures prepared by various preparation techniques at different atomic compositions have higher faradaic efficiency and higher reduction performances for valuable products [2,6–8,10–22,24]. Among these electrocatalysts, Cu is very

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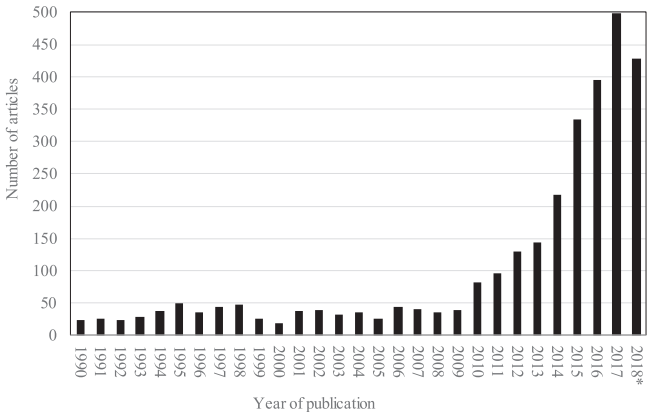

Fig. 1. Number of articles versus date of publication in the "Web of Science Core Collection" database including "CO_2 reduction" in the title of the paper (searched as of 10 September 2018).
*includes the number of articles published in this year till the date of the search.

popular since the initial studies started on Cu and important research works are still being carried out on different forms of Cu electrode because of its high selectivity for hydrocarbons [11,12,14]. In fact, the selection criteria for the Cu and the other metals studied is based on their degree of CO and hydrogen binding energies which determine their selectivities towards valuable products at certain applied potentials [9,18,25]. The useful figure of merit to compare CO_2-reduction activities and selectivities of these electrocatalysts at different conditions is partial current density or rate of production of valuable products. Partial current density or rate of production at certain negative potentials is especially important to determine the dependence CO binding character of metals on the reduction activity as volcano plots (where Au is at the top) (chemical nature vs. electrochemical nature) [26]. These volcano plots suggest that as CO binding strength increases from Ag, Zn to Pt, Cu, Ni, Fe the selectivity ranges from CO to hydrocarbons [27]. On the other hand, the activity may be completely different from unmodified metals if transition metals are functionalized by ligands, and the activity may greatly depend on the proton transfer capability of the ligands [28] other than which the volcano plots suggest. Therefore, based on theoretical backgrounds and partial current density, the knowledge of existence or composition of metals in the electrocatalyst may help us to predict the possible valuable reduction products during electrolysis without the effect of interference by many other cell and operating variables like the type of electrolyte, pH and so on. Obviously, it is extremely difficult to generalize the effect of many different types of electrode designs [5,29–31] with many different electro catalysts in different electrolytes and different type of cells, at different pH and applied potentials. Therefore, to increase the performance of CO_2-electroreduction not only by electrocatalyst synthesis but also by type, operating conditions and design of the electrochemical cell, electrolyte and electrode design are all very important. They are interrelated with each other and the type of electrocatalyst used on the cathode electrode. The interactions between these variables are also studied for highly efficient, selective and stable CO_2-electrolyzers to get the optimum operating conditions. For instance, for a better cathode electrode design, to decrease CO_2 mass transport resistance and increase solubility, carbon-based gas diffusion layers, which also affect catalyst dispersion, can be used as backing layers for electrocatalysts. Optimum gas diffusion electrode (GDE) with highly dispersed catalysts is important for low ohmic losses and high intrinsic activity which therefore lead to high faradaic efficiency and current density that could be scaled up to industrial levels [5,29–31]. For instance, in a continuous single cell electrolyzer with a stainless-steel anode and tinned copper mesh cathode, the effects of K^+ and Na^+ cations and HCO_3^-, Cl^- anions, pH of the catholyte, concentration of the catholyte on the formate generation are well established. The effects of K^+ and HCO_3^- are superior to Na^+ and Cl^- and the negative effect of pH at about 9 is due to CO_3^{-2} formation suppressing the formate production. The parabolic relationship between electrolyte concentration and current efficiency is observed due to mainly competing effects of ionic conductivity and solubility of CO_2 in the electrolyte [32]. In fact, the increase in electrolyte concentration together with modification of anions can dramatically improve energy efficiency by lowering ohmic resistance. As seen in these two cases of GDE and electrolyte, although some of the relationships between these variables may be well established, there can be many complexities in the electrolysis process if additional catalytic or operating variables are considered.

As it is explained above, since a great number of experimental results have been reported in the literature with so many different catalytic variables and operational conditions, it is too difficult to visualize at first sight the general trends and patterns which are quite likely to be hidden in this enormous data pool. On the other hand, data mining can provide the discovery of such valuable knowledge by clustering, classification and regression. For instance, artificial neural networks are quite popular for predictive purposes that have been applied in a variety of different fields; i.e., the field of catalysis (to help to design new catalysts and to understand catalytic structures) [33]. Moreover, applying decision trees for classification purposes is also quite common for understanding the hidden patterns and for indicating how to maintain the experimental variables leading to higher levels of an output variable [34,35]. Indeed, we have successfully employed various data mining based techniques for a variety of different complex systems such as optimization of catalytic variables for selective CO oxidation [36], water gas shift reaction [37], steam reforming of methane [38], dry reforming of methane [39] as well as to optimize direct alcohol fuel cells for achieving maximum power [40] and to determine the conditions leading to the highest biodiesel yield [41]. There are also successful applications of data mining methods in the area of CO_2 utilization as reported in the literature; for example, to predict CO_2 capture of ionic liquids [42], to estimate CO_2-related thermodynamic properties in solution environment [43] and to explore the intrinsic trends of CO_2 solubility in various mixed solutions of trisodium phosphate (based on the experimental data extracted from the literature) [44].

In this work, we systematically reviewed the recent articles published in the literature on electrocatalytic reduction of CO_2 for the elimination of greenhouse gases and producing valuable products, and built a database containing 471 data points from 34 different publications. First, we statistically reviewed the database and applied an exploratory data analysis using box and whiskers plots [45]. Then, we applied decision tree analysis to determine the conditions leading to higher electroreduction efficiency and rate as well as the selectivity of the product for the aim of industrial scale up. It should be noted that the approaches proposed in this study are quite different from volcano plots, since volcano plots ignore many design parameters in the actual electrolysis system. Besides, this study aims to add (integrate or utilize) these parameters with the catalyst composition and different supports, and to show the significances of these parameters on the performance variables. Our study also aims to combine electrode design, reactor design, catalyst design parameters in a model which will be much more complex compared to volcano relationship.

2. Materials and methods

2.1. Database construction

First, numerous articles on electrocatalytic reduction of CO_2 were reviewed, and a database of 471 data points was prepared by collecting the experimental results reported in 34 recent articles found through sources such as Elsevier, Wiley, ACS and Springer. The details of these publications, experimental parameters, maximum faradaic efficiencies and maximum rates reported in each reference are given in Table 1.