Vol. 22, No. 2(2023) Sim2387
Revista Mexicana de Ingeniería Química

Practical approach to identify electrochemical parameter in aqueous Potassium ferricyanide by solving the multi-variable Cottrell equation via genetic algorithms

Enfoque práctico para la identificación de los parámetros electroquímicos en una solución de ferrocianuro de potasio via algoritmos genéticos

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Received: July 7, 2023; Accepted: July 29, 2023

Abstract
Parameters optimization of emerging electrochemical processes is crucial for improving efficiency and cost. Herein, a procedure based on the genetic algorithms (GA) search method was proposed to solve the fundamental Cottrell equation. First, a basic GA background is provided to help students and researchers understand the basic concepts of such evolutional algorithms and how this can be applied in their field of expertise. Then, the study was conducted considering measured chronoamperometry data of potassium ferricyanide, as electroactive species, at the platinum working electrode. The number of electrons (n), species concentration (C), and diffusion coefficient (D) were the three unknown solved variables that were obtained through optimization. The crossover function and population size effect were deeply studied on the final value of these electrochemical parameters. The results show that Intermediate and Heuristic crossover stochastic functions had the best performance in solving the multi-objective function, according to the root mean square error (RMSE) outcome. Thus, it was concluded that GA is a feasible tool that can be adopted to solve complex and multivariable problems in electrochemistry. Furthermore, it should be highlighted that GA can be adopted to determine chemical and electrochemical parameters in emerging technologies such as energy conversion devices.
Keywords: Genetic algorithm, chronoamperometric, Cottrell equation, crossover functions, heuristic.

Resumen
La optimización de los parámetros de los procesos electroquímicos emergentes es crucial para poder mejorar la eficiencia y los costos. En este trabajo, se propuso un procedimiento basado en el método de búsqueda de algoritmos genéticos (AG) para resolver la ecuación fundamental de Cottrell. En primer lugar, se proporciona una revisión básica de GA para ayudar a los estudiantes e investigadores a comprender los conceptos básicos de dicho algoritmo evolutivo y como se pueden aplicar en sus campos de especialización. Después, el estudio se realizó considerando los datos de una medición de cronoamperometría en un electrodo de platino en ferricianuro de potasio, como especie electroactiva. Las tres variables se obtuvieron a través del proceso de optimización fueron: el número de electrones (n), concentración de especies (C) y el coeficiente de difusión (D). El efecto de la función de recombinación y tamaño de población sobre los valores finales de los parámetros electroquímicos fueron estudiados a detalle. Los resultados mostraron que las funciones de recombinación estocásticas que presentaron el mejor desempeño en la resolución de la función multiobjetivo fueron la intermedia y heurística, de acuerdo con el resultado del error cuadrático medio (RMSE). Por lo tanto, se concluyó que un algoritmo genético es una herramienta factible que puede adoptarse para resolver problemas complejos y multivariables en electroquímica. Además, es importante resaltar que los AG se pueden adoptar para determinar parámetros químico y electroquímico en tecnologías emergentes como son los dispositivos de conversión de energía.
Palabras clave: algoritmo genético, cronoamperometría, ecuación de Cottrell, función de recombinación, heurístico.

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https://doi.org/10.24275/rmiq/Sim2387
ISSN:1665-2738, *issn-e*: 2395-8472

1 Introduction

Most electrochemical University courses contain fundamental concepts for determining D values through a given measured experimental dataset. Moreover, the majority of electrochemical analysis tools taught in the classroom consider that at least one or two variables are known. This is, to some extent, an academic limitation. Undergraduate and graduate students should be familiarized with the fundamentals of chemical and electrochemical engineering issues with application in the industry sector, where it is usually almost impossible to know the values of species concentrations or other variables in advance. For these reasons, incorporating hot topics and powerful tools such as GA into University courses should be amazing. These algorithms are capable of solving simultaneous equations with several unknown variables with acceptable computing time and also can be used for optimization applications.

Diffusion is generally the rate-limiting step in many electrochemical systems (Wang, *et al*., 2018). Therefore, determining D values is needed to fully understand the redox couple of the electroactive species (Geng *et al*., 2022; Saw *et al*., 2018; Sikeyi *et al*., 2021). Furthermore, many techniques have been proposed to obtain the diffusion coefficient under a specific framework (Chayambuka *et al*., 2021; Deng *et al*., 2022; Hasegawa *et al*., 2021). For example, Shao *et al*. studied the diffusion characteristics of OH- ions, an active species participating in different chemical reactions, by adopting laser-induced fluorescence at high temperatures. To this end, they used a planar laser-induced fluorescence laser (ArF, 193 nm) coupled with lenses and mirrors to observe the released OH- radical from the photochemical dissociation of water (Shao *et al*., 2021). The main disadvantage of this technique is the equipment cost and the applied high temperatures. On the same issue, Belgodere *et al*. reported implementing *in situ* Raman microspectroscopy to successfully estimate the diffusion coefficient of CO_2 in aqueous solutions at room temperature (Belgodere *et al*., 2015). The experiments were carried on in fused silica capillaries with salinity conditions of 0 to 6 mol NaCl per kilogram of water. D was calculated by numerical analysis of the measured Raman peaks of CO_2 and H2O. The aforementioned method can be considered promising regarding its simplicity and short-time measurements, but it should be mentioned that materials presenting fluorescence can not be analyzed by this technique. In this sense, several researchers have proposed using electrochemical methods to estimate the diffusion coefficient of analytes (Black, Zhang, Reid, & Bartlett, 2022; Kim *et al*., 2021; T. Q. Nguyen & Breitkopf, 2018). Iranzo *et al*. proposed for the first time the adoption of electrochemical impedance spectroscopy (EIS) to determine the distributed relaxation time (DRT) in a 50 cm^2 Polymer Electrolyte Membrane Fuel Cell (PEMFC), which is related to electrochemical and diffusion processes. A Gauss distribution with a radial basis function discretized the measured EIS input data (Iranzo *et al*., 2021). The authors stated that the obtained data had a significant value because it can be used to describe the main drawbacks limiting fuel cell efficiency qualitatively.

Chronoamperometry (CA) is also an electrochemical technique widely used to determine kinetic parameters, including the D value of electroactive species. This method is more convenient than EIS because only uses current and voltage signals instead of frequency and sinusoidal input as is the case of EIS.

For example, it has been demonstrated that CA is versatile in characterizing sensors. Moreover, in recent work, the D valuer of nicotine was calculated employing the Cottrell equation (Zaki *et al*., 2022).

$$i(t) = \frac{nFACD^{1/2}}{\pi^{1/2} * t^{1/2}} \tag{1}$$

where i is the measured current (A), F is the Faraday constant (C mol^{-1}), A is the electrode working area (cm^2), t is the time (s), while n, C and D have already been defined here above. The calculated values were too close to those obtained by cycling voltammetry analysis.

Recently, Jiankang *et al*. developed a method to optimize parameters in studying nitrogen gas crossover and accumulation at the anode of PEMFC using machine learning methods (Wang *et al*., 2022). Firstly, the authors simulated a two-dimensional steady-state mechanistic PEMFC model in COMSOL Multiphysics to construct a database of the six parameters under study. Then, several machine learning algorithms were trained to solve the multi-objective equation. As a result, they observed a reduction in the nitrogen gas crossover coefficient close to 50%, while the power efficiency was improved by ca. 20%.

The CA method has also been used to determine D and the nucleation process of electrodeposited aluminium in chloroaluminate ionic electrolytes (Al_2Cl_7) with the aid of the Cottrell equation (Peng *et al*., 2021). Interestingly, the calculated D value could be used to estimate the density of nucleation centres based on the model proposed by Gunawardena *et al*. (Gunawardena *et al*., 1982). This way, it was possible to calculate the grain size of electrodeposited films by using equation (2):

$$r = \left(\frac{1}{\pi N}\right)^{0.5} \tag{2}$$

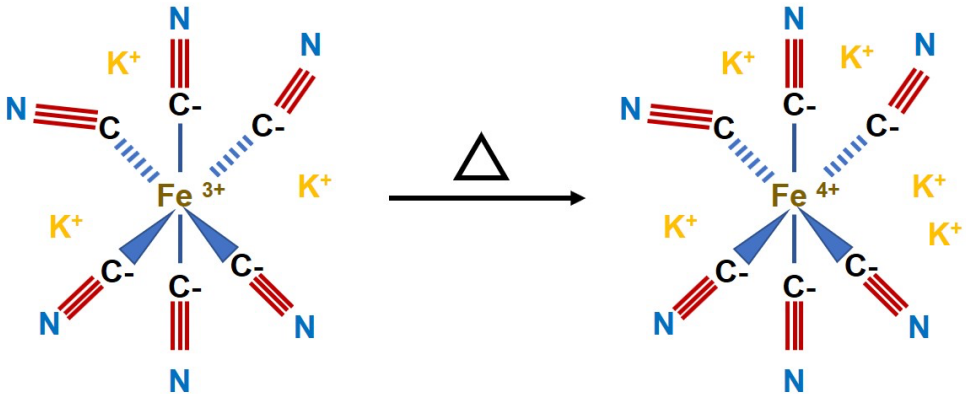

Figure 1. Potassium ferricyanide reaction mechanism in aqueous solvent.

where r is the average grain radius (m), and N is the density of nucleation centres (m^{-2}).

Ferricyanide or Hexacyano ferrate (III) is a widely studied molecule in the electrochemical process for biological and engineering applications (Cheah & Chernev, 2021). Also, this chemical compound was used as a stabilizer in electroless copper electrodeposition in EDTA/THPED. Lu *et al*. observed that potassium ferricyanide delays the deposition of Cu. They stated that this behaviour is due to the competitive adsorption between ferricyanide and OH- species (Lu *et al*., 2019). Interestingly, it has been demonstrated that highly ordered pyrolytic graphite compounds could be electrochemically analyzed using ferricyanide to calculate kinetic parameters and obtain gravimetric capacitance (Iamprasertkun *et al*., 2020). So, ferricyanide has been extensively used, as an electroactive specie, to elucidate electrochemical reactions, and D is commonly measured by cyclic voltammetry or CA.

Thus, it can be inferred that D can be determined either by using expensive and often unavailable equipment or by solving complex equations using a numerical approach with experimental data as input. On this matter, research groups worldwide have shown a growing interest in adopting GAs to solve non-linear equations with multiple unknown variables (Gao & Lu, 2021; Li & Zhao, 2021; Song *et al*., 2020; Y. Zhang *et al*., 2020). A prominent work was developed by Zhu *et al*., where an EIS model was recognized via a machine-learning support vector. The research showed that machine learning has tremendous potential in electrochemical research because this approach can efficiently figure out the values of unknown variables and can be used to optimize electrochemical parameters as was observed in (Zhu *et al*., 2019). Artificial intelligence has also been adopted to identify degradation parameters in lithium-ion batteries through experimental EIS measurements (Zhang *et al*., 2020). State of charge and state of health are some of the main battery parameters studied, which can be obtained by analyzing the EIS data determined with an equivalent circuit model (Choi *et al*., 2020). In this sense, machine learning has been adopted because it allows the computation of more than three variables simultaneously with good precision in a reasonable time. It should be mentioned that EIS equations are highly non-linear, and numerical solutions can also be adopted, but this is highly time-consuming. According to the aforementioned information, GA plays a vital role in current days because it can be implemented in real-world applications such as the prediction of electrical energy generation from photovoltaic systems, waste management, trajectory, scheduling optimization, and so on (Gallego-Martínez *et al*., 2022; Lara-Cerecedo *et al*., 2023; Pourreza Movahed *et al*., 2020).

In this work, it is proposed for the first time the implementation of GA to solve the multi-objective Cottrell equation considering three unknown variables: i) n, ii) C, and iii) D. The input of the functions was the current (i), measured from CA experiments. To this end, we use the experimental data of the electrochemical redox process of potassium ferricyanide at the surface of the Pt working electrode. From Figure 1 it can be seen that the potassium ferricyanide ($K_3Fe(CN)_6$ molecule has three potassium cations and one ferricyanide anion (Menolasina, 2005). It should be noted that when potassium ferricyanide is in an aqueous solution, the bond between the cyanide and potassium is broken and tends to form octahedrally coordinated $[Fe(CN)_6]^{3-}$ ion. Furthermore, this coordination compound is easily oxidized by adding a K^+ ion to form potassium ferrocyanide or by adding electrons. In this regard, experimental chronoamperometry data was used to study the potential of GA to obtain the electrochemical parameters.

The algorithm was solved with the aid of the Matlab software optimization Tool kit. The results confirmed that machine learning is a powerful tool

with the capacity to solve variables with great accuracy in a short time. Thus, this work demonstrated the versatility of GA to solve electrochemical equations fed with experimental data, obtaining the parameters of interest to understand the electrode-electrolyte phenomena. The main contribution of this work was the parameter extraction from a simple and rapid technique using commercially available software with a Toolbox designed to conduct optimization tasks. The former is relevant because practitioners do not need to have special training in programming and they can focus on proposing the boundaries for the parameters. Furthermore, researchers could use homemade electrochemical boards to conduct cyclic voltammetry and CA tests to estimate electrochemical parameters. It should be emphasized that the proposed methodology can be used to solve other electrochemical problems such as electrochemical impedance spectroscopy data extraction, fuel cell data model identification, and so on. The research questions are: how convenient is using GA to determine electrochemical parameters from a chronoamperometric date set? and what are the benefits of adopting a commercial GA toolbox?. Herein, the methodology section explained in detail the procedure implemented to solve the multivariable Cottrell equation, while the analysis of the obtained data was discussed in the result section. Finally, future work was presented in the conclusions section.

2 Theoretical background and related works

A GA is an optimization and random search technique based on evolution theory and natural selection, and this idea was used for the first time by John Hollan 1970s (Koohestani, 2020; Nguyen *et al*., 2022). This approach starts with random individuals or chromosomes from a population that evolves through recombination and mutation to produce offspring which inherit the best parents' characteristics (Gao & Lu, 2021; Katoch *et al*., 2021). Because the offsprings are better than the parents they have more chances to survive. This idea was adopted to minimize or maximize a fitness mathematical function where the best values are founded by conducting an iterative process. The fitness function is the function that uses the best individuals to produce an improved output. The search space of solutions to achieve the optimization problem is computed by considering two main operators: i) crossover and ii) mutation.

The crossover operator takes chromosomes to produce new offspring by recombining their parents, expecting an individual with the best characteristics of their ancestors (Kannan *et al*., 2010; Maghawry *et al*., 2021). Therefore, this operator extracts the best attributes or information of both parents, resulting in an enhanced generation that may reduce the exploration time. There are different types of crossover such as single-point, two-point, and multi-point crossover operators and this depends on the number of points chosen where the genetic material will be exchanged. For example, in the two-point crossover, two random points will be selected.

Meanwhile, the mutation operator modifies the genes of a single individual to create a new chromosome (to extend the range of searching) which is part of the new generation, all this to reduce the search time. Mutation operators maintain diversity by introducing variation, which avoids local optimal. The crossover operator has been reported to be vital in improving the GA because it minimizes the number of genotypes in the predefined population (Skobiej & Jardzioch, 2019). In this regard, researchers have been developing and proposing several crossover functions to improve the robustness of the GA. Because crossover is responsible for creating a new solution from the recombination of chromosomes, the study of different crossover proposals is normally found in the literature to find the best algorithm that satisfies the stop criteria in a shorter time. For instance, Pinho and Saraiva analyze the effect of three crossover operators (one-point, multi-points, and uniform crossover) in the GA applied in selecting switch allocation in a power distribution system (Pinho & Saraiva, 2020). The authors have found that multi-point crossover does not significantly alter the processing time as the number of points increases. Instead, an improvement in the optimization problem has been observed.

The Heuristic crossover operator is another well-known function widely employed in evolutionary algorithms. This operator produces an offspring that is in line with the best parent, and its displacement depends on the fitness function of two parent chromosomes, according to the following equation:

$$\text{offspring} = \text{Best parent} + \beta(\text{best parent} - \text{worst parent}) \tag{3}$$

where β is a random number between 0 and 1.

Muyiwa *et al*. have studied the effect of the Heuristic crossover in an evolutionary algorithm applied for clustering wireless sensor networks (Oladimeji *et al*., 2017). The results show that this operator improves the optimization problem aiming to reduce and balance energy consumption among sensors and equipment. Meanwhile, the Laplace crossover is a function commonly used in real-coded GA which follows the Laplace probability distribution (ul Haq *et al*., 2020). This probabilistic distribution is also called the double exponential distribution. Interesting work has been developed by Mouhamed *et al*., where Heuristic GA solves a multi-

objective optimization problem. The authors compare the Heuristic and the two-point crossover operators, finding that the former performs better (Ouamri & Azni, 2019).

In this sense, Postolov *et al*. have implemented a metaheuristic approach based on the Laplace crossover to solve the optimization of a short-term hydro-thermal-solar problem (Postolov *et al*., 2022). A pair of offspring have been generated from their parents by considering a uniformly random number. The numerical results show that the optimized parameters increase the feasibility and reduce the cost of the system. From the literature review, it can be deduced that this is the first attempt to use GA to solve the Cottrell equation and in this way obtain the electrochemical parameters. Although there are other developed optimization algorithms this work focuses on studying the GA and the effect of population size and crossover operator. A commercially available optimization toolbox (Matlab) was utilized as a strategy to conduct GA operations; the latter can motivate practitioners with limited skills in programming to adopt this methodology to solve engineering problems in their field.

3 Methodology

The proposed optimization problem for variable searching consisted in an algorithm that minimizes the multi-objective function and performs a local optimal search. A set of chronoamperometric data extracted from the literature (Pine-Instrument-Company., 2000) was used to assess the versatility of GA. The data set is part of the well-known reference guide for electrochemistry developed by Pine Instrument where the setup and data analysis of different electrochemical tests are explained in detail. The selected CA signal corresponds to the electrochemical reaction of potassium ferricyanide on the Pt working electrode surface. The best possible solution was determined by calculating the error of each model. The optimization toolbox setup is very friendly and asks about some terms such as Pareto and crossover fraction. The first is related to the fraction of elite members to keep on the Pareto front while the crossover fraction indicates the parent population fraction involved during the offspring. To find the best solution, the iterative GA considered that the fitness individuals or chromosomes have a crossover fraction of 0.5, while the Pareto set fraction was set to the same value. This setup guarantees diversity between each generation (Hassanat *et al*., 2019). The selection function was set to the tournament and mutation was adapt feasible, generating random adaptative directions for the last generation.

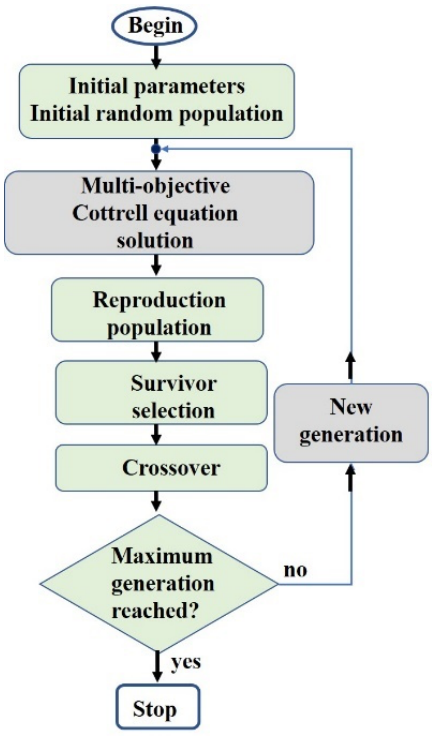

Figure 2. Basic flow chart for the GA.

The Cottrell equation was solved by considering no constraints, and the upper and lower bond for [n, C and D] were [1, 0.5×10^{-3}, 1×10^{-6}] and [2, 10×10^{-3},11×10^{-6}], respectively. To determine the population size effect different random individuals were used to initiate the algorithm in each trial run. So, the population size was investigated from 500 to 2500 in accordance to (Sipper *et al*., 2018). This population was considered constant throughout the simulation. Furthermore, the crossover genetic operator was also changed to study the effect of the optimal search result. This was done to study the advantages of each optimization process.

The stopping criteria, when the code reached the maximum generation number, was set to 600. The aforementioned value was determined by conducting a preliminary computing test and was concluded that 600 generations give sufficient data with acceptable computing time. It should be mentioned that generations more than this value are very time-consuming and there was no significant difference in the determined error. The robustness of the optimal solutions where evaluated by the crowding distance which measures the closeness of an individual to its neighbors. The simulations were executed with the commercially available Matlab optimization Tool kit (Community and technical college license) using a computer with 16 GB of RAM and a 5 GHz processor. Because GA is a statistical procedure, the best fitness values solution in each case was determined by considering the simulated function's deviation with

the experimentally measured curve. Thus, the RMSE was calculated for each solution. In the case of n, the chromosomes were set to obtain only integer values. Figure 2 shows the implemented flow chart to solve the Cottrell equation using GA in Matlab. The initial parameters were the problem function definition, followed by declaring the population size and the algorithm setting for the crossover function.

4 Results

The Cottrell equation is solved considering three unknowns: n, C and D. It needs to be highlighted that in some cases, the user may have knowledge of the experimental variables, for example, the analyte concentration. However, to assess the powerfulness of GA, it is considered here that no information related to the parameters is available. In other words, the potassium ferricyanide is considered unknown. For this purpose, the Cottrell equation is written as a multi-objective problem as follows:

$$\begin{cases} f_1(n,C,D)=0 \\ f_2(n,C,D)=0 \\ f_k(n,C,D)=0 \end{cases} \rightarrow \begin{cases} F_1 = min(abs(f_1(n,C,D)=0)) \\ F_2 = min(abs(f_2(n,C,D)=0)) \\ F_k = min(abs(f_k(n,C,D)=0)) \end{cases} \quad (4)$$

where k is the last declared function, the algorithm synchronously calculates all the equations considering the fitness function (the experimental curve) during optimization. In other words, the multi-objective function is created by declaring various equations considering the current and time values extracted from the experimental curve. It must be emphasized that the number of objective function greatly affect the final response of the GA. Using a small number of element lead to D and C values with considerable errors. The full syntax can be seen in the supporting information document. Also, a brief description of the Matlab Optimization Toolbox can be consulted in this document.

The error of each computed case is calculated by using the general machine learning error function (Wang *et al.*, 2021):

$$RMSE = \sqrt{\frac{\sum_{i=1}^{N}(f(n,C,D,X))^2}{N}} \quad (5)$$

where x denotes the solution, and i is the number of data points in the experimental curve. The code for the evaluated function has been written in Matlab as follows:

```
Function y=Cottrell(x)
F=96485
A=0.1963
%Iex= declare the experimental value of
the current at a certain time
%t= declare time
y(1)=min(abs((A.*x(1).*F.*x(2).*
sqrt(x(3))./(sqrt(pi.*t))-Iex));
...
y(i)= min(abs((A.*x(1).*F.*x(2).*
sqrt(x(3))./(sqrt(pi.*ti))-Iexi))
```

Table 1 summarizes the average simulated values for the three electrochemical parameters estimated from the Cottrell Equation. It can be noticed that a small population size has a negative impact on all the implemented crossover functions. Implementing a small population obviously leads to a rapid loss of genetic diversity compared to a large one, because individuals have more chances to mate with close relatives. The latter may result in a population extension presented as a local optimum. Hassanat *et al.* have conducted a deeper study regarding the effect of population size on the optimization of the traveling salesperson problem (Hassanat *et al.*, 2019). They studied three populations: i) small, ii) moderate, and iii) large. The authors conclude that large populations provide diversity that ultimately guarantees global optima. They also found a significant mutation rate when a small population is implemented and vice versa in large populations. It is important to remember that in some cases, large population sizes do not improve accuracy but significantly impact the computational time (Roeva *et al.*, 2013).

Table 1. GA algorithm parameters and average convergence using different approaches.

Crossover function	Population size	n	C (1×10^{-3}, mol cm^{-3})	D (1×10^{-6}, cm^2 s^{-1})	RMSE (1×10^{-3})
Intermediate	500	1	3.061±0.192	5.872±0.643	1.6113±0.0185
	1000	1	2.911±0.051	6.494±0.181	1.6112±0.0427
	1500	1	2.684±0.074	7.641±0.285	1.6112±0.0181
	2000	1	2.713±0.122	7.476±0.443	1.6112±0.0323
	2500	1	2.740±0.115	7.333±0.465	1.6112±0.0324
Heuristic	500	1	3.728±0.167	3.962±0.393	1.6112±0.0435
	1000	1	2.659±0.101	8.162±0.365	1.6112±0.0323

	1500	1	2.872±0.080	6.672±0.1833	1.6112±0.0122
	2000	1	2.763±0.075	7.208±0.253	1.6112±0.0034
	2500	1	2.610±0.019	8.299±0.0163	1.6112±0.0248
Laplace	500	1	3.098± 0.173	5.735± 0.603	1.6112±0.0185
	1000	1	2.856± 0.018	6.748± 0.192	1.6112±0.0028
	1500	1	2.369±0.104	9.806±0.710	1.6112±0.0181
	2000	1	2.735±0.075	7.357±0.671	1.6112±0.0039
	2500	1	3.701±0.361	4.018±0.717	1.6112±0.0063

According to the calculated RMSE the intermediate crossover function delivers the lowest performance when the population size is set to 500. Intermediate crossover creates children as a random weighted average from their parents, as indicated by the following equation (Hakimi *et al*., 2016):

$$\text{offspring} = \text{parent1} + \text{rand} * \text{ratio}(\text{parent2} - \text{parent1}) \quad (6)$$

where x denotes the solution, and i is the number of data points in the experimental curve.

So, under a small population, this operator loses diversity, resulting in convergence in the local optima. On the other hand, Heuristic and Laplace crossover show better performance, attributed to their versatility in choosing the best springs. Moreover, all the obtained solutions fit well with the experimental curve with a non-significant error. Some explanation of this phenomenon is that GA can search for multiple solutions to optimize the problem. Since this work considers three unknown variables, GA provides accurate solutions. The obtained optimized electrochemical model has been compared with the values reported in the Pine Instrument reference guide for electrochemistry (Pine-Instrument-Company., 2000). The mentioned document uses two electrochemical techniques to extract the electrochemical parameters: cyclic voltammetry and chronoamperometry. First, the species concentration was calculated from the analysis of a set of cyclic voltammetric measured at different scan rates. Then, the D coefficient was obtained by substituting the C value and the determined slope from the Cottrell plot in the rearranged equation 1. The comparison was achieved by using the simulated data to construct the chronoamperometric curve and the experimental one (see Figure 3). The curve can be divided into three regions that correspond to transient (I), quasi-transient (II), and stable behaviour (III).

As can be seen, the calculated values match well with the experimental curve of the potassium ferricyanide reaction at the Pt surface. Only a small shift is observed in region I due to the contribution of non-Faradaic currents. So, it is highly recommended that the determination of electrochemical parameters by GA is achieved considering the fitting function that corresponds to regions II and III. Actually, this has been a topic of discussion, and some authors propose using double-potential step chronoamperograms as a feasible approach to incorporate the contribution of the diffusion coefficient of the substrate and the products during the evaluation of an electrode process (Hyk *et al*., 2002; Ikeuchi & Kanakubo, 2000).

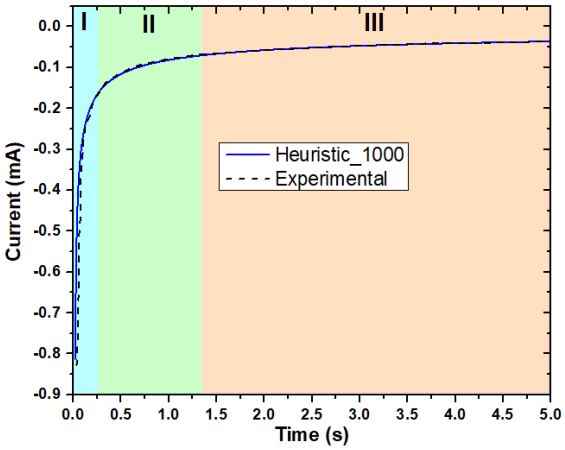

Figure 3. Validation of the calculated data with the experimental chronoamperogram.

Reports in the literature show that D of potassium ferricyanide, calculated from experimental data, can be in the 6.0 $\times 10^{-6}$ to 8 $\times 10^{-6}$ cm^2 s^{-1} interval, depending mainly on the experimental electrochemical test (Pine-Instrument-Company., 2000). For example, a comparison of D values determined from experimental cyclic voltammetry and CA measurements has resulted in 6.057 and 8.19 cm^2 s^{-1}, respectively. Theoretical data demonstrate that most scenarios with the different crossover functions produce D values within the experimental range indicated here. It is to be noted that trial runs with small population sizes display values lower than such range. This behavior has been attributed elsewhere to the lack of individuals that could start mating to form a new optimal generation (Bărbulescu *et al*., 2021; Hassanat *et al*., 2019). Interestingly, when a large population is implemented, the crossover Laplace algorithm shows poor performance in the estimated values. This algorithm is based on the density function Laplace distribution and comprises the location (a) and scale parameters (b), see equation 7. Here the γ coefficient is calculated according to a random number denoted by u. If u is equal or less than 0.5

then $\gamma = a + b * \log(u)$, else $\gamma = a - b * \log(u)$.

$$\text{offspring} = \text{parent1} + \gamma(\text{parent1} - \text{parent2}) \quad (7)$$

When a large population is used, parents are expected to be more random and this is also negatively affected by the γ coefficient which also depends on a random u number, which results in shifted offspring (Katoch *et al*., 2021; Wang *et al*., 2019). This phenomenon was also deeply discussed by Kusum *et al*. who stated that the large b values produce offspring far from their parents (Deep & Thakur, 2007). Considering the aforementioned drawbacks and having in mind the Laplace crossover has many parameters Zhang *et al*. (2020) proposed an improved Laplacian algorithm that improves exploitation and convergence speed.

Figure 4 displays the simulated curve, for potassium ferricyanide reaction, by considering the n, D and C values of 1, 8.19 $\times 10^{-6}$ cm^2 s^{-1}, 2.55 mmol L^{-1}, respectively (Pine-Instrument-Company., 2000). Using the parameters from the literature, it can be observed that the simulated curve also has a displacement in the region I. This feature confirms the fact that the best fitting can be obtained considering regions II and III. This outcome is rather evident, considering that it is almost impossible to know the electrochemical behavior in the transient response.

Considering the parameters' values obtained using the proposed GA, it can be confirmed that the redox couple for ferricyanide occurs by the transfer of one electron. The chemical reaction is achieved according to the following equation (Guo *et al*., 2019; Iamprasertkun *et al*., 2020):

$$[Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-} \quad (8)$$

The ferricyanide anion is adsorbed at the Pt surface, and a single electron is added to reduce the molecule at $Fe(CN)_6^{4-}$ (see Figure S1). The latter causes iron changes its valence state from 3^+ to 4^+, showing a reversible process with a formal potential close to 400 mV vs. the standard hydrogen electrode. Thus, it can be seen that GA can also be used to explain chemical or electrochemical reactions. For example, Charles and coworkers used GA to elucidate chemical reaction networks using species concentration data from batch reactions (Hii *et al*., 2014) while Reiser *et al*. use GA to determine chemical reactions in plasma-assisted methane conversion (Reiser *et al*., 2021). Ferricyanide is commonly implemented as a redox mediator because it exhibits a homogeneous one-electron redox process. From equation 8 and Figure 1 it is evident that the interaction of electrolyte cation species with ferricyanide can slow the chemical process.

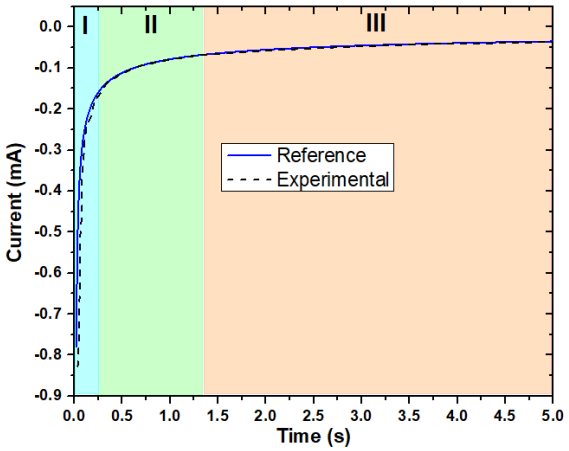

Figure 4. Experimental and simulated curves were plotted considering the reported values of n = 1, D = 8.19 $\times 10^{-6}$ cm^2 s^{-1}, and C = 2.55 $\times 10^{-3}$ mol L^{-1}(Pine-Instrument-Company., 2000).

It should be mentioned that ferricyanide-based electrolytes have been widely used as a standard test to study the electrochemical properties of nanomaterials. For example, Lamprasertkun conducted systematic studies to understand the electrochemistry of highly ordered pyrolytic graphites (Iamprasertkun *et al*., 2020). This group observed a better reversible process for the ferricyanide at high concentrations and dependence of the diffusion coefficient with the concentration. They reported that the D of ferricyanide at the interval of 0.5 to 5 mol L^{-1} is in the range of 2.49×10^{-6} and 7.87×10^{-6} cm^{2}s^{-1}. Similar D values were also reported in the literature for related electroactive solutes, and the authors stated that the electrochemical process is achieved by one-electron (Guo *et al*., 2019). Thus, these results provide fundamental insight into the extensive applicability of GA approach in chemical engineering problems.

Figure 5 compares the computed curve (using the calculated CA parameters from the GA results) and the experimental one. The graph only presents the computed plot of the proposed algorithms with the smallest RMSE. Results from the set of experiments show that the Heuristic crossover operator delivers the best performance in terms of fitting with the experimental data. The best performance not only means better fitting. It also represents the ability of this algorithm to maintain the average RMSE at low values regardless of the size of the population used. As can be seen in almost all cases, the performance of the Heuristic operator is better than the other proposed methods. In other words, the crossover Heuristic function allows parameter estimation with high precision in a short time. Actually, the modelled curve from the Heuristic crossover surpasses the performance of the curve computed by using the parameter values estimated by reference (Pine-Instrument-Company., 2000). This

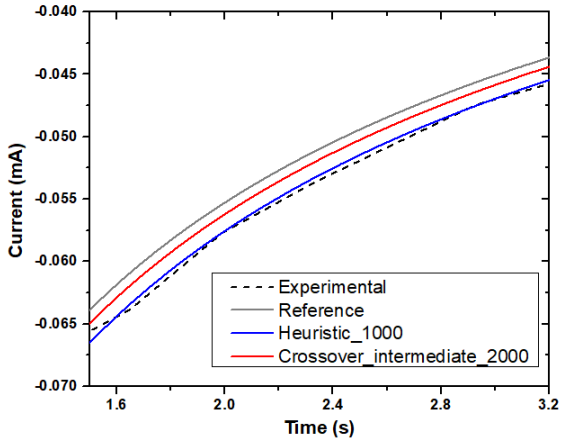

Figure 5. Comparison of curve fitting in region III, using the proposed algorithms.

fact is an outstanding result considering that the multi-objective optimization problem involves three unknown variables.

According to equation (3), the Heuristic crossover is completely different from the intermediate and Laplace operators because the beta parameter multiplies both the factor and the subtraction process of genes from their parents. This provides relevant advantages for the Heuristic operator because it allows for keeping diversity over the whole timeline.

Due to the versatility of Heuristic crossover function in selecting elite individuals, this operator has been widely proposed to modify and study new evolutionary algorithms. For example, Rezaeipanah *et al*. (2021) adopted a hybrid parallel GA to solve timetabling problems. The study shows the advantages of such a crossover algorithm over the uniform and local search functions.

From the results of this work, it can be observed that the crossover operator plays a vital role in the solution of multi-objective optimization problems, and a novel function proposal can reduce the time computing without compromising the accuracy of the results. For instance, a recent work proposed a hybrid GA that uses adjusted and random-order crossover operators to search for the optimal solution in less computational time (Hvattum, 2022). From the above-mentioned discussions, it can be inferred that GA can be applied to several chemical and electrochemical processes either to extract unknown variables or to optimize the most important ones (Hii *et al*., 2014; Reiser *et al*., 2021). The main drawback of this process is the obtention of the mathematical equation or the model that explain the behavior of the phenomena under study.

Conclusions

The present work introduced students to the implementation of a GA using commercially available software to solve the multi-objective Cottrell equation considering three unknown variables: n, C and D. Potassium ferricyanide compound was used as electroactive species, and the CA curve was used to estimate the electrochemical parameters.

To this purpose, the effect of population size and crossover function was studied, focusing on the feasibility of estimating the parameters of interest. The simulation results showed that almost all the trial runs satisfied the expected values (values reported in the Pine Instrument guide). It was observed that population size is a critical factor in the solution of the optimization problem. Moreover, the Heuristic crossover function showed the best performance in terms of fitting for the estimation of parameters. Regarding the research questions it can be concluded that GA is a convenient strategy to determine electrochemical parameters by solving the mathematical equation iteratively and the use of commercial Toolbox permits the practitioner to focus on proposing the boundaries and then data analysis.

Future work includes developing open-access GA codes with an emphasis on the resolution of electrochemical parameters and proposing a user-friendly configuration. Although the Matlab Toolbox works nicely this can be improved by incorporating novel algorithms related to crossover and mutation operators. Besides, statistical analysis might be very convenient to consider.

One limitation of this work could be that practitioners need to know about the physical parameters of the experiments. The main advantage of machine learning was found to be that it is possible to use a large span when upper and low boundaries are declared, compared with numeric methods. But this can be a problem because some optimal solutions might not have real meaning. Although this is a disadvantage of the GA, in real-world applications the users normally know their process and the expected values. For example, if we are dealing with electrochemical impedance spectroscopy parameters identification in batteries the boundaries can be chosen according to the shape of the Nyquist plot.

It should be mentioned that the proposed methodology can be applied to solve other engineering problems such as electrochemical impedance spectroscopy parameters estimation, identification of fuel cell model parameters, and other real-world and hot-topic applications such as batteries and electrolyzers.

Acknowledgment

The authors thank the Polytechnic University of Victoria for providing time and equipment to develop the study.

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