Neural networks approach for simulation of electrochemical impedance diagrams

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A new approach of data simulation using neural networks (NN) has been proposed for electrochemical impedance spectroscopy, applied for copper electrodeposition from sulphate acidic electrolytes. The trained NN, with data obtained in different experimental conditions (electrode potential and thiourea concentrations), have been used to generate impedance spectra for new electrode potential values, within the investigated potential range, as well as to estimate the maximum frequency value on Nyquist plot, by generating supplementary output data for new frequency values, inside the investigated domain of frequencies.

The electrochemical impedance spectroscopy (EIS) is one of the most powerful techniques for investigating the metal electrodeposition and for obtaining kinetic information concerning the elementary steps involved in the electrochemical process. The most frequent approach, used for obtaining quantitative information on the metal electrodeposition mechanism is the simulation of the system impedance considered as a dependent variable of the frequency and of the dc electrode potential. First step in the simulation procedure is to propose an a priori reaction model for the overall electrode process that will be, in a second step, expressed in terms of faradaic impedance components and current density. The main goal of the simulation procedure is to find values of those parameters of the proposed model, which best describe the experimental data. The simulation’s performance is evaluated either graphically, by comparing the calculated impedance diagrams with the experimental ones, or quantitatively, using the mean square error calculation as a performance criterion. The main disadvantage of this approach is that with increasing model complexity, the mathematical solution becomes more and more difficult requiring far reaching simplification.

The neural networks (NN) may be successfully used for modelling systems in which detailed governing rules are unknown or are difficult to formalize, but the desired input-output set is known. On the other side, NN have a remarkable ability of learning, generalization and robust behaviour in the presence of noise.

In this context, a new approach to improve the EIS data simulation for copper electrodeposition by means of NN is proposed. The trained NN, with data obtained in different experimental conditions (electrode potential, and thiourea concentrations), were used: (i) to generate impedance spectra for new electrode potential values, within the investigated potential range, as well as to estimate the maximum frequency value on Nyquist plot, by generating supplementary output data for new frequency values, inside the investigated domain.

Materials and Methods

Electrolyte

A stock solution of acidic copper sulphate was prepared using pure reagents (Merck) and distilled water. The stock solution contains 30 g/l CuSO₄ as CuSO₄ and 100 g/l H₂SO₄. Solutions with various amounts of thiourea concentration (10, 25 and 50 mg/l) were prepared using the stock solution.

Electrochemical measurements

The experimental set-up for impedance spectroscopy measurements consisted of a three-electrode cell, a potentiostat (PS 3 Meinsberg, Germany) and a data acquisition system (Olivetti AT 486 DX computer with a National Instruments AT MIO16 T5 acquisition board). The working electrode was a copper disc electrode (Ø = 3 mm). To ensure reproducibility
between experiments, the exposed surface was polished with 600 and 1200 grit paper, and rinsed with distilled water. For controlling the mass transport, the working electrode was rotated at 1000 rpm. The counter electrode was a platinum foil and a saturated calomel electrode (SCE) was used as reference electrode. Impedance diagrams were recorded in the Nyquist coordinates system, in the 6.8 kHz and 0.022 Hz frequency range, at different potentials between -75 and -175 mV vs. SCE with 25 mV increment. In order to improve the accuracy, measurements were automatically repeated up to 20 times, especially for high frequencies measurements. As a consequence, the extension time of the measurements was more than 2 hr.

Neural networks

The employed NN architecture was of the multi-layer feed-forward structure with back propagation training algorithm used for computing the network biases and weights. Two layers of neurons have been considered, having the tan-sigmoid transfer function for the hidden layer and the purelin transfer function for the output layer. The quasi-Newton Levenberg-Marquardt algorithm was used for training the NN and an early stopping method was applied for preventing the NN overfitting and for improving generalization.

Results and Discussion

The investigated system has been considered as having three input variables: the d.c. amplitude component of the sinusoidal applied voltage, the signal frequency and the thiourea concentration. The d.c. amplitude component of the obtained sinusoidal current together with the real and imaginary components of the resulting electrochemical impedance have been taken as output variables. First, the NN have been used for investigating the prediction ability of the trained NN to infer the output variables corresponding to input data not present in the training set, i.e. to generate new values of the system response, for inputs different from the experimental data used in the training step.

For this purpose, in a first attempt, the frequency range used both to train and to test the NN prediction ability, was restrained to the interval from 2.2 Hz to 6.8 kHz. The set of experimental data has been divided in two subsets: one for training the network (90% of the available data) and the other for testing its generalization ability (rest of 10% of the available data). The testing subset has been extracted uniformly distributed within the original experimental set. It can be seen from Fig. 1, for output current amplitude, and in Fig. 2, for the electrochemical impedance (as Nyquist plots), a good fit between the experimental and NN simulated data, proving that a successful training was achieved.

As the good agreement between the experimental and NN simulated electrochemical impedance, in the frequency range from 2.2 Hz to 6.8 kHz is good, the same procedure was applied for an extended frequency range, namely from 0.022 Hz to 6.8 kHz.

![Fig. 1—Comparison between experimental and NN simulated data, for absolute values of current. Experimental conditions: sinusoidal frequency ranging from 2.2 Hz to 6.8 kHz, thiourea concentration, 10 mg/l.](image)

![Fig. 2—Nyquist plot presenting the comparison between experimental and NN simulated data. Experimental conditions: sinusoidal frequency ranging from 2.2 Hz to 6.8 kHz; thiourea concentration c=10 mg/l.](image)
The obtained results are presented in Fig. 3, for a
given thiourea concentration and at three different
electrode potentials. As it can be seen, the
concordance between the experimental and NN simulated data is better for the first capacitive loop,
corresponding to the charge transfer, than for the
second one, attributed to the adsorption of an
intermediate species on the electrode surface. The
discrepancies observed in the domain of the second
loop could be due to the longer duration of the
experiment at low frequencies than that at high
frequencies (first loop), and, consequently, to a
decrease of the reproducibility due to the electrode
surface growth.

In order to test the NN generalization capability,
the second subset of experimental data (10% of the
original experimental set) was operated. A
comparison between the experimental and NN simulated data
for the two frequency ranges (0.22 Hz to 6.8 kHz) and
for all output variables: current amplitude, real part
and imaginary part of the electrochemical impedance
shows a good prediction capability of the trained NN.
The agreement between experimental data and NN
simulated data for current amplitude is found better
than that for real and imaginary part of the electro-
chemical impedance at both frequency ranges. How-
ever, among the two frequency ranges, the results
in the case of restrained frequency range (2.2 Hz
to 6.8 kHz) are better. The reason for this may be
more complex behaviour of the system in case of the
wider frequency range.

Additional investigation has been performed to
study the prediction capability of the trained NN for
generating outputs of the electrochemical system for
input variables having values situated between the
experimental values used in the training or testing
steps. Thus, different values for the dc amplitude and
for the frequency of the input electrode potential have
been supplied to the NN and the obtained results are
presented in Figs 4 and 5.

The obtained results fit to a shape in conformity
with the expected one (qualitatively inferred by in-
duction) for the electrochemical impedance. This
agreement proves that trained NN were able to predict
well the electrochemical impedance of a complex
system, otherwise more difficult to be described using
analytical models.

The prediction capability of the trained NN was
also exploited to provide exact values for important
parameters used for electrochemical system charac-
terization, i.e. the double layer capacitance, the
electrolyte resistance etc. Thus, in a first attempt, the
frequency corresponding to the apex of the first capaci-
tive loop from the Nyquist plot was estimated. An
example is presented in Fig. 6, where, using the NN
predicted values of the real and imaginary part of the
electrochemical impedance, it was possible to evaluate
with an improved precision the frequency corre-
sponding to the apex (280.746 Hz) than in the absence
of these supplementary values of electrochemical
impedance.
Fig. 5—Nyquist plot presenting NN predicted values of the electrochemical impedance for different input values for the electrode potential. Experimental conditions: sinusoidal frequency ranging from 0.022 Hz to 6.8 kHz; thiourea concentration c=10 mg/l.

In all investigated cases, the trained NN present a good fit between the NN simulated output data (network response) and the original experimental process data (targets) of the training subset (correlation coefficients exceeding the value of R=0.99). The favourable fit was also preserved for the testing subsets of data, demonstrating a good generalisation property of the NN (correlation coefficients exceeding the value of R=0.96).

Conclusions

The large potentiality offered by the NN for modelling the complex process behavior was investigated for the case of copper electrodeposition. The obtained results present certain incentives for the use of this method, because, in spite of the complex mechanism governing the process, the level of predicted values accuracy was acceptable.

Results show a good ability of the NN to be trained using the experimental data set and a good capability to use the assimilated knowledge for generalization. When tested on data not met in the training step, the results show excellent fit for the output current amplitude and good fit for the real and imaginary parts of the electrochemical impedance. It is worth mentioning that, as the process becomes more complex, for example at frequencies corresponding to the second impedance loop, the success of obtaining good results strongly depend on the level of confidence of the training set of experimental data. Nevertheless the trained NN, by itself, may be used to point out possible outliers of the training or testing set of data and propose them for filtering.

The aptitude of the NN to generate the response of the system for input values, different from the training set, with fairly good accuracy, may be highly appreciated. Its use offers the possibility to enrich the usually limited experimental set of data, as the governing rules are intrinsically contained in the trained NN structure. For example, a better estimation of the frequency corresponding to a maximum on the electrochemical impedance Nyquist plot is just one of the possible answers supplied by the NN.

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References