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Research Article

Some Applications of Bayes' Rule in Probability Theory to Electrocatalytic Reaction Engineering

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Bayesian methods stem from the principle of linking prior probability and conditional probability (likelihood) to posterior probability via Bayes' rule. The posterior probability is an updated (improved) version of the prior probability of an event, through the likelihood of finding empirical evidence if the underlying assumptions (hypothesis) are valid. In the absence of a frequency distribution for the prior probability, Bayesian methods have been found more satisfactory than distribution-based techniques. The paper illustrates the utility of Bayes' rule in the analysis of electrocatalytic reactor performance by means of four numerical examples involving a catalytic oxygen cathode, hydrogen evolution on a synthetic metal, the reliability of a device testing the quality of an electrocatalyst, and the range of Tafel slopes exhibited by an electrocatalyst.

1. Introduction

In a comprehensive overall treatment of the subject matter, Bockris and Khan [1] discuss electrocatalysis with respect to various physicochemical properties of substance and surface, for example, exchange current density, work function, bond strength, metal complexes, trace elements adatom effects, enzymatic catalysis, poisons, crystal face effects, and so forth, under the aegis of "phenomenological electrode kinetics". In the domain of ERE, the assessment of electrocatalyst (EC) performance also includes additional parameters related to catalyst preparation (i.e., possible defectiveness in specimens), cell construction, and human factors affecting reactor output.

This paper was written with this dichotomy in mind, from the vantage point of the electrochemical engineer, whose responsibilities dealing with production quota, the possibility of (temporary) reactor breakdown, safety, and environmental considerations reach well beyond purely scientific quantities. Major tools for dealing with these responsibilities are provided by probability-based (e.g., statistical) methods. Bayes' rule is one such tool, whose specific application to scenarios with EC is the subject of this article.

2. Brief Theory

Following a concise definition [2] for the purposes of this paper, Bayes' rule for two events may be expressed as

$$P(A/B) = \frac{P(B/A)P(A)}{P(B)}, \tag{1}$$

where $P(A/B)$ is the probability of event A occurring if event B has already occurred, and

$$P(B) = P(B/A)P(A) + P(B/A')P(A'), \tag{2}$$

which is the probability of event B occurring, given the conditional probabilities (likelihoods) $P(B/A)$ relating it to event A and $P(B'/A)$ relating it to its opposite event A'. In an EC reactor a case for Bayes' rule would exist, for instance, when the loss of effectiveness in an EC may or may not be due to premature detachment of the catalytic layer. If A is the event of detachment and B is the event of deterioration (demise) of the EC, then B/A would be the event of demise due to layer detachment, A' the event of a nondetachment cause of deterioration, and B/A' the event of deterioration due to a nondetachment cause. In terms of event probabilities, (1) yields the probability $P(A/B)$ that

Table 1: Postulated distribution pattern of 137 failure occurrences over a fixed time period in three independently operating (hypothetical) electrolytic plants using identical catalytic oxygen cathodes (Application 1).

Source of failure	Number of cathode failures over a fixed period of operation		
	Plant 1 (B_1)	Plant 2 (B_2)	Plant 3 (B_3)
A_1: Catalyst surface area(1)	12	14	10
A_2: Pore volume(2)	7	8	9
A_3: Binder content(3)	9	5	7
A_4: Catalyst content(4)	6	4	5
A_5: Human error(5)	14	11	16
Total number of failures	48	42	47

(1) Electrolytic carbon type P33: specific surface area is less than stipulated 1000 m^2/g.
(2) Electrolytic carbon type P33: specific pore volume is less than stipulated 2.3 cm^3/g.
(3) PTFE binder content in electrode layer is less than stipulated 10%.
(4) CoTAA (dibenzotetraazaannulen cobalt II) catalyst content on carbon is less than stipulated 15%.
(5) Careless stack assemblage and general operation.

deterioration would occur as a result of layer detachment and not due to a different cause, for example, the decomposition of a binder, or the splitting of the electrode frame, and so forth. If $A_1, A_2, \ldots, A_n$ are mutually exclusive and exhaustive events, (1) and (2) are generalized to

$$P(A_k/B) = \frac{P(B/A_k)P(A_k)}{\sum_{k=1}^{n} P(B/A_k)P(A_k)}, \tag{3}$$

taking into account all possible causes of deterioration (the denominator of (3) is also known as the total probability theorem [3]). A lucid discussion of the merits of Bayesian methods by Bulmer [4] and a short set-theoretic proof by Arnold [5] are amply complemented by a sizeable literature on probability and statistics dealing with the subject matter.

Specific exploratory applications to electrochemical processes and technology at various levels of complexity are relatively recent [6–10]. The paper illustrates, via four independent examples, the (potential) utility of Bayes' rule in ERE. Due to the currently insufficient availability of appropriate experimental information in the research literature, hypothetical numerical data are employed with the sole purpose of indicating the course of analysis to which appropriate experimental data could be subjected. With the intention of stimulating at least a modest appetite at present for Bayes' rule, the illustrations are realistic but uncomplicated on purpose.

3. Illustration of the Utility of Bayes' Rule for ERE

3.1. Application No. 1: Estimating the Most Likely Location of Oxygen-Cathode Failure. Table 1 contains the failure-frequency map of identical oxygen cathodes, assumed to possess the structure described by Wiesener and Ohms [11]. These mutually independent failures are stipulated to have occurred in three independently operating electrochemical plants. Denoting $A_1, A_2, \ldots A_5$ as the source-of-failure events and B_1, B_2, B_3 as the plant location events, the probability of failure arising, for example, from human error is given by

$$P(A_5) = \sum_{k=1}^{3} P(A_5/B_k)P(B_k) = \frac{14}{48}\frac{48}{137} + \frac{11}{42}\frac{42}{137} + \frac{16}{47}\frac{47}{137} = \frac{41}{137} = 0.2993, \tag{4}$$

which is about 30%, and Bayes' rule:

$$P\left(B_j/A_5\right) = \frac{P\left(A_5/B_j\right)P\left(B_j\right)}{P(A_5)}, \quad j = 1,2,3, \tag{5}$$

yields the probability of failure in any one of the three plants caused by human error: $P(B_1/A_5) = 14/41 = 0.3415$; $P(B_2/A_5) = 11/41 = 0.2683$; $P(B_3/A_5) = 16/41 = 0.3802$. Thus, (next time) failure due to human error can be expected to be the least likely in Plant 2 and the most likely in Plant 3, although not significantly so with respect to Plant 1. The entire set $P(B_k/A_j)$, $j = 1,2,3$, $k = 1,2,\ldots,5$ of likelihoods, obtained in a manner similar to (5) is shown in Table 2. The relatively largest failure probability, about 43%, can be expected in Plant 1 on account of insufficient PTFE binder content in the electrode layer. The contents of Table 2 would guide plant operators in attempting to eliminate (or at least to reduce the extent of) the most likely cause that can be expected in each plant. They would also indicate what cautionary measures would be advisable in the design of future plants.

3.2. Application No. 2: The Effect of Prior Probability on the Anticipated Viability of an EC-Generated H_2 Evolution Process. A recently developed electrocatalyst for a hydrogen evolution process, made up of certain synthetic metals, is expected to possess an exchange current $i_0 \approx 100\,\mu A/cm^2$ at design operating conditions in a pilot scale electrolyzer. Inspection of Trasatti's [12] "volcano plot" [13, 14] suggests that its catalytic property would presumably fall between that of iridium and gold. It is further anticipated that the novel

Table 2: The complete set of probabilities computed via (5) in Application 1.

Source-of-failure events	$P(B_j/A_k)$		
	B_1	B_2	B_3
A_1	0.3333	0.3889	0.2778
A_2	0.2917	0.3333	0.3750
A_3	0.4286	0.2381	0.3333
A_4	0.4000	0.2667	0.3333
A_5	0.3415	0.2683	0.3902

Table 3: The effect of prior probability $P(B)$ on decision possibilities related to a new CE (Application 2).

$P(B)$%	$P(B/A)$%	$P(B/A')$%
20	67.4	2.5
40	84.6	6.3
60	92.5	13.2
70	95.1	19.1
80	97.1	28.8
90	98.7	47.6

$P(B/A)$: the probability that a CE will be deemed acceptable upon the Q_2 test, if the results of the Q_1 test were positive.
$P(B/A')$: the probability that a CE will be deemed acceptable upon the Q_1 test, even if the results of the Q_1 test were negative.

catalyst would be less expensive than Ir and Au, it would exhibit good dimensional/geometric stability as well as resistance to parasitic reactions due to possible contamination, and resistance to possible nonuniformity in current distribution. The design team postulates that if, on a pilot-plant scale, electrode specimens will show no loss in catalytic activity up to the passage of $Q_1 \approx 600\,\text{kAh/dm}^2$ electric charge per unit area, then there should exist an a priori chance that a catalyst-carrying electrode (CCE), selected randomly from a lot of identically prepared specimens, can sustain its catalytic activity, at an acceptable level, up to the passage of $Q_2 \approx 1200\,\text{kAh/dm}^2$. During the Q_1 tests, 91% of the electrodes were found to be acceptable, but 89% of electrodes, which later failed the Q_2 tests, did not perform in a satisfactory manner. The design team (i) would proceed to consider commercial-scale implementation if there is at least a 95% chance that a survivor of the Q_1-test would keep its catalytic activity up to the passage of Q_2, (ii) would abandon further research if favourable results were obtained in only one-fifth or less of the Q_1 tests.

The set of events of interest here, involving a randomly selected CCE, is defined as follows:

A: results obtained during the passage of Q_1 are positive,
A': results obtained during the passage of Q_1 are negative,
B: the CCE is acceptable,
B': the CCE is unacceptable,
A/B: Q_1-results were positive for an acceptable CCE,
A/B': Q_1-results were positive for an unacceptable CCE,
A'/B: Q_1-results were negative for an acceptable CCE,
A'/B': Q_1-results were negative for an unacceptable CCE,
B/A: a CCE which showed positive Q_1-test results is found acceptable,
B/A': a CCE which showed negative Q_1-test results is found acceptable.

Consequently, the stipulations can be expressed in terms of their probabilities as follows: $P(A/B) = 0.91$; $P(A'/B') = 0.89$; $P(A/B') = 1 - - P(A'/B') = 0.11$. Bayes' rule yields, therefore,

$$P(B/A) = \frac{0.91P(B)}{0.91P(B) + 0.11[1 - P(B)]},$$
$$P(B/A') = \frac{0.09P(B)}{0.09P(B) + 0.89[1 - P(B)]}. \quad (6)$$

Here, $P(B)$ is the prior probability of a CCE being acceptable. Its value, if not known experimentally, would be a matter of the designers' judgment. Table 3 indicates that in order to satisfy the $P(B/A) \geq 95\%$ and $P(B/A') \geq 20\%$ decision criteria simultaneously, the prior probability of a CCE passing the Q_2-test would have to be somewhat higher than 70%. If the abandonment criterion were raised to a stricter $P(B/A') \geq 25\%$ probability, $P(B)$ would have to be at least 77% for satisfying the two continuance conditions. Such results provide the design team with important knowledge for establishing proper testing protocols.

3.3. Application 3: Probing Claims Regarding the Reliability of a Catalyst Tester. A device for testing defects in a certain electrocatalyst (EC) is envisaged to be advertised by the catalyst producer, claiming that it is 97% reliable if the EC is defective, and 99% reliable when it is flawless. Independently from any testing device and based upon earlier experience, 4% of said EC may be expected to be defective upon delivery. In order to ascertain the true reliability of the device, Bayes' rule is applied to basic event set A: the EC is defective; A': the EC is flawless; B: the EC *is tested* to be defective; B': the EC *is tested* to be flawless, equipped with the full set of conditional events of interest here with their probabilities:

B/A: EC is (known to be) defective, and tested defective, $P(B/A) = 0.97$,

B'/A: EC is (known to be) defective, but tested flawless, $P(B'/A) = 1 - -P(B/A) = 0.03$,

B/A': EC is (known to be) defective, but tested defective, $P(B/A') = 1 - -P(B'/A') = 0.01$,

B'/A': EC is (known to be) flawless, and tested flawless, $P(B'/A') = 0.99$.

The probabilities of events to be computed via Bayes' rule, shown in Table 4, point to the (vexingly) high possibility of rejecting flawless EC's (about 20%) and the (vexingly) low possibility of identifying defective EC's (about 80%) when the tester indicates defectiveness. These findings, hidden by the advertisement without Bayes' rule, should discourage its adoption for routine use.

3.4. Application 4: Probing Claims Regarding Tafel Slopes in an Electrocatalytic Oxidation of Methanol Process Envisaged for Fuel Cells. This example is motivated by an experimental study of Pt:Mo dispersed catalysts (PMDCs) for the electro-oxidation of methanol in acid medium [15], assuming that a

Table 4: Probabilities of flawlessness/defectiveness expected from an EC tester (Application No. 3).

Event	Bayes' rule	Event probability
EC tested defective, but found flawless	$P(A'/B) = \dfrac{P(B/A')P(A')}{P(B/A')P(A') + P(B/A)P(A)}$	0.1983
EC tested flawless, and found flawless	$P(A'/B') = \dfrac{P(B'/A')P(A')}{P(B'/A')P(A') + P(B'/A)P(A)}$	0.9987
EC tested flawless, but found defective	$P(A/B') = \dfrac{P(B'/A)P(A)}{P(B'/A)P(A) + P(B'/A')P(A')}$	0.0013
EC tested defective, and found defective	$P(A/B) = \dfrac{P(B/A)P(A)}{P(B/A)P(A) + P(B/A')P(A')}$	0.8017

$P(A/B') + P(A'/B') = P(A/B) + P(A'/B) = 1$; $P(A) = 0.04$; $P(A') = 1 - 0.04 = 0.96$.

different research team claims in a new experimental catalyst development program a 65–70 mV/dec Tafel slope range at low current densities, and a 255–265 mV/dec at high current densities (in contrast with the 30–35 and 230–250 mV/dec ranges, resp. in the cited study). The polarization method chosen for investigating the claim is assumed to be 89% reliable when the claim cannot be verified and 99.5% reliable when the claim can be verified. Defining events A: the PMDC exhibits Tafel slopes below the claimed ranges and B: the PMDC is found to exhibit Tafel slopes below the claimed ranges, the complementary events A': the PMDC exhibits Tafel slopes within the claimed ranges and B': the PMDC is found to exhibit Tafel slopes within the claimed ranges establish the basis for applying Bayes' theorem. Following the pattern shown by the previous applications, the conditional probabilities are $P(B'/A) = 0.11$, $P(B/A') = 0.005$, $P(B/A) = 0.89$ and $P(B'/A') = 0.995$.

The research team is assumed to report that 96% of the new PMDC possess the claimed Tafel slope ranges; Bayes' theorem yields $P(A'/B) = 0.1188$; $P(A/B') = 0.0046$; $P(A'/B') = 0.9954$; $P(A/B) = 0.8812$. The about 12% probability that a new catalyst complies with the claim although the polarization experiment indicates otherwise raises at least a reasonable doubt about the claim or the reliability of the experimental procedure, in spite of the satisfactory $P(A/B')$ and $P(A'/B')$ values.

4. Discussion and Final Remarks

Perhaps the most striking feature of Bayes' rule is the amount of information that can be gleaned from a few uncomplicated probability ratios (the fact that Bayesian methods are at present more than two hundred years old is equally impressive). Within the Bayesian framework, a prior event probability is updated to a posterior probability of that event by means of a likelihood. The latter provides the (conditional) probability of corroborating the a-priori stated hypothesis; this aspect is numerically illustrated in the Appendix.

The examples presented in this paper provide a small "window" to the realm of Bayesian methods whose further exploration in electrochemical science and engineering requires further work. Bayes' rule is just one of many other mathematical devices of applied probability theory with potential interest to the field.

Appendix

Bayes' Rule: Short Analysis and Illustration via Application No. 3

Let AB and BA denote the combined event of both events A and B occurring, the order of occurrence being immaterial. The veracity of the statement $P(AB) = P(BA) = P(B/A)P(A) = P(A/B)P(B)$ and of (1) immediately follows. Accounting for complementary events A' and B' the (total) probabilities $P(A) = P(A/B)P(B) + P(A/B')P(B')$ and $P(B) = P(B/A)P(A) + P(B/A')P(A')$ are mirror images of each other. In Application No. 3 $P(B/A)P(A) = (0.97)(0.04) = 0.0388$ is the posterior probability of an EC being defective vis-à-vis prior probability. $P(A) = 0.04$. Similarly, $P(B/A')P(A') = (0.01)(0.96) = 0.0096$ is the posterior probability of EC-defectiveness vis-à-vis prior complementary probability $P(A') = 0.96$; the total probability of event B is $0.04 + 0.0096 = 0.0484$. Bayes' rule yields $P(A/B) = 0.0388/0.0484 = 0.8017$, that is the posterior probability that an EC tested defective is, indeed, defective. It is appreciably less than the claimed (i.e. prior) probability of 0.97.

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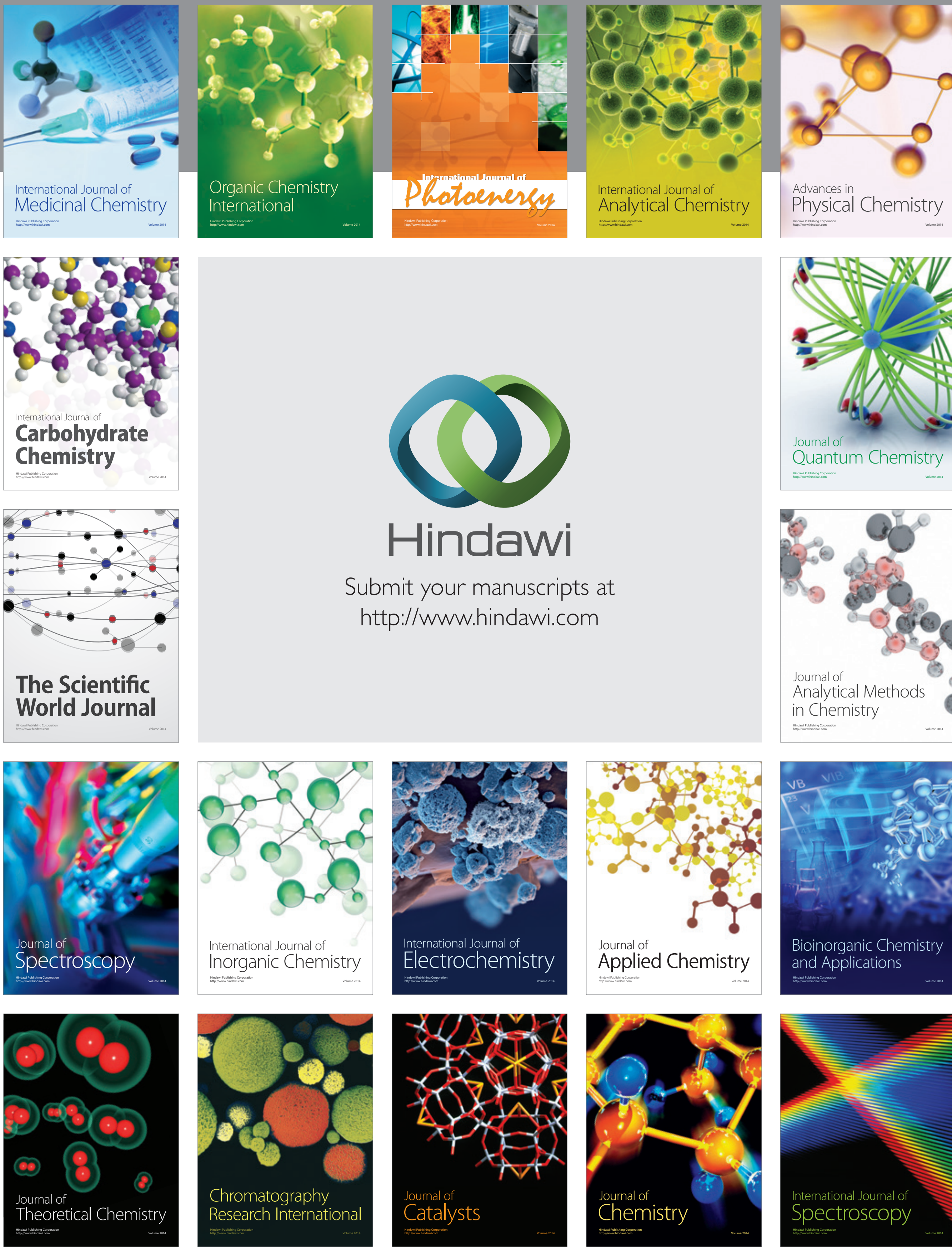

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