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# On An Applications of Bayes' Rule in Probability Theory to Electrocatalytic Reaction Engineering

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## Abstract

Bayesian methods stem from the rule of linking prior probability and conditional probability (likelihood) to posterior probability by Bayes' rule. The posterior probability is an 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 describes 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 dependable of a device testing the quality of an electrocatalyst, and the range of Tafel slopes exhibited by an electrocatalyst.

## Keywords

Prior Probability, Posterior Probability, Conditional Probability, Mutually Exclusive Events, Mutually Exhaustive Events

## 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 instance, exchange current density, poisons, work function, bond strength, crystal face effect, trace elements adatom effects, enzymatic catalysis, metal complexes and so forth, under the aegis of "phenomenological electrode kinetics".

In the domain of ERE (Electrocatalytic Reaction Engineering), the assessment of EC (electrocatalyst) performance also includes additional parameters which are related by catalyst preparation (i.e., possible defectiveness in specimens), cell construction and reactor output is effected by human factor.

This paper was written by keeping his thing in mind, that 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 methods for dealing with these responsibilities are provided by probability-based (e.g., statistical) methods. Bayes' rule is one such tool, whose definite application to scenarios with EC (Electrocatalyst) is the subject of this article.

## 2. Brief Theory

By summarizing the 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 occurrence of event A if event B has already occurred, and

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

This is the probability of occurrence of event B, given the conditional probabilities (likelihoods) P (B/A) which is related to event A and P (B'/A) related to event A' which is opposite to it.

A case for Bayes' rule would exist in case of EC reactor, for instance, when the effectiveness loss in EC an (Electro-catalyst) may or may not be due to earlier detachment of the catalytic layer. If the event of detachment is A and the event of demise (deterioration ) of the EC is B, then due to layer detachment the event of demise would be B/A, the event of a non-detachment cause of deterioration is A', and the event of deterioration due to a non-detachment cause is B/A'. In terms of probabilities of event, (1) yields the probability P (A/B) that as a result of layer detachment deterioration would occur 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 A1, A2... An are mutually exclusive and exhaustive events, (1) and (2) are generalized to

Table 1: In three independently operating (hypothetical) electrolytic plants postulated distribution pattern of 137 failure occurrences over a fixed time period using identical catalytic oxygen cathodes (Application No 1)

***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.*

| 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 | 12 | 14 | 10 |
| $A_2$ :Pore volume | 7 | 8 | 9 |
| $A_3$ :Binder content | 9 | 5 | 7 |
| $A_4$ :Catalyst content | 6 | 4 | 5 |
| $A_5$ Human error | 14 | 11 | 16 |
| Total number of failures | 48 | 42 | 47 |

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

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 investigating applications to electrochemical processes and technology at various levels of complexity are relatively recent [6–10].

Four independent examples are described in this paper, 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 hiding 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 Electrocatalytic Reaction Engineering

## 3.1. Application No. 1

"Estimating the Most Likely Location of Oxygen-Cathode Failure"

Table 1 contains the identical oxygen cathode's failure frequency map, assumed to possess the structure described by Wiesener and Ohms [11].

These mutually independent failures are specified to have occurred in three independently operating electrochemical plants. Denoting A1, A2...A5 as the failure source events and B1, B2, B3 as the plant location events, the probability arising due to failure, for example, from human error is given by

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

This is about 30 percent.

The Bayes' rule is:

$$P\left(B_i / A_5\right) = \frac{Pi\left(A_5 / B_i\right)P(B_i)}{P(A_5)} \quad \text{Where i=1, 2,}$$

Probability of failure caused by human error in any one of the three plants is:

$$P\left(B_1 / A_5\right) = \frac{14}{41}$$

$$=0.3145;$$

$$P\left(B_2 / A_5\right) = \frac{11}{41}$$

$$=0.2683; \quad (5)$$

$$P(B_3 / A_5) = \frac{16}{41}$$

$$=0.3802;$$

Thus, (next time) failure can be expected to be the least likely in Plant 2 due to human error and the most likely in Plant 3due to human error, although not significantly so with respect to Plant 1. The entire set P( Bk /Ai), where i=1,2,3, and k=1,2,...,5 of likelihoods, obtained in a same manner as in (5), is shown in Table2. The relatively largely failure probability, about 43%, can be expected in Plant1on account of insufficient PTFE binder content in the electrode layer. The Table 2 contents would guide plant operators in attempting to exclude (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 in the design of future plants would be advisable.

## 3.2. Application No. 2

"The Effect of Prior Probability on the Anticipated Viability of an EC-Generated H2 Evolution Process"

A recently developed electrocatalyst made up of certain artificial metals for hydrogen development process, is expected to possess an exchange current i0≈100μA/cm2 at design operating conditions in a pilot scale electrolyze.

Organization 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 catalyst would be of low price as compare to iridium and gold, it would contest good dimensional/geometric stability as well as resistance to parasitic reactions due to possible contamination, and resistance to possible no uniformity in current distribution.

***Table 2.*** *The complete set of probabilities computed via (5).*

| Source of failure events | $P(B_i / A_k)$ | | |
|---|---|---|---|
| | $B_1$ | $B_2$ | $B_3$ |
| $A_1$ | 0.3333 | 0.3889 | 0.2778 |
| $A_2$ | 0.2197 | 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.*

| 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 upon

The Q2 test, if the result of Q1 test were positive.

P(B/A'):the probability that a CE will be deemed upon

The Q1 test, if the result of Q2 test were negative

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 Q1≈600 kAh/dm2 electric charge per unit area, then there should exist a priori chance that a catalyst-carrying electrode (CCE) selected randomly from a lot of specimens, which are identically prepared, can maintain its catalytic activity, at an acceptable level. During the Q1 tests, 91% of the electrodes were found to be acceptable, but 89% of electrodes, which later failed the Q2 tests, did not perform in a satisfactory manner. The design team (i) would proceed to consider commercial-scale implementation if there is at least 95% chance that a survivor of the Q1-test would keep its catalytic activity up to the passage of Q2, (ii) would abandon further research if favourable results were obtained in only one-fifth or less of the Q1tests.

The set of events which would be interested here, involve CCE which are randomly selected, is defined as follows:

A: results obtained during the passage ofQ1are positive,

A': results obtained during the passage ofQ1are negative,

B: the CCE is acceptable,

B': the CCE is unacceptable,

A/B: Q1- for an acceptable CCE result were positive,

A/B':Q1- for an unacceptable CCE results were positive,

A'/B: Q1-for an acceptable CCE results were negative,

A'/B': Q1-for an unacceptable CCE results were negative,

B/A: a CCE which showed positive Q1-test result is found acceptable,

B/A': a CCE which showed negativeQ1-test results is found acceptable.

Consequently, the stipulations in terms of their probabilities can be expressed as follows:

$$P(A / B) = 0.91; P(A' / B') = 0.89;$$

$$P(A / B') = 1 - P(A' / B') = 0.11$$

Baye's rule therefore yields,

$$P(B / A) = \frac{(0.91)P(B)}{(0.91)P(B) + (0.11)[1 - P(B)]}$$

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

Here, P(B) is the prior probability of a CCE being acceptable. Its value, would be a matter of the designers' judgment if not known experimently. Table 3 indicates that in order to satisfy the P (B/A) ≥95% and P (B/A') ≥20% decision criteria simultaneously, the prior probability of a CCE passing the Q2-test would have to be somewhat higher than 70%. If the abandonment criterion were raised to a stricter P (B/A') ≥25% probability, P (B) would have to be at least 77% for satisfying the two continuance conditions. Such results provide the design team for establishing proper testing protocols with important knowledge.

### 3.3. Application No. 3

"Probing Claims Regarding the Reliability of a Catalyst Tester"

In a certain electrocatalyst (EC) a device for testing defects is visualized to be advertised by the catalyst producer, claiming that if the EC is defected then it is 97% reliable, and when it is flawless then it is 99% reliable. Independently from any testing device and based upon earlier experience, 4% of said EC may be expected to be defective upon delivery.

Bayes' rule is applied to basic event set in order to establish the true reliability of the device, 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 attention 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 teste 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 Table4, 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, invisible by the advertisement without Bayes' rule, should dishearten its adoption for routine use.

### 3.4. Application No. 4

"Probing Claims Regarding Tafel Slopes in

An Electrocatalytic Oxidation of Methanol Process Envisaged for Fuel Cells"

By an experimental study of Pt: Mo dispersed catalysts (PMDCs) for the electro-oxidation of methanol in acid medium [15], this example is motivated, assuming that a different research team claims in a new experimental catalyst development program at low current densities Tafel slope range is 65–70 mV /dec, and at high current densities it is 255–265 mV/dec (in contrast with the 30–35 and 230–250 mV/ dec ranges, resp. in the cited study).

When the claim cannot be verified, for investigating polarization method is choosen. The claim is then

assumed to be 89% reliable and when the claim can be verified then it is assumed to be 99.5% reliable. Defining events

A: below the claimed range the PMDC exhibits Tafel slopes and B: below the claim ranges the PMDC is found to exhibit Tafel slopes, the complementary events A': within the claimed ranges the PMDC exhibits Tafel slopes and B': within the claimed ranges the

***Table 4.*** *Probabilities of flawlessness/defectiveness expected from an EC tester.*

| Event | Baye's rule | Event probability |
|---|---|---|
| EC tested defective, But found flawless | $P(A'/B)=\frac{P(B/A')P(A')}{P(B/A')P(A')+P(B/A)P(A)}$ | 0.1983 |
| EC tested flawless, And found flawless | $P(A'/B')=\frac{P(B'/A')P(A')}{P(B'/A')P(A')+P(B'/A)P(A)}$ | 0.9987 |
| EC tested flawless, But found defective | $P(A/B')=\frac{P(B'/A)P(A)}{P(B'/A)P(A)+P(B'/A')P(A')}$ | 0.0013 |
| EC tested defective, And found defective | $P(A/B)=\frac{P(B/A)P(A)}{P(B/A)P(A)+P(B/A')P(A')}$ | 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

PMDC is found to exhibit Tafel slopes, range establish the basis for applying Bayes' theorem. Following the pattern shown by the previous applications, the conditional probabilities are

$$P(B'/A)=0.11; P(B/A')=0.005; P(B/A)=0.89 \text{ And}$$

$$P(B'/A')=0.995$$

The research team is assumed to report that 96% of the new PMDC possess the claimed Tafel slope ranges; Bayes' theorem yields

$$P(A'/B)=0.1188; P(A/B')=0.0046; P(A'/B')=0.9954;$$

$$P(A/B)=0.8812;$$

About 12% probability that a new catalyst complies with the claim that, the polarization experiment indicates otherwise raises at least a reasonable doubt about the claim or there liability of the experimental procedure, in spite of the

Satisfactory P (A/B') and P (A'/B') values.

## 4. Discussion and the Final Remarks

The most impressive feature of Bayes' rule perhaps is the amount of information that can be gleaned from a few uncomplicated probability ratios (the fact that Bayesian methods present are equally impressive about more than two hundred years ago). A prior event probability is updated to a posterior probability of that event within the Bayesian framework by means of a likelihood. The latter provides the (conditional) probability of supporting the a-priora stated hypothesis.

The examples which are presented in this paper provide a small "window" to the realum of Bayesian methods, whose further exploration in electrochemical science and engineering requires further work. So if we say that Bayes' rule is just one of the many other mathematical devices of applied probability theory with potential interest to the field then it is not wrong.

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