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Multi-q pattern classification of polarization curves

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HIGHLIGHTS

- Multiple polarization curves of two stainless steels are experimentally acquired.
- The multi-q approach automatically classifies the profiles using Tsallis entropy.
- A success rate of 80–90% was achieved using only 2% of the original data.

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ABSTRACT

Several experimental measurements are expressed in the form of one-dimensional profiles, for which there is a scarcity of methodologies able to classify the pertinence of a given result to a specific group. The polarization curves that evaluate the corrosion kinetics of electrodes in corrosive media are applications where the behavior is chiefly analyzed from profiles. Polarization curves are indeed a classic method to determine the global kinetics of metallic electrodes, but the strong nonlinearity from different metals and alloys can overlap and the discrimination becomes a challenging problem. Moreover, even finding a typical curve from replicated tests requires subjective judgment. In this paper, we used the so-called multi-q approach based on the Tsallis statistics in a classification engine to separate the multiple polarization curve profiles of two stainless steels. We collected 48 experimental polarization curves in an aqueous chloride medium of two stainless steel types, with different resistance against localized corrosion. Multi-q pattern analysis was then carried out on a wide potential range, from cathodic up to anodic regions. An excellent classification rate was obtained, at a success rate of 90%, 80%, and 83% for low (cathodic), high (anodic), and both potential ranges, respectively, using only 2% of the original profile data. These results show the potential of the proposed approach towards efficient, robust, systematic and automatic classification of highly nonlinear profile curves.

1. Introduction

Several results of experimental techniques in materials science and engineering are available in the form of profiles. Despite the crucial importance of these types of data, the use of statistics on profiles is rare, as the adequate statistical

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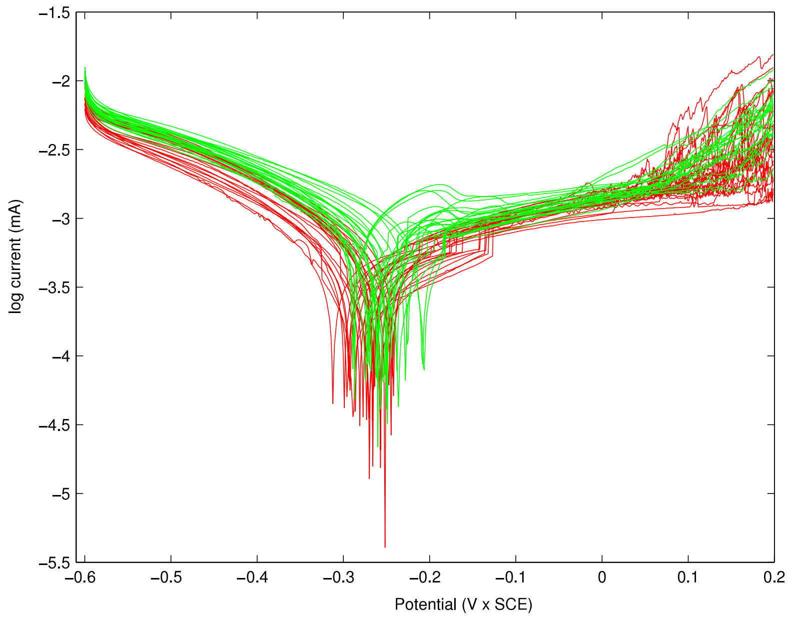

Fig. 1. 48 experimental polarization curves of stainless steels 304 (red) and 316 (green). Each curve consists of 800 sample points. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

techniques themselves are under development [1–3]. Useful applications of profile analysis include outlier detection and classification/clustering of groups of results, taking into account the inherent stochasticity of the experimental data.

Since the use of statistics for realistic profile datasets is currently somewhat scarce, the evaluation and comparison of experimental results is ordinarily performed by subjective criteria, e.g., after performing three to five runs of an experiment to identify representatives. In the case of profiles, a physical model with a related adjustment of parameters is a good indication of pertinence to a target group. In this situation, however, the analysis is mainly focused on the parameter values instead of profiles themselves. We here explore systematic data analysis techniques suited for *complex* or *highly nonlinear* profiles, i.e., when there is no simple model description or parameters to represent the entire profile curve.

In the fields of corrosion and materials science, there are numerous examples of data with complex profile shapes: the aforementioned polarization curves, impedance diagrams, voltammograms, electrochemical noise records and so on. Despite this profusion of profile data, the work of Strutt et al. [4] is a rare example of profile analysis from corrosion, albeit the studied profiles were related to the geometric shape of corroded interfaces, and not electrochemical data as in the present work.

Polarization curves, or, more generally, current–potential plots, have crucial importance in corrosion studies as well as in electrochemistry. They are essential for measuring the global kinetics of electrodes. A number of electrochemical parameters can be obtained from these tests, from charge transfer, passivation, corrosion current density, to mass transport properties. As expected, for any set of experimental results, dispersion always occurs. Even a stable reaction performed under stringent control of experimental procedures, such as the ferri/ferrocyanide redox reaction, can present significant scattering [5]. Moreover, the level of scattering in polarization curves naturally increases as the localized corrosion takes place, which exhibits random nature. Another challenging case is that the surface of commercial grades of steels, which has wide industrial interest, has inherent heterogeneity of their metallurgical aspects. Furthermore, certain stochastic phenomena such as pitting produce electrochemical current variations that produce overlap in the experimental curves, rendering them almost inseparable. However, these fluctuations can also be useful to describe the type and the intensity of corrosion attack [6,7]. Thus, for some corrosion resistant alloys (CRA) such as stainless steels, the evaluation of parameters from polarizations curves near pitting potential is an important procedure to classify their corrosion resistance.

Having had success in employing Tsallis statistics [8] to the classification of image patterns as well as other applications [9], we devise a similar multi-q approach based on such statistics to propose a method to classify highly nonlinear profiles from corrosion tests, such as those in Fig. 1. The primary goal of any classification method is to assign a class label (e.g., material type) to a given data sample (e.g., image or profile). In our case, the profiles are the polarization curves and the output label is one of two stainless steels. Despite having slightly different chemical compositions, the polarization of both materials is very similar, especially in the cathodic region and in the potential immediately past the corrosion potential region. This similarity produces overlapping curves which require a systematic approach to classify, an analysis that has not been routinely carried out in this field.