# Anodic Polarization Curves Revisited

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# Anodic Polarization Curves Revisited

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ⓈSupporting Information

**ABSTRACT:** An experiment published in this *Journal* has been revisited and it is found that the curve pattern of the anodic polarization curve for iron repeats itself successively when the potential scan is repeated. It is surprising that this observation has not been reported previously in the literature because it immediately brings into question the long accepted and well-known explanations involving a passive film. A qualitative and plausible explanation is provided from surprisingly simple principles for this new finding. Some important pedagogic conclusions have been derived from this work. It is noteworthy that the somewhat complicated phenomenon can be simply explained, thus providing two important lessons to students. First, even well-accepted scientific work studying simple processes may be incomplete and worthy of further study, and second, such processes may be explained simply at the undergraduate level. The contents of the paper also confirm that presenting curricular contents in a new and more correct manner is beneficial, interesting, and that research in curricular contents represents one of the important forms of educational research.

**KEYWORDS:** *Graduate Education/Research, Upper-Division Undergraduate, Physical Chemistry, Misconceptions/Discrepant Events, Problem Solving/Decision Making, Electrochemistry*
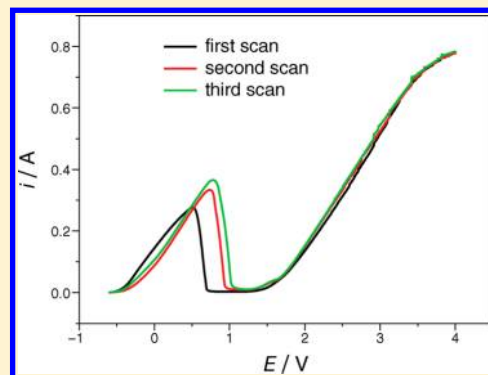
Typical anodic polarization curves for iron are well-known and the explanation provided in this *Journal*[1] some 20 years ago has been generally accepted and remains unchallenged to this day. We have revisited the experiment and the experimental results are presented in the Supporting Information. The sharp drop in the anodic current at a critical potential $E_P$ (Figure 1A) manifests its passivity. However, unlike previous workers, we noticed an interesting phenomenon in that the curve pattern repeats itself successively when the potential scan is repeated immediately after the previous scan has been completed (Figure 1B). This observation immediately refutes the usually accepted explanation for the curve pattern that is based on the static passive film theory. We note that phrases such as "dynamic passive film"[2] and "metastable oxide layers"[3] have been used previously in the literature but the occurrence of this repeating pattern has not been mentioned. Clearly any theory of anodic curves must explain this new finding and therefore the mechanism of anodic passivation given in the literature (e.g., refs 1 and 2) is clearly inadequate.

One observation, clearly seen in Figure 1A, is that there is no current in the passive region from $E_P$ to $E_D$. Thus, there should be no electric field present in the solution as the free ions in solution will be transported by the presence of an electric field. The predominant explanation for the presence of the passive region is that a passive oxide film is formed on the surface of the metal, which prevents further reaction. This explanation seems reasonable if Figure 1A is considered in isolation. However, it is at odds with the observation of a repeat curve pattern as shown in Figure 1B because such a film would cause

irreversible behavior. Thus, the present theory cannot account for all properties of anodic polarization.

Theories that do not involve static films have been proposed, involving reaction velocity adsorption, modification,[4] and other concepts.[5,6] It may be that some at least of these alternative theories have been developed because researchers have observed this repeat curve pattern and as a result rejected the static passive film theory, but this has not been explicitly stated.

Kinetic models[5,7,8] with simplifications and detailed mathematical treatments have been proposed that to some extent reproduce quantitatively the passivation effect in the active region, such as is demonstrated by Malloy.[7] But such models cannot explain the presence of the passive region from $E_P$ to $E_D$ in Figure 1A where the electric current is consistently low in a typical anodic polarization curve. Although it should be noted that the term "passive film"[6,8] is often used in descriptions of kinetic models where their success originates from the steady-state postulate, the steady-state postulate is simply a principle used in dynamic simulations, so kinetic models offer only a numerical model that explains the experimental data rather than provides a theoretical explanation.
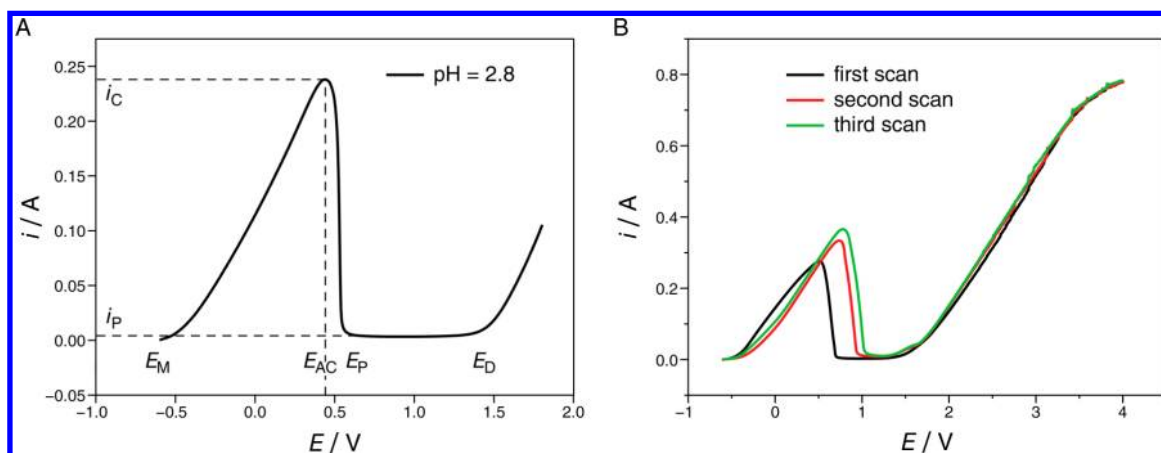
**Figure 1.** (A) Anodic polarization curve for iron where the concentration of $KNO_3$ is 1.25 M and pH = 2.8: $E_M$ is the starting potential; $E_{AC}$ is the potential at which the anodic current reaches its maximum; $E_P$ is the potential where the anodic current first drops to its minimum, and $E_D$ is the potential at which the current begins to increase. $i_C$ and $i_P$ are the maximum and the minimum current, respectively. (B) The pattern repeats after each successive scan.

## ■ DISCUSSION

### Explanations for the Passive Region

The solution is neutral whether there is current or not. However, this does not mean that there is no concentration gradient near the double layer especially when a potential is applied. To understand why there is no current in the passive region between $E_P$ and $E_D$ (Figure 1A), two factors are important, namely, the concentration gradient between the electrode and bulk solution and the electric field between electrodes, both of which provide a driving force for ion transportation. A higher concentration gradient increases the ion diffusion rate and produces a higher electric current. Likewise, as another independent effect, a higher electric field increases the ion migration rate and also produces a higher electric current. It seems contradictory that the current is low at the passive region where the concentration gradient and the electric field are high. Here we propose an explanation by considering the local concentration gradient and an induced opposite electric field.

First, from the perspective of the local concentration gradient, it can be considered that the concentration gradient between the bulk solution and the electrodes is high in the passive region. Even though the concentration gradient is high at the diffusion layer in the higher-potential region, the local concentration gradient near the electrode in the electrical double-layer is low because a large number of ions are concentrated within this region, and the ions cannot diffuse out because they accumulate very fast and are held in position by the higher voltage, though they will be released on reducing the voltage.

An important feature of a series circuit is that the current is the same everywhere. So, the low local concentration gradient near the surface of electrodes is also responsible for the low current in the passive region. Diffusion limited by high voltage as described above should be the basis for the success of any kinetic explanation.

Second, from the perspective of the electric field, it can be assumed that the electric current is high when the electric field is high as long as the insulating oxide cannot be formed quickly on the anode, which is the case in the passive region. However, at high anodic potential, the concentration of iron ions is high near the anode in the double-layer as shown in Figure 2, and
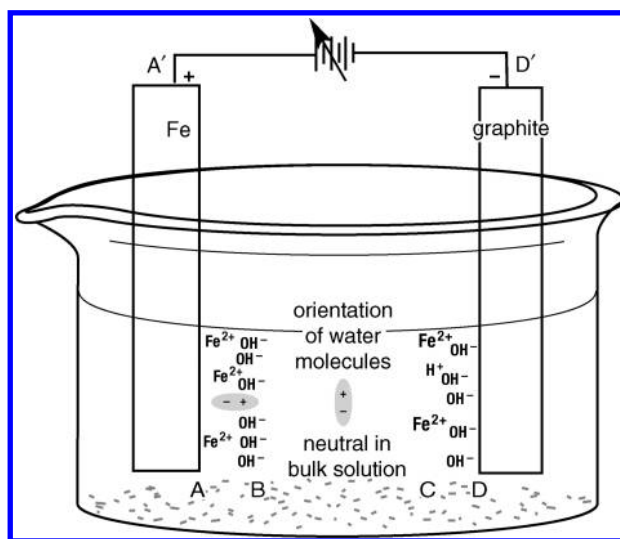


**Figure 2.** The concentration gradients near the electrodes. A, D, A′, D′ are used to indicate regions at the apparatus. B and C indicate where bulk solution begins. The local concentration gradients indicated near the electrodes are low.

the iron ions are congested near the anode being unable to release their charges (or electrons for iron metal) due to their close proximity to each other. Usually, high potential differences lead to rapid electrochemical reaction. Here, however, the dynamics caused by the congested ions hinders the electrochemical process. This also results in a low local concentration gradient because the ions cannot diffuse out efficiently; that is, the chemical reaction at the electrodes is slow and the diffusion of the ions is also slow because of the outside potential, thus the driving voltage $V_{A'D'}$ provided in Figure 2 maintains different concentrations of anions and cations at cathode and anode, respectively, and cannot release the charges of the ions. In other words, the $Fe^{2+}$ ions are trapped on the iron surface because of the driving voltage $V_{A'D'}$. Thus, when there is no current as in the passive region for a typical case, $Fe^{2+}$ is retained near the anode as shown in Figure 2.

The charge on the electrode should migrate to the electrode surface. The outside voltage, $E_{A'D'}$, provided by the outside circuit keeps the ions on the surface of the electrode and they

will only be released in the next cycle of the scan. Hence, inside the anode from A to A′ in Figure 3 the electric-field lines
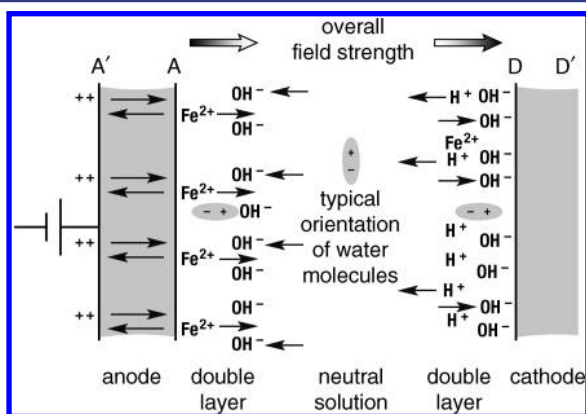


**Figure 3.** The effect of trapping $Fe^{2+}$ on the surface of the anode and the cancellation of the electric-field lines, shown by stick arrows. The cancelation of field lines in the electrode is equivalent to the physical convention in electrostatics that the field lines will avoid going through any conducting surfaces. Indeed they are always outside such surfaces. The electric-field lines in the bulk solution have also been canceled out. The darkness of the shaded arrows symbolizes the transition in field strength through the double-layer region between the bulk solution and the edge of the electrode.

provided from point A′ are canceled out by those provided by the surplus $Fe^{2+}$ on the metal surface, just as a metal case shields out an electric field. Thus, the electric field provided by the outside circuit is canceled by an induced field produced by $Fe^{2+}$, whatever the value of the outside potential, because the ion concentration of the surface ion will be altered according to the variation of the outside voltage. So, there is no electric field in the anode from A′ to A (Figures 2 and 3), and the current is cut off for a range of voltages from $E_P$ to $E_D$ (Figure 1A) in a manner analogous to the effect of a switch in a series circuit, that is, the voltage difference $V_{A'A} = V_{D'D} = 0$ (Figure 2) because of the absence of an electric field. Even with the static film theory, there needs to be a mechanism for the insulating oxide to shield out the electric field taking into account the fact that it does not conduct electricity. If an insulating film can only cut off electricity but cannot cut out an electric field, the ions in the bulk solution will remain under the influence of the field.

Because the concentration of the surface ion is altered according to the outside voltage, the level curve that is observed over a large range of outside voltage from $E_P$ to $E_D$ in Figure 1A can be readily explained. The above phenomenon can be related to the fact that there is no electric field outside a capacitor connected to an electric cell (similar to Figure 3) or within a metal box with the electric field outside. Thus, besides the low local concentration gradient near the electrodes, the electric current is also cut off by an induced electric field even when the potential provided at the anode is high and the induced electric field is varied according to changes in the outside voltage. This fact is not accounted for explicitly by the kinetic treatment and can be considered as an effective "dynamic passive film" if for consistency, the term "passive film" is to be kept.

If the $Fe^{2+}$ ions on the electrode surface can diffuse out at a certain speed, there would be a current flow in the circuit. This is why there is low current from $E_P$ to $E_D$ where the curve is somewhat different from Figure 1A as is found for other metal

ions with different mobility. For the typical case in Figure 1A, the effects of the above-mentioned local concentration gradient and an induced antielectric field (Figure 3) are coupled together perfectly. Different metals give different shapes of the anodic polarization curve because the balance between these two effects is different. When the potential difference between A′ and D′ is removed, the concentration in the solution becomes uniform and ready for another cycle of the scan. In fact, when the potential difference between A′ and D′ is removed, some $Fe^{2+}$ ions may still be trapped on the surface by $O^{2-}$ ions, for example, in the form of a passive film of $Fe_3O_4$. Such facts are the basis of literature reports[2] that support passive film theory. But the existence of a passive film of iron oxides has only a minor effect in anodic polarization phenomenon as will be made clear in the next sections.

## Open Circuit Analogy

It follows from the above discussion that we can consider a typical passive region with a varied electric potential difference to be analogous to an open circuit where there is no current because the potential on the anode surface always stays the same as the potential on the positive pole whatever its value (Figure 4). When electrons are removed from the electrode, the
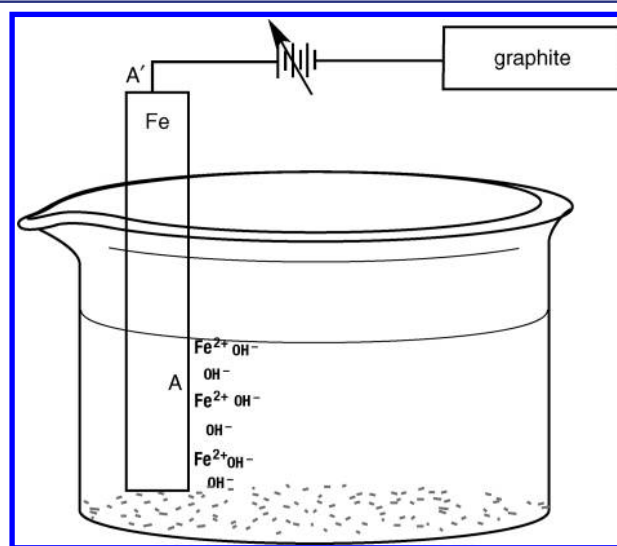


**Figure 4.** Open circuit and $Fe^{2+}$ distribution near the electrode.

resulting $Fe^{2+}$ ions should appear at the surface. In both an open circuit and a passive region, more $Fe^{2+}$ ions may appear at the surface when the potential of the positive pole increases.

According to the Nernst equation (eq 1),

$$E_{A'} = E_A = E^\circ + \frac{RT}{zF}\ln\frac{[Fe^{2+}]}{[Fe]} \tag{1}$$

the ion will continue to be transported to the electrode surface until the potential on the surface (labeled A in Figure 4) is equal to the potential of the positive pole. But the response time for this process in the anodic experiment is very short, and thus, the quantity of ions diffusing out of the surface is so small that it can be neglected. Whereas for an open circuit, the ions are held still on the surface by the outside potential and no diffusion can occur.

Because there is little chance in an open circuit or passive anode to diffuse out the $Fe^{2+}$ ions, the induced opposite electric field switches off the circuit by opening the "switch" between

points A′ and A. The current will be zero because the voltage difference between A and A′ in Figure 4 is zero.

In our experiments, the successive scans were taken immediately and also after a delay, and the same iron electrode was used day after day. There is no significant difference between the results obtained with or without a delay. The current is zero in the passive region because the condition at the anode changes rapidly with outside voltage during the scan. This is good evidence that the response of the anode to the outside voltage is instantaneous; that is, if the response cannot be adjusted to the change of the applied voltage, there should be a current between $E_P$ and $E_D$ in Figure 1A even within a single scan. The presence of this typical zero current passive region shows that the condition at the electrode surface responsible for the anodic polarization phenomenon changes in accord with the relevant outside driving potential difference, and the responding time is fast enough in adjusting the conditions to match the change in potential difference.

An important feature of the circuit should be emphasized. It is neutral in the vicinity of every point in the metal whether the current is present or not. In a similar manner, it is neutral in the vicinity of every point in the solution whether there is current or not, and whether there is a concentration gradient or not. Thus, while the ions around the cathode and anode may be more concentrated than in the bulk solution, the solution between A and D in Figure 2 is still neutral as the conduction medium never becomes charged even though there is significant charge flow. It is a basic principle that ions in neutral media can be driven by an electric field. When there is no current in the solution, there is also no electric field. So, in the typical case of a zero current passive region, the solution from A through to D in Figure 2 behaves like an open battery, which is electronically neutral and presents no electrical field in the bulk solution. However, a main difference exists as it is chemical energy that keeps the potential difference from positive pole to negative pole for an open battery. By contrast, it is the driving force provided by the potential difference from outside at A′ and D′ that maintains the ion concentration difference from anode to cathode at A and D thus facilitating the formation of the passive region (the potential difference from A′ to A is zero).

### Static Oxide Film and the Effective "Dynamic Passive Film"

When the iron is placed within a solution of concentrated sulfuric acid, no air bubbles are observed after several seconds, showing that "the passive film" does have the effect of protecting the metal. However, a static passive film would cause irreversible behavior and the concept needs to be modified. When iron treated with concentrated sulfuric acid is subsequently put into a solution of dilute sulfuric acid, then air bubbles appear after a short initial time, showing that the concept of a static passive film is inaccurate and should be changed to the concept of "a dynamic passive film" even though releasing of the bubbles is much slower than that obtained with a fresh iron bar. Thus, it is clear that a "dynamic passive film" is consistent with such reversible behavior, whereas the static film is not.

The explanation provided by the old static passive film theory for this phenomenon is that "the oxide film" formed on iron cannot resist dilute acid effectively. But a more reasonable explanation would involve limitations in ion transportation. It seems more likely that the real explanation is consistent with the principles stated previously. The strong oxidation capability

of concentrated sulfuric acid acts similarly to the high voltage difference of $V_{A′D′}$ and causes $Fe^{2+}$ ions to be trapped on the iron surface. But dilute acid facilitates the dissolving of the basic "passive oxide film" as the voltage difference of $V_{A′D′}$ is changed toward the region between $E_M$ and $E_P$ in Figure 1A and some $Fe^{2+}$ ions are diffused away.

However, it is a totally different matter in the anodic polarization experiment. The iron treated with concentrated sulfuric acid still gives almost the same anodic polarization curve as a fresh iron bar, thus showing that ion transport limitations must be responsible for this passivation because the outside driving force increases the transport effects. Thus, the electrode potential that provides the impetus for ion transportation has been provided from outside, giving a similar result to that provided by dilute acid for ion diffusion.

These experimental observations show that both the presence of the oxide film and limitations of ion transport affect metal passivation, but in various ways that depend on the specific situation. Both the inclusion of concentrated sulfuric acid and the provision of a high potential at the anode have similar but different effects as they both provide strong oxidation conditions but behave somewhat differently. We accept that there might have been some irreversible nature and that this can be accounted for by the static passive film theory. The oxidation rate of iron does decrease when iron treated with concentrated sulfuric acid is subsequently reacted with dilute acid, which reflects the irreversible nature of the static passive film. However, the curve shape and the peak height of the active anode current for the anodic polarization experiment are not so affected, which shows that the effect of transport limitation is more important when transport driving power $V_{A′D′}$ is provided from outside. The above observations are consistent with the conclusion of Bojinov et al.[5] that the prepassive dissolution (from $E_M$ to $E_{AC}$ in Figure 1A) of iron is largely controlled by mass transfer, rather than by electrode reaction, which means that a static passive film cannot be the decisive feature of anodic polarization.

### Summary of Experimental Evidence

Further experimental data support the theoretical discussion given above. When the successive scanning experiment is continued on the same anode, the same curve pattern containing both peak and passive region always reappears, thus showing that the experiment is reversible. This is counterintuitive to static passive oxide film theory because the passive oxide film should persist in the active region and should prevent iron from taking part in any subsequent reaction. The breakdown of the oxide film was given as one reason for the rise of the anodic current at $E_D$.[1] However, if the formation of a passive film is the only reason for passivation, then the final zone in the polarization curve where the electrode begins to pass current again (caused by oxidation of $O^{2-}$) is unlikely to be due to physical imperfections such as cracks because the passive film could be reformed at these cracks under strong oxidation conditions thus reverting the system to the passive state. In fact, the same polarization curve pattern is repeated at each subsequent scan even though the maximum scan potential does not reach $E_D$ indicating that the reappearance of the active region is not caused purely by fresh cracks.

The present theory involving local concentration gradient and the induced electric field account for the fact that the same pattern shown in Figure 1A repeats itself in each potential scan

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from $E_M$ to $E_D$. As the power potential sweeps periodically from the value found in the active region to that in the passive region, the ion distribution near the surface of the electrode changes with imposed potential and the polarization curve is repeated. The two factors, local concentration gradient and the induced opposite electric field, are therefore coupled together in a complementary fashion. Thus, if the local concentration near the electrode is not high enough as in the case of the active region from $E_M$ to $E_P$ in Figure 1A, then the induced electric field is also not important.

In addition, the static oxide film theory does not account for experimental data obtained from other metals. Anodic passivation is quite commonly observed for metals, although the anodic curves[2] are not as typical as observed for iron shown in Figure 1. It is not surprising that different metals give different passivation curves as they have different mobility. For example, the mobilities of $Na^+$ and $Fe^{2+}$ are different. The fact that anodic passivation is commonly observed for metals emphasizes that it is more likely to be caused by the reversible transport nature of these ions than by the formation of irreversible passive oxide films. It is also worth noting that the typical passive curve shown in Figure 1A for iron only appears at electrolyte concentration ranges where the concentration is dilute but still capable of conducting electricity, showing the importance of transportation conditions (Figure 3 in the Supporting Information). Indeed each scan is different (Figure 1B) because pH (Figures 1 and 2 in the Supporting Information) and the concentration (Figure 3 in the Supporting Information) change. When ion concentration is high (Figure 3 in the Supporting Information) the passive effect might be suppressed and there are enough ions to respond to the driving potential to generate a current. The experiments were conducted without solution stirring, which enhances the concentration difference between different scans. Any supporting electrolyte that is present changes the transportation conditions and has a significant effect on current conduction. Thus, at higher electrolyte concentrations with strong conductivity, the passive curve is not so well characterized as that in Figure 1A, consistent with the fact that transportation effects are important for passivation. As the concentration increases, the passive region will finally disappear at the end of many of the subsequent scans even though the tarnished film still existed, presumably because the ion concentration became higher and more ions are available to respond to the outside voltage and thus improve conductivity. Thus, the obstacles for ion migration are then overcome, but not purely because of the dissolution of the static passive oxide film. It is reasonable to propose that transportation limitations result in an effective "dynamic passive film" of an ion layer but not a dynamic formation and disappearance of a real "static passive film".

Although the oxide film has been characterized by some techniques,[2] it was also noted[9,10] that the hydrated iron oxides formed in the experiment are soft and do not prevent further oxidation. So, the static film is not so effective that it can prevent the generation of current. It is no surprise that the oxide film could be characterized by sophisticated techniques as the tarnished film on the scanned iron anode and on the iron treated with concentrated sulfuric acid can be seen even by the naked eye. Whether the active region from $E_M$ to $E_P$ or the passive region from $E_P$ to $E_D$ in Figure 1A is involved, the tarnished oxide is still there, showing little evidence for the effect of the formation and disappearance of the static film but rather showing the likelihood of the presence of a reversible ion layer. The tarnished oxide could not fully prevent the appearance of the active region in the anodic polarization curve, which is experimentally proved by the reappearance of the same curve pattern when repeating the experiment with the same iron anode.

Our new theory concerning anodic curves can be applied to more complex phenomena and this is discussed in detail in the Supporting Information.

## ■ CONCLUSIONS AND PEDAGOGIC IMPLICATIONS

Simple experiments including those using iron treated with concentrated sulfuric acid as anode were revisited. The anodic polarization curve for iron has been measured and it is found that the curve pattern repeats itself successively when the potential scan is repeated. This periodic phenomenon has not been previously emphasized in the literature though terms such as "dynamic passive film" are commonplace. Logical explanations for this repeating curve pattern are provided here based on simple well-known principles such as (i) the charged particle must move if an electric field is present; (ii) the current is equal everywhere in a series circuit; (iii) there is no charged area in metal or solution whether there is current or not; and (iv) the electric-field shielding principle. Taking into account facts such as that passive property is common in metals and that the shape of the anodic polarization curve is dependent upon ion concentration and metal, all these observations are consistent with our explanation. The known complex facts, such as the sustained periodic current oscillations in passivation region from $E_{AC}$ to $E_P$ in Figure 1A, are explained simply as a special case of the anodic polarization curve and are detailed in Supporting Information.

This work apart from its intrinsic importance offers important lessons to students and others. First, that even when an experiment has been carried out many times with consistent results, it can be worthwhile to revisit the work. Occasionally, as in the present case, new results can be obtained, but even if not, much can be gained by repeating the work because the thought processes of the original experimenter can be followed. Thus, this process of replication can represent a beneficial learning strategy and can deepen understanding even if important new revisions are not established. Further comments of the pedagogic implications of this work, based on our experience[11−16] are given in the Supporting Information.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Experimental details, application of the principles proposed here to more complex phenomena, and pedagogic implications of this work. This material is available via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

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