Fundamental research on the voltammetry of polycrystalline gold

Yang, S.

Citation

Yang, S. (2024, April 9). *Fundamental research on the voltammetry of polycrystalline gold*. Retrieved from https://hdl.handle.net/1887/3731809

The Legend of Murloc

一个简单误判引发的蝴蝶效应。
The butterfly effect triggered by a simple misjudgment.

The Mystery of a Million Stars

关键，　The key is,
不在于他们在哪，　not where they are,
而在于他们如何存在。 but how they exist.

The Lost Heart of the Electric Grove

复杂背后的本质是简单。
The essence behind complexity is simplicity.

Perplexities of the Identification Center

万物皆有独特印记。
All things bear their distinctive imprints.

Anecdotes from the Scapegoat Farm

多重解读，浅见皆替罪。
Multiple interpretations, Shallow perspective as scapegoats

Chasing the Invisible Man

你的速度决定它的存在。
Your speed determines its presence.

5

Summary

Since the application of voltammetry techniques have been expanded from its original use with mercury electrodes to a wide range of solid materials, modern voltammetry has evolved into an indispensable technique. It offers valuable insights into the electrochemical properties and behavior of materials, and therefore has had a big impact in various field like materials science, energy storage, corrosion studies, and sensor development. In a voltammogram, the correct interpretation of the current response is exceptionally crucial when the applied potential is changed by the potentiostat, but not always easy to unravel. Historically, gold was the focal point in some of the earliest discussions in electrochemical surface science, notably in the studies of Frumkin, Butler, Browden and Rideal, which took place simultaneously with initial research on mercury.[1] The knowledge gained by the interpretation of the electrochemical behavior of gold has had a profound impact on many modern scientific fields.[1-3]

In this thesis we investigated the relationship between the type of oxide and the oxygen evolution reaction (OER) activity by combining *in situ* Raman and voltammetry measurements (**Chapter 2**). We explored the behavior of the oxide reduction peaks using Rotating Ring-Disk Electrode (RRDE) and Electrochemical Quartz Crystal Microbalance (EQCM), thereby uncovering important details of the structural reconstruction of gold oxides (**Chapter 3**). Additionally, we evaluated the distribution of surface charges in the presence of chemical adsorption events and even in the oxygen reduction reaction (ORR) catalytic process using EQCM (**Chapter 4**). In this Chapter, the primary objective is to summarize the findings described in this thesis, and share some insights from our findings.

The separated reduction waves observed for gold oxides indicate the reduction of distinct types of oxide, rather than reductions of the so-called inner and outer oxide layers.

The experimental exploration of oxide formation in electrochemistry can be traced back to the 1930s. The introduction of the “charge-curve” method, initially employed by Bowden and Rideal[4] for measuring the double layer capacitance at Hg, independently saw applications to the study of electrochemical processes at Pt and Au by Frumkin *et.al.* and by Butler *et. al.*

in the early 1930s.[1, 5] A significant stride was taken in the 1960s by Will and Knorr,[6] who advanced our understanding of electrochemical surface processes at noble metals through the use of potentiostats. This method, an extension of the potential-sweep approach (i.e. voltammetry) already employed in polarography at DME, offered a new avenue for exploring interfacial processes at noble metals. The adoption of controlled-potential techniques, facilitated by electrochemical instrumentation, grants a level of control that is crucial for studying anodic oxide film formation at metals — an advantage not easily achieved through the examination of oxide film formation from the gas phase or with controlled current methods.

In the exploration of the oxide layer formation and reduction, electrochemists have made connections between different reduction waves and distinct oxide layers. This line of thought traces back to Shibata's findings on the reduction of thick-film Pt oxide reduction, where he discerned between the quasi-2d oxide film (α state) and the thick (β) oxide during a potential sweep towards negative potentials.[7, 8] Shibata proposed that the thick (β) oxide would be situated between the bulk metal and a layer of newly deposited metal atoms on the exterior of the remaining β oxide, arising from the reduction of the α state oxide.

Burke and Roche, however, introduced an alternative model known as the hydrous oxide model.[2, 9] According to the Burke model, a thick metal oxide comprises an inner monolayer (compact and anhydrous) and an outer oxide layer (dispersed and hydrous). In the hydrous oxide model, the inner oxide layer is reduced first before the outer oxide layers. Although these papers lacked any direct experimental evidence linking the oxide layers with the reduction peaks, these paved the way for further research, encompassing a broader range of materials to probe their various oxide layers by tracing reduction peaks.[10, 11] As a direct consequence, voltametric data have been mistakenly regarded as a convenient means to distinguish between the inner anhydrous oxide layer and the outer hydrous oxide layer.[2]

In **chapter 2**, our exploration delved into analysis of the reduction peaks of gold oxide across the entire pH scale, revealing a significant flaw in the existing hydrous oxide model. First of all the O_2 reduction peak has been frequently misconstrued as an oxide reduction peak in the common literature, leading to severe misinterpretations in the analysis of oxide layer structure. While it is evident that gold oxides possess inner and outer components, the critical question that thus far has not been answered is whether electrochemical reduction of these inner and outer components is responsible for the observation of multiple gold oxide reduction waves observed in the voltammogram.

We therefore conducted a more in-depth investigation into the reduction chemistry of gold oxide, employing a combination of cyclic voltammetry and surface-enhanced Raman spectroscopy. Ultimately, we confirmed the presence of two distinct types of oxides (α oxide and β oxide). This oxide classification was pinpointed by systematic tracing of the gold oxide reduction behavior and by conducting *in situ* surface-enhanced Raman spectroscopy (SERS). In addition, we investigated the relationship between the OER activity and in relation to the type of oxide present and found that the two oxides are both pivotal for the OER, yet lead to different OER pathways. Thereby, this discovery significantly contributed to our understanding of why the OER activity on gold varies considerably as a function of pH.

The anomalous potential shifts that are observed in in case of the gold oxide reduction waves are not caused by mysterious ion effects from the electrolyte; Instead, these accurately reflect the way gold oxides undergo self-reconstruction processes.

Presently, our comprehension of the metal oxide structure on the atomic–scale mainly relies on *ex situ* spectroscopic techniques in vacuum,[12-14] and computations on well-defined and highly symmetrical metal surfaces. However, during catalysis, the corrosion and reconstruction of the metal oxide surface give rise to the formation of amorphous structures. These amorphous structures significantly differ from the original well–defined crystalline materials studied in vacuum and by computations.[14-17] At present the scientific community knows very little about the atomic structure of real metal oxide catalysts, especially at the solid liquid interface where electrocatalysis occurs. Therefore how the structure of amorphous oxides changes during a catalytic process is seen as one of the most challenging scientific questions .[14]

In **Chapter 2**, we corrected the traditional hydrous model, which mistakenly regarded different gold oxide reduction peaks as the reduction process from distinct oxide layers. The disruption of that model has prompted us to reconsider the true underlying reasons behind the non-Nernstian behavior , i.e. abnormal potential shift, of the gold oxide reduction waves. This is crucial because many interpretations of non-Nernstian behavior on oxides in the past were built upon misinterpretations related to the hydrous model. For these reasons, we present our findings in **Chapter 3**.

In Chapter 3, we explored the intriguing "non-Nernstian behavior" characterized by anomalous potential shifts in the oxide reduction peaks of CVs. Our exploration was facilitated by employing advanced *in situ* techniques, including Rotating Ring-Disk Electrode (RRDE) and Electrochemical Quartz Crystal Microbalance (EQCM). These tools enabled us to probe deeply into the intricacies of the amorphous oxide structure within realistic catalytic environments.For instance, we could pinpoint the moment of Au^{3+} detection in the oxide reduction process by observing the reduction current of Au^{3+} on the ring during an RRDE experiment. By investigating the moment of mass loss on EQCM, we gained insights into the role of these Au^{3+} ions in stabilizing the interface between oxides and solutions. In the end, the data from various techniques interconnected, revealing that Au^{3+} cations play a crucial role in the chemistry of gold oxide. They form bonds with nucleophiles present within the amorphous gold oxide layer and the electrolyte solution, thereby dominating the interactions at the solid-liquid interface.

In this study we introduce an important connection between the non-covalent states of metals (ionic and hydrous metal cations) within covalent oxides and the dynamic evolution of oxide structures by tracing the non-Nernstian behaviors of gold oxide reduction. This newfound connection lies the basis for a more accurate understanding of the electrochemical behavior of oxides. This shows that is possible to trace structural changes caused by metal ions within amorphous metal oxides by investigating the Non-Nernstian behavior of such oxides. It serves as a reminder that understanding the manner in which metals are bound within the metal oxide (ionic bond, covalent bond or hydrogen bond) is crucial for comprehending the dynamic behavior of such metal oxides under realistic operating conditions.

Exploring the surface charge distribution during chemical adsorption/desorption and catalytic processes is possible by employing EQCM.

Inspired by the work in the preceding two Chapters (which focused on the potential range where oxides exist in voltammetry), the focus of chapter 4 lies with the relatively negative potential ranges where no oxides are present—specifically, the electrochemical double layer potential range. Here a new investigation was built from the ground up to understand the electrochemical behavior at the double layer region on gold. Thus, **Chapter 4** came into being.

Our original comprehension of the electric double layer structure at interface comes from surface tension measurements on mercury, where the potential of zero charge (PZC) is pinpointed as the potential corresponding to the maximal surface tension on an electrocapillary curve.[18] Variations in the surface excess charge will induce a redistribution of ions, resulting in the non-Faradaic currents that can be observed in a CV. Because there is a correlation between excess charge and non-Faradaic current, it allows us to investigate excess charge by current response without surface tension measurements. The correlation is crucial for solid electrode, as surface tension measurements are impossible on solid materials. Thus electrochemical capacitance measurements calculated from the current responses in a voltammogram have played a crucial role in understanding the electrochemical interface structure on the electrode surface, particularly for solid electrodes.

However the presence of Faradaic current resulting from the chemical adsorption/desorption of ions poses a challenge to the accuracy of capacitance measurements, given that chemical processes frequently occurs at solid electrodes. While numerous modified GCS models discuss the double layer structure by incorporating adsorption/desorption involving electron transfer, it must be emphasized that we still lack a precise understanding of how excess charge is built up exactly in the presence of chemical adsorption/desorption.

The use of the EQCM may allow for new insights into our understanding of electrochemical interfaces. The potential use of QCM as a mass sensor was first demonstrated by Sauerbrey in 1959. Nomura and Okuhara extended the applicability of QCM to liquid based systems in their 1982 publication, initiating the development of EQCM for the field of interfacial electrochemistry.[19] Initially, QCMs were predominantly utilized as monitors for thin film deposition to control the film thickness. The initial application of EQCM measurements is rooted in the existence of a correlation between Faradaic charge involving electrochemical deposition and the mass change. However, increasing research has revealed that EQCM can also detect the electrostatic attraction of both ions and cations.[20, 21] These efforts have inspired our investigation into the distribution of excess charge on the gold surface. This was primarily accomplished through the combination of voltammetry and EQCM measurements.

In **Chapter 4**, we introduce the utilization of EQCM as an innovative approach to discern and quantify the electrode excess free charge. The EQCM exploits the oscillation frequency of a quartz crystal as a sensitive indicator of mass changes on a gold electrode. By capitalizing on the frequency response of the quartz crystal to the electrostatic attraction of free charges, this method may provide a means to identify the potential regions where a positive and a negative excess charge exist, respectively. Through a comparison of the frequency response recorded by the EQCM and the capacitance recorded by cyclic voltammetry, we can estimated the amount of excess free charge and the Faradaic charge in the entire pH scale. Furthermore, by examining the correlation between the excess free charge and the frequency response, we have constructed excess free charge distribution diagrams for both Ar and O_2 saturated solutions.These diagrams aim to visually depict how the excess charge may fluctuate at specific pH levels and applied potentials before and during catalysis.

The experimental results are exciting because through this study, we not only gained insights into the distribution of surface charges (excess charges and bound charges) in the presence of chemical adsorption without interference from Faradaic currents but also surprisingly discovered that this method of testing excess charge distribution may still be possible even during the oxygen reduction process.

Our discoveries in this thesis underscore the need for further in-depth research. Firstly, the Burke model involving different oxide layers was proposed based on the oxide reduction behaviors of various Nobel metals. **Chapter 2** reveals inaccuracies in applying the Burke model to gold, necessitating an examination of its applicability to other metals. Secondly, the relatively limited influence of electrolyte ions on the gold oxide reduction behavior opens avenues to explore the relationship between Non-Nernstian behaviors and oxide structure changes (**Chapter 3**). Investigating the role of electrolyte ions in Non-Nernstian behaviors for more complex metal oxides poses an intriguing question on how metal cations from oxide play a role. Thirdly, our work indicates significant differences of interface environments for oxygen evolution/reduction on gold. Consequently, understanding these electrode structural changes becomes crucial for explaining the high overpotential of these reactions (**Chapter2-4**). Lastly, **Chapter 4** demonstrates that EQCM may be used to explore excess free charge on gold during ORR. This raises the intriguing possibility of investigating excess free charge on various materials and in different electrochemical reaction processes.

Besides, these three Chapters we mentioned earlier inspired us to reconsider more complex questions about how we comprehend the connection between applied potential and current in voltammetry. For example, how do we interpret changes in the shapes of redox peaks over different time scales, such as measurement time? How do we precisely identify the spatial distribution of active species in different homogeneous and heterogeneous processes in voltammetry? And Why do we sometime observe an imbalance between oxidation and reduction charges in voltammetry?

References

1. Conway, B. E., *Prog. Surf. Sci.* **1995,** *49* (4), 331-452.
2. Laurence D. Burke, L. D. B., Electrochemistry of hydrous oxide films. *Modern Aspects of Electrochemistry* 1986 pp 169-189.
3. Bard, A. K.; Zoski, C. G., *Analytical Chemistry* **2000,** *72* (9), 346A-352A.
4. Bowden, F. P.; Lowry, T. M., *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character* **1929,** *125* (798), 446-462.
5. Butler, J. A. V.; Armstrong, G.; Kendall, J., *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character* **1932,** *137* (833), 604-621.
6. Will, F. G.; Knorr, C. A., *Zeitschrift Fur Elektrochemie* **1960,** *64* (2), 258-269.
7. Shibata, S., *Electrochim. Acta* **1977,** *22* (2), 175-179.
8. James, S. D., *Journal of the Electrochemical Society* **1969,** *116* (12), 1681-&.
9. Burke, L. D.; McRann, M., *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1981,** *125* (2), 387-399.
10. Baten, S. M. A.; Taylor, A. G.; Wilde, C. P., *Electrochim. Acta* **2008,** *53* (23), 6829-6834.
11. Doyle, R. L.; Lyons, M. E. G., *Journal of The Electrochemical Society* **2013,** *160* (2), H142-H154.
12. Cheng, X.; Fabbri, E.; Nachtegaal, M.; Castelli, I. E.; El Kazzi, M.; Haumont, R.; Marzari, N.; Schmidt, T. J., *Chem. Mater.* **2015,** *27* (22), 7662-7672.
13. Wang, J.; Gao, Y.; Kong, H.; Kim, J.; Choi, S.; Ciucci, F.; Hao, Y.; Yang, S.; Shao, Z.; Lim, J., *Chem. Soc. Rev.* **2020,** *49* (24), 9154-9196.

14. Ding, H.; Liu, H.; Chu, W.; Wu, C.; Xie, Y., *Chem. Rev.* **2021,** *121* (21), 13174-13212.
15. Yang, S.; Hetterscheid, D. G. H., *ACS Catal.* **2020,** *10* (21), 12582-12589.
16. Gerken, J. B.; McAlpin, J. G.; Chen, J. Y.; Rigsby, M. L.; Casey, W. H.; Britt, R. D.; Stahl, S. S., *J. Am. Chem. Soc.* **2011,** *133* (36), 14431-42.
17. Bergmann, A.; Jones, T. E.; Moreno, E. M.; Teschner, D.; Chernev, P.; Gliech, M.; Reier, T.; Dau, H.; Strasser, P., *Nat. Catal.* **2018,** *1* (9), 711-719.
18. Hamann, C. H.; Hamnett, A.; Vielstich, W., *Electrochemistry*. 2nd completely rev. and updated ed. ed.; Weinheim : Wiley: 2007.
19. Buttry, D. A.; Ward, M. D., *Chemical Reviews* **1992,** *92* (6), 1355-1379.
20. Levi, M. D.; Salitra, G.; Levy, N.; Aurbach, D.; Maier, J., *Nat Mater* **2009,** *8* (11), 872-5.
21. Levi, M. D.; Sigalov, S.; Salitra, G.; Elazari, R.; Aurbach, D., *J Phys Chem Lett* **2011,** *2* (2), 120-4.