Quantitative Analysis of Homogeneous Electrocatalytic Reactions at

IDA Electrodes: The Example of $[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Bn}}_2)_2]^{2+}$

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Abstract

Interdigitated array (IDA) electrodes have been applied to study the EC' (electron transfer reaction followed by a catalytic reaction) reactions and a new method of quantitative analysis of IDA results was developed. In this new method, currents on IDA generator and collector electrodes for an EC' mechanism are derived from the number of redox cycles and the contribution of non-catalytic current. And the fractions of bipotential recycling species and catalytic-active species are calculated, which helps understanding the catalytic reaction mechanism. The homogeneous hydrogen evolution reaction catalyzed by $[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Bn}}_2)_2]^{2+}$ (where $\text{P}^{\text{Ph}}_2\text{N}^{\text{Bn}}_2$ is 1,5-dibenzyl-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane) electrocatalyst was examined and analyzed with IDA electrodes. Besides, the existence of reaction intermediates in the catalytic cycle is inferred from the electrochemical behavior of a glassy carbon disk electrodes and carbon IDA electrodes. This quantitative analysis of IDA electrode cyclic voltammetry currents can be used as a simple and straightforward method for determining reaction mechanism in other catalytic systems as well.

Keywords: Interdigitated array (IDA) electrodes; EC' reaction; mechanism; quantitative analysis

Introduction

IDA electrodes work similarly to traditional rotating ring-disk electrodes (RRDE) with two closely spaced but separately operated working electrodes, the generator and collector. With properly controlled potentials on the two working electrodes, redox couples can be reduced (or oxidized) on generator, and subsequently diffuse to collector where the reverse reaction can occur (Figure 1(a)). The main difference between IDA and RRDE is that the communication between generator and collector on IDA electrodes is in both directions due to the diffusion mass transfer mode, rather than convective in the RRDE, whose collector doesn't affect the generator current (Figure 1(b)). The small spacing between generator and collector digits (several microns in IDA instead of several hundred microns in RRDE) results in largely enhanced currents due to the continuous redox cycling between them. While the larger distances between the ring and disk electrodes, compared to the microfabricated IDAs, makes them less sensitive to short lived intermediates except at very high rotation velocities that tend to induce turbulence in the solution. In addition RRDEs are bulky, need to use a lot more solutions and samples, and not convenient to transfer into the glove box.

Extensive research has been done on IDA electrodes with much of the literature describing their fabrication and characterization[1-16] while pursuing smaller features, higher collection efficiencies and more redox cycling. Digital simulations and analytical methods for modeling the behavior of IDA electrodes have been reported [17-22]. A wide variety of applications exploit the high sensitivity of IDAs including the detection of products from generator, e.g., H_2O_2 detection in O_2 reduction reaction and H^+ from electrooxidation of methanol[23-25] as in RRDEs. Fast and efficient redox cycling

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4 between the IDA generator and collector electrodes works like a “signal amplifier”
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6 enabling its use as a sensor for trace detection[1,14,26-36]. Some other applications
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8 include the measurement of electron conduction through polymer films[14,37], selective
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10 functionalization of the IDA digits[38-40], electrooptical measurements[41], biological
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12 cell detection via the impedance and capacitance changes between two working
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14 electrodes[42-44] and electrical stimulation of muscle tissue[45].
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18 Specifically, when it refers to the EC' (electron transfer reaction followed by chemical
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20 steps) reaction, as will be discussed in this paper, traditionally the RRDE could be used to
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22 detect the reaction efficiency[46,47]. However, the low collection efficiency of the
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24 RRDE (30%-40%) limits its application in detecting the short-lifetime or low-
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26 concentrated reaction intermediates, especially for the catalysts with low catalytic rates
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28 and current response. Besides, the mass transfer of RRDE reaction relies on the strong
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30 external force on the electrode, which generates much noise and lowers the sensitivity of
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32 electrodes. In contrast, the high sensitivity of IDA electrodes makes it a good candidate
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34 for studying the catalytic reactions, especially the low activity reactions.
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38 Most research with IDA electrodes involves either qualitative estimation or simple
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40 quantitative analysis of calculating the collection efficiency, number of redox cycles or
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42 electrode impedances. However, these simple calculations are not sufficient to provide
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44 information for complex reactions, e.g. EC' (electron transfer reaction followed by
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46 chemical steps), unless a digital simulation is applied. Without some prior knowledge of
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48 the reaction mechanism and good guesses on rate constant values the digital simulation
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50 process is not straightforward. In this paper, a new method of analyzing the IDA results
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52 of EC' reaction was derived. A simplified reaction rearrange model is proposed and with
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this model the information of active reaction species and species in bipotential mode could be calculated, which therefore helps understanding the reaction mechanism.

Experimental

Chemicals and Apparatus

$[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Bn}}_2)_2][\text{BF}_4]_2$ and $[\text{H}^+-\text{DMF}]\text{OTf}/\text{DMF}$, the acid used for the hydrogen reduction reaction, were provided by the Center for Molecular Electrocatalysis, Pacific Northwest National Laboratory. Ferrocene (Sigma-Aldrich), tetrabutylammonium hexafluorophosphate (NBu_4PF_6) ($\geq 99.0\%$, Sigma-Aldrich) and acetonitrile ($\geq 99.8\%$, Sigma-Aldrich) were used as purchased. Electrochemical experiments were performed with a bipotentiostat (Ivium Technologies, Netherlands).

Carbon IDA Fabrication

Carbon IDA electrodes were fabricated on oxidized silicon wafers at the Center for Nanoscale Materials at Argonne National Laboratory. Each IDA used herein have 50 generator digits and 51 collector digits. The carbon IDA digits were $1000\text{ }\mu\text{m}$ long with various widths and gap sizes. The widths are between $1.2\text{ }\mu\text{m}$ to $3\text{ }\mu\text{m}$, and the size of the gaps is between $3\text{ }\mu\text{m}$ and $4.8\text{ }\mu\text{m}$, as indicated in the figures. Details of the carbon IDA fabrication were published in a previous paper^[48].

Results and Discussion

1) Quantitative Analysis of IDA Currents

A quantitative analysis of the IDA currents is desired and important for describing and understanding the reaction mechanism. In this section we explore the current responses at

IDA electrodes for an EC' reaction (as shown in scheme 1), where O is the electrocatalyst, S is the substrate, ES is the intermediate, P is the product, and k , k_f , k_r and k_{cat} are electron transfer rate constant, chemical reaction forward rate constant, chemical reaction reverse rate constant and catalytic reaction rate constant, respectively.

The concept of redox cycles, where the currents on both generator and collector are enhanced by diffusional feedback, is introduced to facilitate the understanding of the IDA current calculations that will be utilized in this section. The number of redox cycles (Rc_{dual}) at IDA electrodes has been defined by Niwa et al [49]. In his paper, the number of redox cycles was obtained by operating IDA electrodes in both dual-potential mode and open-circuit mode. Here the dual-potential mode means that both the generator and collector are operated with proper potentials and enables the redox cycling between them, while in the open-circuit mode the collector is set open circuited and reaction takes place only on generator electrode. Calculation equation is shown in equation (1),

$$Rc_{dual} = i_g / i_o \quad (1)$$

where i_g and i_o are the limiting currents of the generator operated in the dual-potential mode and open-circuit mode respectively without the existence of catalytic reaction. Rc_{dual} reflects the efficient transfer of electroactive species between generator and collector and is affected by the geometry, specifically the gap size between two adjacent IDA electrodes. When operated in the dual-potential mode without catalytic reactions, the current at the generator electrode is given as $i_g = i_o \times Rc_{dual}$, according to equation (1); and the current on the collector is then $i_c = i_g \times \phi$, where i_c is the collector current and ϕ is the measured collection efficiency of the IDA electrode, the ratio of the steady state current on collector to the steady state current on generator.

Similar to the cycling of compounds between generator and collector, the catalytic reaction in solution also drives the mass transfer cycling (or called feedback) of redox couples on IDA electrodes operating in the open-circuit mode. In order to quantify the cycling of compounds in catalytic reactions, the number of redox cycles of IDA electrodes in open-circuit mode with the existing of catalytic reaction (Rc_{cat}) is defined in equation (2), where i_{cat} is the catalytic current at the IDA generator electrode in open-circuit mode. The catalytic current (i_{cat}) on IDA generator electrode operated with the collector open-circuited is represented as $i_{cat} = i_o \times Rc_{cat}$ from a rearrangement of equation (2).

$$Rc_{cat} = i_{cat} / i_o \quad (2)$$

In this paper, both redox cycles, Rc_{dual} and Rc_{cat} , are accounted to investigate and predict the currents at IDA electrodes.

Based on the simple circumstances (IDA operated in dual-potential mode without catalytic reaction, and IDA operated with the collector open-circuited and with the existing of catalytic reaction) discussed as above, the expression for IDA currents with EC' reactions in the dual-potential mode is obtained by a simplification of the reactions occurring in the IDA system. Focusing on the IDA generator with EC' reactions, the reactions on it are treated as the sum of two contributions (Figure 2).

1) The first component is named as “pure open-circuit mode”. It assumes that a fraction of catalyst, c , participates in the catalytic reactions (EC') on the generator with no influence from the collector. The current obtained from this component is similar to that in the single working electrode system.

2) The second component is named as “pure dual potential mode”, in which the remaining catalyst fraction, $1-c$, is assumed that only participates in the straightforward redox cycling (i.e. electron transfer reaction) on generator and collector, and does not influence the catalytic reaction.

The real reaction mechanism may have both catalytic-active intermediate and inactive intermediate produced, so further assumption is made that the fraction of active intermediate is a , as shown in Figure 2. It is then clear that c includes both active and inactive intermediates where the fraction of catalytic-active intermediates ($a \times c$) would participated in the catalytic reaction, while all the other molecules ($1-c+c \times (1-a)$) are almost completely collected at the collector electrodes since the collection efficiency is usually higher than 95% for IDA electrodes with small gaps and assumes that the inactive intermediate is also electroactive.

The two processes on the IDA electrodes operated in the dual-potential mode are assumed to be independent of each other as described above in the simplified scheme. Therefore, the collector current is simply composed of the feedback current from “pure dual-potential mode” (Expression (3)), plus the collection current for the inactive intermediate from “pure open-circuit mode” (Expression (4)).

$$(1-c) \times i_o \times R_{c_{dual}} \times \Phi \quad (3)$$

$$[c \times (1-a)] \times i_o \times R_{c_{dual}} \times \Phi \quad (4)$$

While the generator current is composed of the catalytic current from “pure open-circuit mode” (Expression (5)), plus the feedback current from communication with the collector in “pure dual-potential mode”, i_o/ϕ .

$$c \times i_o \times Rc_{cat} \quad (5)$$

Therefore the generator and collector currents of the IDA electrode, operated in the dual-potential mode with an EC' reaction, can be expressed as below:

$$\frac{i_c}{\Phi} = [(1 - c) + c \times (1 - a)] \times i_o \times Rc_{dual} = (1 - a \times c) \times i_o \times Rc_{dual} \quad (6)$$

$$i_g = \frac{i_c}{\Phi} + c \times i_o \times Rc_{cat} = [(1 - a \times c) \times Rc_{dual} + c \times Rc_{cat}] \times i_o \quad (7)$$

The a and c parameters can be calculated from the experimental cyclic voltammograms using the known i_c , i_g , i_o , Rc_{dual} and Rc_{cat} values and equations (6) and (7).

2) Electrochemical Detection of Hydrogen Evolution Reaction

Electrocatalysts enable the interconversion of energy between chemical bonds and electrical current. To lower the cost of producing hydrogen from water much research has been focused on replacing rare and costly platinum with synthetic coordination compounds containing more earth abundant elements, such as the $[\text{Ni}(\text{P}^{\text{R}}_2\text{N}^{\text{R}'}_2)_2]^{2+}$ series of electrocatalysts (where $\text{P}^{\text{R}}_2\text{N}^{\text{R}'}_2$ is 1,5-R'-3,7-R-1,5-diaza-3,7-diphosphacyclooctane)[50-52], that are designed as a mimic of [FeFe]-hydrogenase enzymes in nature for hydrogen reduction or oxidation. Among these, the hydrogen evolution catalyst $[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Bn}}_2)_2]^{2+}$ (where $\text{P}^{\text{Ph}}_2\text{N}^{\text{Bn}}_2$ is 1,5-dibenzyl-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane - abbreviated as NiPhBn), even though has a low turn over frequency for hydrogen production ($<0.5 \text{ s}^{-1}$)[53], but attract a lot of attentions due to its role in understanding proton coupled electron transfer in this series of $[\text{Ni}(\text{P}^{\text{R}}_2\text{N}^{\text{R}'}_2)_2]^{2+}$ catalysts[53]. In this part of paper we will use NiPhBn catalyst as an

example to study its EC' mechanism in more detail using electrochemical techniques that are different than methods used previously.

According to the previous study by Appel, et al [53], the NiPhBn catalyst has a “two proton and two electron” steps in its reaction mechanism for hydrogen evolution. The electrocatalysis reaction in non-aqueous solvents with protonated dimethylformamide ($[H^+ \cdot DMF]OTf/DMF$) as the proton source was proposed to proceed by the following mechanism: 1) biprotonation of NiPhBn catalyst, where the second protonation reaction is easier than the first leading to one simultaneous biprotonation step [53]; 2) the biprotonated catalyst is subsequently reduced by two electrons; 3) the reduced biprotonated catalyst slowly converts to a catalytically-active form to release a H_2 molecule returning the catalyst to its initial form. Particularly, as determined by NMR [51,53], the protonation step takes place first at the exo positions of the $P^{Ph}_2N^{Bn}_2$ ligand and forms the exo-exo $[Ni(P^{Ph}_2N^{Bn}_2H)_2]^{4+}$ intermediate (Scheme 2). However this exo-exo form is not active for H_2 production since the two protons are pinned up by the two pendant amines and cannot approach the metal center and to form metal hydride bonds and release H_2 molecules. Therefore it is believed that this exo-exo intermediate slowly converts into the endo-endo isomer (Scheme 2), eliminating H_2 and returns to the original $[Ni(P^{Ph}_2N^{Bn}_2)_2]^{2+}$ form [53]. This slow isomerization from catalytic inactive exo-exo to active endo-endo structure results a slow rate of H_2 generation.

The regular big working electrode, glassy carbon disk electrode, was firstly used to detect the basic electrochemical performance of the NiPhBn catalyst. Cyclic voltammograms of the NiPhBn catalyst with and without the presence of acid were obtained at different scan rates as shown in Figure 3. Two reversible one-electron transfer peaks are present in the

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4 absence of acid (black curves in Figure 3), corresponding to the reduction of NiPhBn^{2+}
5 and NiPhBn^{1+} whereas with the addition of protonated DMF, as a strong acid, shifts the
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7 reduction of the protonated catalyst (NiPhBnH_2^{4+}) to significantly more positive
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9 potentials indicative of strong proton binding to the complex [53]. Furthermore, possible
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11 intermediates were observed when investigating the catalytic reaction at different scan
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13 rates with the low acid concentrations. Relatively fast scan rates and low acid
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15 concentrations showed a peak at -0.70 V vs. $\text{FeCp}_2^{+/0}$ (the potential reference for all the
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17 potentials reported in this paper) as well as a hump at around -0.55 V. Increasing the acid
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19 concentration diminishes the peak current at -0.70 V while the peak current at -0.55 V
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21 increased (Figure 3(a)). These two waves are attributed to the reduction of the
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23 NiPhBnH_2^{4+} exo-exo and NiPhBnH_2^{4+} endo-endo intermediates, respectively. Larger
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25 acid concentrations promote faster formation of the exo-exo isomer resulting in a greater
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27 production of the endo-endo isomer, demonstrating the coexistence and interconversion
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29 between the endo and exo isomers, as shown in the Scheme 3. Additionally, slow scan
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31 rates at very low acid concentrations produced waves at around -0.80 V and -1.10 V
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33 (Figure 3(b) red curve). These reproducible humps may demonstrate the existence of the
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35 singly protonated catalyst and its reduced forms (Scheme 3, dash boxes.), that were
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37 originally proposed but not detected [53]. The formation of the singly protonated catalyst
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39 may be very slow and so only appears at slow scan rates and low acid concentrations.
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50 As mentioned earlier, IDA electrodes with dimensions in the 1 to 10 micron range and
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52 operating in generation and collection mode function differently in comparison with a
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54 rotating ring-disk electrode. Figure 4 shows the possible reactions that may take place on
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56 IDA electrodes when it is applied to investigate the catalytic proton reduction reaction
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with NiPhBn. In the absence of a catalytic reaction (no H^+ in the solution), $[Ni(P^{Ph}_2N^{Bn}_2)_2]^{2+}$ (abbreviated as Ni^{2+} in Figure 4) gets reduced and eventually produces $[Ni(P^{Ph}_2N^{Bn}_2)_2]^0$ (Ni^0 in Figure 4) on the generator. The Ni^0 reduction product can either diffuse into the bulk or get reoxidized at the collector surface if the appropriate potential is applied (Figure 4(a)). A corresponding cyclic voltammogram of NiPhBn (Figure 5 in black curves) reveals that the catalyst shows two reduction waves on the generator and two corresponding oxidation waves on the collector. Then, a catalytic reaction is initiated when Brønsted acids are present in the solution. In this circumstance some fraction of the reduced and protonated catalyst produced at the generator will evolve H_2 while another fraction will be re-oxidized at the collector. Therefore, the chemical oxidation occurring in solution as the final step in turnover competes with the Faradaic re-oxidation reaction at the collector, with both channels contributing to feedback at the generator (Figure 4(b)). Catalytic H_2 production starts with a low reaction rate in case of a low H^+ concentration, offering a weak Ni^{2+} feedback to the generator. As what could be predicted, the collector would takes a larger share of reduced catalyst from the generator and sustain a high collection efficiency. With more H^+ added into the solution, it leads to a faster catalytic H_2 production and therefore a rapider species communication between the reduction reaction on generator and catalytic reaction in solution. Spceices are easier reacting with H^+ than diffusing to the collector. Therefore, the collection efficiency decrease with more H^+ added to the solution.

The red curves in Figure 5 show the affect of catalytic reactions on the IDA currents. In accordance with the results from glassy carbon electrodes, the reduction potential of protonated catalyst is at more positive potentials than $NiPhBn^{2+}$ reduction (near -0.7 V vs.

$\text{FeCp}_2^{+/0}$). The slow scan rate curve (0.01 V/s) in Figure 5(b) demonstrates that the continuous increase of the currents on both generator and collector may resulted from the more abundantly generated reaction intermediates with the slow scan, NiH^{3+} , NiH_2^{4+} -exo, etc, as shown in scheme 3. These intermediates are observed as multiple humps in the current-potential curve, in accordance with the red curve in Fig.3(b). It should be pointed out that currents on both the generator and collector were lower than those in the absence of protons. The lower currents indicate that the catalytic reaction in this solution is not fast enough to provide efficient feedback of regenerated catalyst at the collector.

In order to clearly detect any possible intermediates formed after protonation, the IDA was operated by holding the generator at a constant negative potential (-1.4V or -1.6V vs. $\text{FeCp}_2^{+/0}$) and the collector was scanned from the same potential in the positive direction in order to oxidize any possible products formed on the generator. Figure 6 shows these results at different scan rates. Without protons in the solution the generator and collector currents reproduced two mirror image waves expected for the reduction and reoxidation of the catalyst (Figure 6, black curves). In the presence of acid, the catalyst was immediately protonated and was reduced with a constant current on generator until all H^+ were depleted near the electrode surface and no protonated catalyst could form. Simultaneously the reduced protonated catalyst from generator electrode could either produce H_2 in solution or diffuse to collector and got reoxidized. So following these possible reactions, the generator showed the catalytic current and the corresponding current on collector (Figure 6, red curves). Specifically, Figure 6(b), the big hump near -0.7 V for the slow scan rate corresponds to the oxidation of biprotonated catalyst as is already established and the two small humps that appear near -1.1V and -0.8V we assign

to the reaction of the singly protonated catalyst (NiPhBnH^{3+}). At the faster scan rates (0.5V/s) the single-protonated intermediates are not detected, however the oxidation of biprotonated catalyst still appears near -0.7 V (Figure 6(a)). The sharp current increase near -0.4V is related to the reaction of un-protonated catalyst due to the depletion of acid near the electrode surface.

3) Calculations on IDA Result of EC' reactions

Figure 7 shows the calculated dependence of a and c values with potential, i.e. the change of the active intermediate fraction and the fraction of “pure open-circuit mode” from the experiments above. The a and c values both reach a near steady state at potentials of about -1.3V.

Figure 8 shows the comparison of a and c values for different IDA electrodes with similar approximations of diffusion distances (D) of 4.2, 3.8, 3.5 and 3.9 μm calculated from equation (8)[21,49] at four different H^+ concentrations.

$$D = \text{width} / 4 + \text{gap} \quad (8)$$

The fraction of “pure open-circuit mode” current, c , is larger with higher H^+ concentration in the solution. Obviously, a larger acid concentration increases the H_2 production rate and therefore accounts for a larger involvement of “pure open-circuit mode” in the catalytic reaction. The active intermediate fraction, a , is around 0.65~0.77 at all investigated H^+ concentrations, as shown in Figure 8(b). The changes of the fraction of active intermediate(s) (a) is not straightforward since it is influenced by both the consumption for H_2 production and the conversion of inactive intermediates to active catalyst[53]. On the one hand, larger H^+ concentration will promote the catalytic reaction and continuously consume the active intermediate as well as increase inactive ones; on

another hand, the accumulated inactive intermediate is increasingly converted to the active form. So the obtained a value is a general representation of all these influences.

The above calculation of IDA currents provides a simple way to quantitatively explore the relationship between the reactants and intermediates. Information about how much active intermediate is generated in the electrochemical reaction and how much the catalytic reaction contributes to the IDA currents is inferred from the analysis of the IDA currents for this specific EC' reaction. It should be pointed out that in this simplified model the calculated $a \times c$ values would be relatively larger than predicted if the inactive intermediate is not electroactive.

Conclusion

The IDA electrode currents in the dual-potential mode for an EC' reaction were simplified as the sum of the “open-circuit mode” current and the “dual-potential mode” current for generator and “dual-potential mode” for collector. This assumption allows the IDA currents to be represented by combinations of the noncatalytic current, catalytic current, fraction of active intermediate and fraction of “pure open-circuit mode”. Therefore, the fraction of the active intermediate in the catalytic reaction could be determined by combining the experimental currents with the theoretical IDA current expressions. The fraction of active intermediate under different conditions was calculated for the electrocatalyst $[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Bn}}_2)_2][\text{BF}_4]_2$, to be 0.65-0.77. This simple analysis is applicable in other electrochemical systems with following chemical steps.

Besides, carbon IDA electrodes were applied to investigate the electrochemical behavior of the homogeneous hydrogen evolution electrocatalyst $[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Bn}}_2)_2][\text{BF}_4]_2$. Catalytic

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4 currents were measured with cyclic voltammetry at relatively low H^+ concentrations at
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6 different scan rates using both a glassy carbon disk electrode and carbon IDA electrodes.
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8 In addition to the commonly observed diprotonated catalytic intermediate, the results
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10 from the slow scan rates provide evidence for the existence of singly protonated reaction
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12 intermediates.
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Captions of Figures and Schemes

Figure 1. Diagrammatic sketches of cross sections of electrodes and their working principles. (a) IDA electrodes. (b) RRDE.

Figure 2. Diagram presenting the assumptions for the IDA dual-potential working mode. The c represents the fraction of catalyst contributing to the “pure open-circuit mode” reaction on the generator electrode and the a is the fraction of catalytic active catalyst, e.g. NiPhBn, in solution.

Figure 3. Cyclic voltammograms for 0.08 mM NiPhBn at a glassy carbon disk electrode (3 mm dia) in 0.2 M NBu₄PF₆ acetonitrile solution with various H⁺ concentrations. Ferrocene was added into the solution as a inner reference showed reversible currents at 0V. Reference electrode: Ag wire; counter electrode: glassy carbon rod. (a) 0.5 V/s scan rate; (b) 0.01 V/s scan rate.

Figure 4. Diagram of the working principle of IDA electrodes. a) simple feedback, b) feedback with a catalytic reaction with substrate (H⁺) in solution (EC' mechanism).

Figure 5. Cyclic voltammograms for IDA electrodes with 1.3 μm width and 4.7 μm gap in 0.12 mM NiPhBn, 0.2 M NBu₄PF₆ acetonitrile solution. The potential of collector is constant at -0.4V vs. FeCp₂⁺⁰. Reference electrode: Ag wire; counter electrode: glassy carbon rod. (a) 0.5 V/s scan rate; (b) 0.01 V/s scan rate. Solid: generator; open: collector.

Figure 6. Cyclic voltammograms for IDA electrodes with 3.0 μm width and 3.0 μm gap in 0.11 mM NiPhBn, 0.2 M NBu_4PF_6 acetonitrile solution. The potential of generator is constant at -1.5V vs. $\text{FeCp}^{+/0}$. Reference electrode: Ag wire; counter electrode: glassy carbon rod. (a) 0.5 V/s scan rate; (b) 0.01 V/s scan rate. Solid: generator; open: collector.

Figure 7. Calculated a and c values versus potential calculated from cyclic voltammograms in Figure 5. Working electrode: IDA with 1.3 μm width and 4.7 μm gap; reference electrode: Ag wire; counter electrode: glassy carbon rod. Solution: 0.12 mM NiPhBn, 0.2 M NBu_4PF_6 in acetonitrile. The potential of collector is constant at -0.4V vs. $\text{FeCp}_2^{+/0}$.

Figure 8. Comparison of calculated a and c values at various acid concentrations at electrodes with different diffusion distances. Working electrode: carbon IDA electrodes; reference electrode: Ag wire; counter electrode: glassy carbon rod. Solution: 0.12 mM NiPhBn, 0.2 M NBu_4PF_6 in acetonitrile. The potential of collector is constant at -0.4V vs. $\text{FeCp}_2^{+/0}$.

Figure(s)

(a)

(b)

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.