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Seyed S. Jamali

University of Wollongong, sjamali@uow.edu.au

Simon E. Moulton

University of Wollongong, smoulton@uow.edu.au

Dennis E. Tallman

North Dakota State University

Jan Weber

Boston Scientific

Gordon G. Wallace

University of Wollongong, gwallace@uow.edu.au

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Abstract

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Keywords

electro, local, oxidation, detection, evolution, reduction, platinum, studied, scanning, electrochemical, microscopy, purpose, h₂

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Electro-oxidation and reduction of H₂ on platinum studied by scanning electrochemical microscopy for the purpose of local detection of H₂ evolution

Sina S. Jamali^{1,2}, Simon E. Moulton^{1,3*}, Dennis E. Tallman⁴, Jan Weber⁵, Gordon. G. Wallace^{1*}

¹ARC Centre of Excellence for Electromaterials Sciences, University of Wollongong, NSW, Australia.

²ARC Research Hub for Australian Steel Manufacturing, Faculty of Engineering & Information Sciences, University of Wollongong, Wollongong, NSW, Australia.

³Faculty of Science, Engineering and Technology, Swinburne University of Technology, Hawthorn, Victoria, Australia.

⁴Department of Coatings and Polymeric Materials, North Dakota State University, Fargo, ND, USA.

⁵Boston Scientific, G. Martinolaan 50, 6229 GS, Maastricht, Nederland.

Keywords: scanning electrochemical microscopy; H₂ detection; H₂ electro-oxidation; H₂ electro-reduction; H₂/H⁺ redox recycling.

Abstract

Electrochemical detection of H₂ using scanning electrochemical microscopy (SECM) has shown to hold great promise as a sensitive characterization method with high spatial resolution for active surfaces generating H₂. Herein the factors contributing to the current that is measured by SECM in generation/collection mode for H₂ detection are studied. In particular the concentration gradient of H₂ at the substrate, the H₂/H⁺ recycling between the SECM tip and substrate and hemispherical profile of H₂ diffusion have been discussed. It was postulated that H₂/H⁺ recycling plays a dominant role in the oxidative current measured in

generation/collection mode of SECM when the microelectrode is positioned in close vicinity of substrate.

Introduction

One of the unique capabilities of scanning electrochemical microscopy (SECM) compared to other scanning probe techniques is the electrochemical interaction with active species that can be sensed via an oxidation or reduction reaction. SECM in surface generation/tip collection (SG/TC) mode interacts with reducible and/or oxidisable species released from the substrate and thereby provides information on local concentration of the species [1]. In tip generation/substrate collection (TG/SC) mode with large substrates (relative to the tip size) the collection efficiency is essentially 1, meaning that the entire electroactive species generated at the tip is electrochemically converted and sensed at the substrate [2]. However, in the reverse situation, SG/TC mode, because of disproportional size factor between tip and substrate, only a fraction of electroactive species generated at the substrate is detected at the tip. It is also suggested that in small tip/substrate separation, the feedback effect may also contribute to the current being measured by the SECM tip. A series of systematic studies by Albery et al in 60s-80s examined similar concept on rotating ring-disk electrodes and the effect of diffusion and kinetic of the chemical reactions on efficiency of generation/collection of electroactive species [3-6].

Sensing H_2 via electro-oxidation at SECM tip has been utilized for studying corrosion of metals [7–11] and electro-catalytic activity of surfaces [12]. SECM in SG/TC mode has been applied elsewhere in the reverse order for screening hydrogen oxidation reaction (HOR) [13,14] where the H^+ generated electro-catalytically at the substrate was reduced to H_2 at the tip and the reduction current was measured. Also the same approach has been utilized for investigating the catalytic activity of surfaces for H_2 oxidation [15,16]. Redox activity of H^+/H_2 within the thin layer between the probe and the substrate can be utilized to monitor consumption and/or generation rates of H_2 at the catalytic surfaces [17]. Despite the attention that generation/collection mode of sensing H_2 and/or H^+ has received, the redox activity of H_2/H^+ and the factors contributing to the current sensed by SECM tip has not been fully studied.

In order to acquire reliable quantitative results from H₂ sensing by SECM in G/C mode it is essential to study the redox activity of H₂/H⁺ couple and its contribution into the overall current sensed at SECM tip. This paper presents a fundamental study on sensing H₂ through electro-oxidation near the surface of a Pt substrate in aqueous electrolyte. The tip to substrate separation and diffusion profile of the electroactive species are critical factors that determine the magnitude and resolution obtained by SECM in G/C mode. Herein SECM is used to visualize the diffusion profile of H₂ and the redox properties of H⁺/H₂ proximal to the H₂ source. Also the relationship between H₂ oxidation current measured at the SECM tip and the H₂ generated at the substrate is studied.

Experimental

Scanning electrochemical microscopy (SECM) was performed using CH instruments SECM model 920D. A 10 μm Pt ultra-microelectrode (UME) and an Ag/AgCl were used as working and reference electrodes, respectively. Substrates were Pt disk electrodes with 50 μm and 65 μm diameter which were fabricated by mounting the Pt wire in epoxy and abrasion of the cross-section with 240, 600, 1200 and 4000 grit SiC emery successively.

SECM images in constant height mode were obtained by rastering the tip in the x-y plane and recording the tip current against tip location. Distance between the tip and substrate was adjusted using a digital zoom microscope manufactured by MEIJI Techno model MS50.

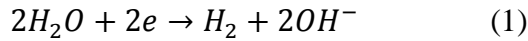
In SG/TC mode, the probe was biased at 0.0 V (Ag/AgCl) for direct detection of H₂ evolution via the H₂ electro-oxidation at the probe. The potential of 0.0V was purposefully chosen in order to eliminate the interference from O₂ reduction at more negative potentials [18] and Pt UME oxidation and deactivation at more positive potentials [19].

All electrochemical measurements were conducted in 0.1 M NaCl solution at room temperature, 22±2 °C.

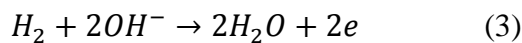
Results and discussion

In order to use SECM in SG/TC mode as a quantitative tool for measuring H₂ at a surface, it is essential to calibrate the oxidative current measured by the UME with reference to the reduction current generating H₂ at the substrate. Herein the relationship between H₂ oxidation

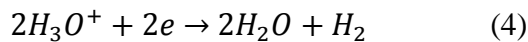
current measured at the SECM tip and the reduction current consumed for generation of H₂ at the substrate is studied. H₂ is initially generated at the surface in neutral or alkaline pH by reduction of water, reaction (1), causing further alkalization:



The H₂ generated at the substrate is then sensed by SECM UME tip via electro-oxidation, reactions (2) and (3), causing acidification:



Reaction (2) can neutralize the OH⁻ generated at the substrate within the gap between tip and substrate. If reaction (2) exceeds reaction (1), it results in an acidic pH which changes the mechanism and kinetics of H₂ oxidation reaction. In acidic electrolytes, hydrogen is produced by hydronium ion reduction, reaction (4).



From the above reactions it is clear that the pH plays a major part in both the H₂ generation and its electro-oxidation. Figure 1 shows a cyclic voltammogram of a 10µm Pt UME at 5µm distance from a 50µm diameter Pt disk substrate. The substrate was biased at -1.0V (Ag/AgCl) to generate H₂ and UME potential was cycled between -0.8 V and +0.5 V (Ag/AgCl). Figure 1a shows a potential scan of the UME tip starting at -0.8 V (corresponding with t=0 on Figure 1b) towards +0.5 V (corresponding with t=140 on Figure 1b). The data was recorded after several initial scans to obtain a more stabilised condition. The minimum oxidative current is measured at the most positive potential in Figure 1a (indicated by an asterisk) which also corresponds with the minimum current due to reduction of H₂ generated at the Pt substrate (Figure 1b - asterisk).

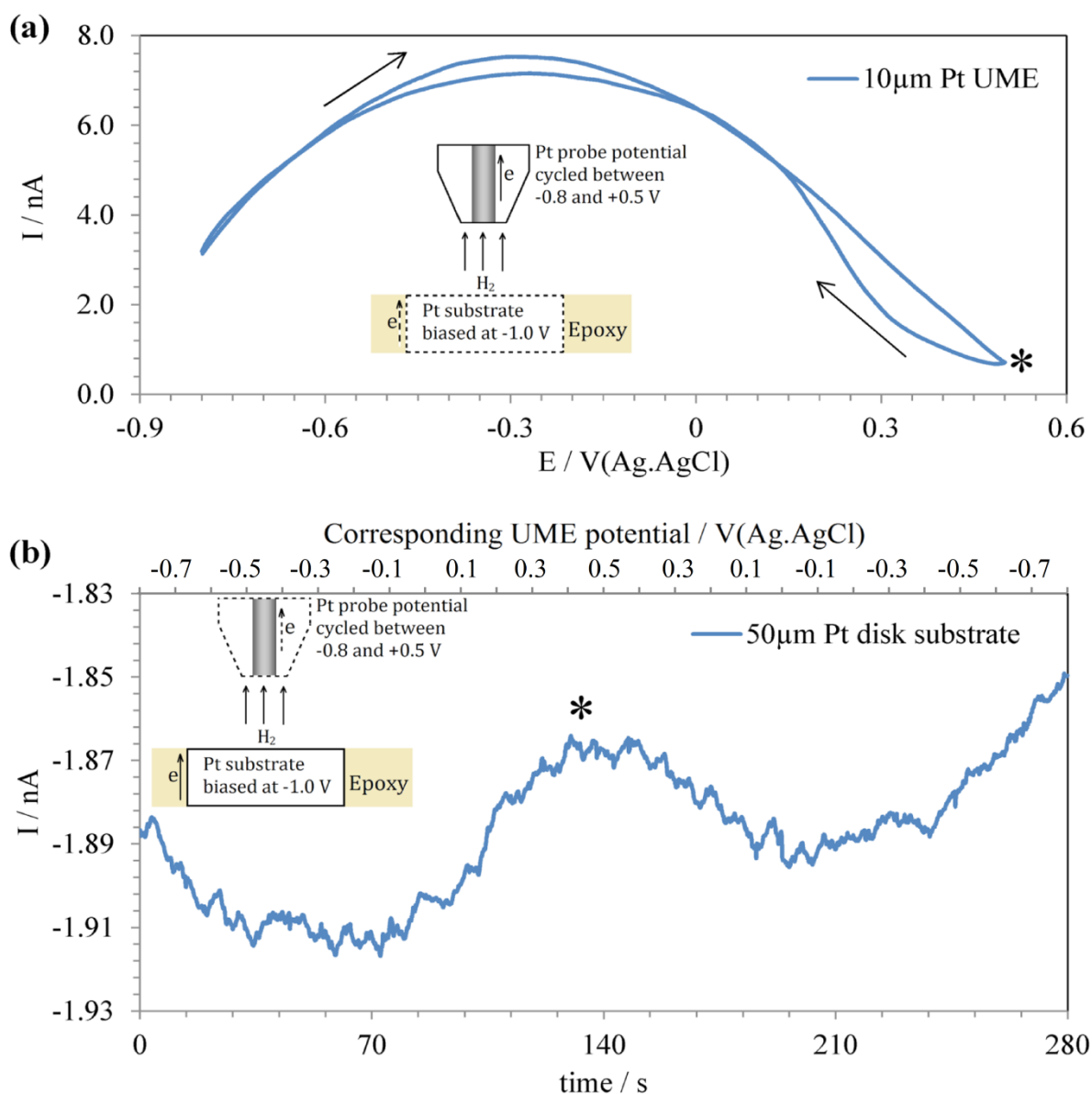


Figure 1 (a) Cyclic voltammety (CV) using a 10 μm Pt UME as SECM tip at 5 μm distance from a 50 μm diameter Pt disk substrate and (b) the reduction current measured at the substrate. Substrate was biased at -1.0V (Ag/AgCl) to generate H₂. Current generated by substrate is calculated per surface area of UME tip (approx. 78.5 μm^2). Scan rate was 5mV/s and the stabilized CV was collected after performing several cycles. The asterisks in (a) and (b) correlate with the minimum current measured at the tip and substrate respectively.

Figure 1 indicates that the oxidative current measured by the UME tip (Figure 1a) is larger than the associated H₂O reduction current measured at the substrate (Figure 1b). This suggests that the UME tip is detecting more H₂ than is being generated directly below the UME tip (Figure 2-vertical solid arrow). One explanation for this can be the lateral diffusion

of H_2 parallel to substrate towards the UME which is also oxidized and contributes to the current measured by the UME tip (Figure 2). Earlier findings showing spherical diffusion of H_2 are consistent with this hypothesis [10]. The second contributing phenomenon is the feedback effect (Figure 2 - broken arrows) caused by H_2/H^+ redox activity within the small separation gap between substrate and the UME tip. It is noteworthy that the H_2/H^+ recycling may also increase the reduction current measured at the substrate, however compared to the UME in which the recycling is effective at the entire surface of electrode (due to its smaller size compared to the substrate), at the substrate H_2/H^+ recycling occurs only at a fraction of surface and therefore is not as significant.

Figure 1b also shows the variation in substrate reduction current when the UME tip (positioned just above the substrate) potential is cycled between -0.8 V and +0.5 V. The smallest reduction current indicated by the asterisk in Figure 1b is produced when the UME tip is biased at +0.5V (Figure 1a – asterisk) which indicates the least effective potential range for H_2 oxidation reaction (HOR). This is most likely due to passivation of the Pt surface on the UME tip and the loss of metal sites for H_2 adsorption at highly positive potentials [9]. The peak reduction current in Figure 1b is generated when the tip is biased in the range -0.4V to -0.2V (Figure 1a – around $t=70s$ and $t=210s$) indicating this is the most efficient potential range for H_2 oxidation reaction (HOR). At this potential the HOR happens more effectively at the tip resulting in a less alkaline pH within the gap between the tip and substrate [10]. The less alkaline pH also favours H_2 generation taking place at the substrate resulting in a more effective reduction reaction which in turn produces larger current measured at the substrate. The HOR and its reverse reaction are both fast in an acidic electrolyte, but significantly slower in an alkaline electrolyte [20]. This is because HOR is kinetically diffusion controlled in acidic and neutral pH whereas in alkaline pH the reaction becomes electron transfer (kinetically) controlled [20]. In alkaline media there is also a second descriptor of the catalytic activity for H_2 electro-catalysis on Pt, the binding of surface hydroxyl groups which slows down the HOR [21].

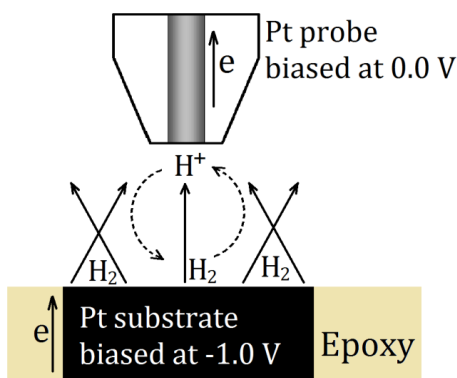


Figure 2 Schematic representation of electro-oxidative H₂ sensing showing the contribution of a large area in H₂ supply at the Pt probe and redox regeneration of H₂/H⁺ within the separation gap between substrate and the probe. Pt substrate is negatively biased (e.g. -1.0 V (Ag/AgCl)) to generate H₂ while the probe is biased positive to H₂/H⁺ reduction potential (e.g. 0.0 V (Ag/AgCl)) to electro-oxidize H₂.

A further experiment was conducted to examine the effect of diffusing H₂ from distant domains (lateral diffusion) and also the feedback effect from H₂/H⁺ regeneration on the HOR current measured by the tip. In case the lateral diffusion dominates, the oxidative current should decrease by reducing the gap between tip and substrate. In contrast, if the feedback effect from H₂/H⁺ regeneration is a significant contribution then reducing the gap between tip and substrate should increase the oxidative current exponentially. Figure 3 shows the approach curve of a 10 μm Pt UME collected on a 65 μm Pt disk substrate. The substrate was biased at -1.0V to generated H₂ and the tip was biased at 0.0V to oxidise the H₂. The increase of current by reducing the tip/substrate separation is primarily a result of increasing H₂ concentration in proximal to the substrate.

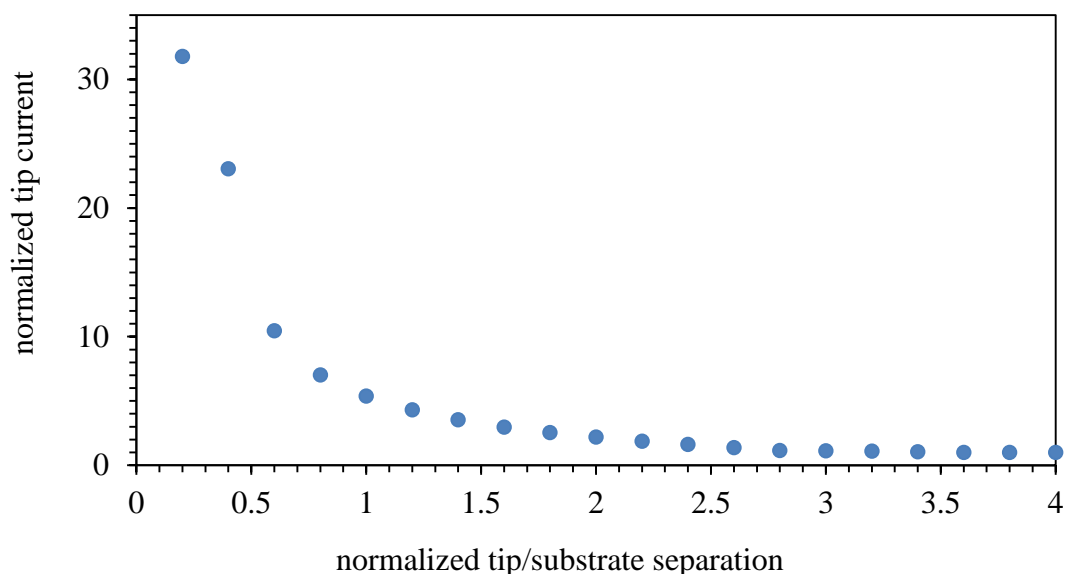


Figure 3 Amperometric approach curve using a 10 μ m Pt UME as SECM tip biased at 0.0V (Ag/AgCl) and a 50 μ m dia. Pt disk biased at -1.0V (Ag/AgCl) as substrate and source of H₂ generation.

This current will be further influenced by the local pH in the gap due to the neutralization effect. The steady H₂ generation at the Pt substrate would result in an alkaline local pH in the vicinity of substrate surface in the absence of neutralizing reactions (2) and (3) at the SECM tip. As the tip approaches the substrate, neutralization reactions would decrease the pH thus accelerating the H₂ generation. The local pH gradient in the gap will depend on tip-substrate distance. By definition, this increase in tip current is not purely a feedback effect as it is not only a result of redox electron mediator regeneration. The strong increase of current in the vicinity of Pt substrate also indicates that feedback current from H₂/H⁺ redox regeneration (shown by broken arrows in Figure 2) is a major contribution to HOR current measured by the tip in close proximity of substrate (e.g. <10 μ m). The lateral diffusion of H₂ is probably more important at higher tip/substrate separation.

The electrochemical model proposed in Figure 2 illustrates how H₂ generation from surrounding domains contributes to the HOR current that is measured at the UME probe (solid radial arrows). It also demonstrates the redox regeneration of H₂/H⁺ within the separation gap between substrate and the UME probe (broken arrows). This redox

regeneration may also influence the substrate reduction current when the probe is appropriately biased to effectively oxidize H_2 . This increase of reduction current can be seen as a more negative current at the substrate in Figure 1b. The solid vertical arrow shows the H_2 generated at the substrate which is directly detected (collected) at the UME probe.

The proposed model in Figure 2 is visualised by acquiring SECM images of H_2 distribution profile at different distances from the Pt substrate. Figure 4a illustrates the distribution of H_2 concentration that is generated at a $65\mu\text{m}$ diameter Pt disk substrate at different tip/substrate separations. The micro Pt substrate (Figure 4b) was biased at -1.0 V (Ag/AgCl) to produce a consistent rate of H_2 generation while the UME tip was biased at 0V (Ag/AgCl) and rastered across the Pt substrate in x and y direction. It is evident from Figure 4a that H_2 diffuses spherically from its source towards the bulk electrolyte. An important implication of Figure 4a for H_2 sensing using SECM in HOR mode is the loss of resolution as tip/substrate separation increases. It is noteworthy that the diffusion occurs as a result of a concentration gradient which is the case when the tip is positioned near the edge of a substrate. The lateral concentration gradients will arise since no H_2 is generated on the insulator surrounding the active substrate. With the tip positioned near the edge of the substrate, H_2 will diffuse out of the gap between the tip and substrate decreasing the H_2 concentration and the tip current. Also when the tip is positioned over the epoxy insulator where no H_2 is produced, then lateral diffusion of H_2 into the gap region may occur if the tip is near the edge of the active substrate. This will increase the tip current leading to the “diffusional broadening” of the substrate image generated by SECM.

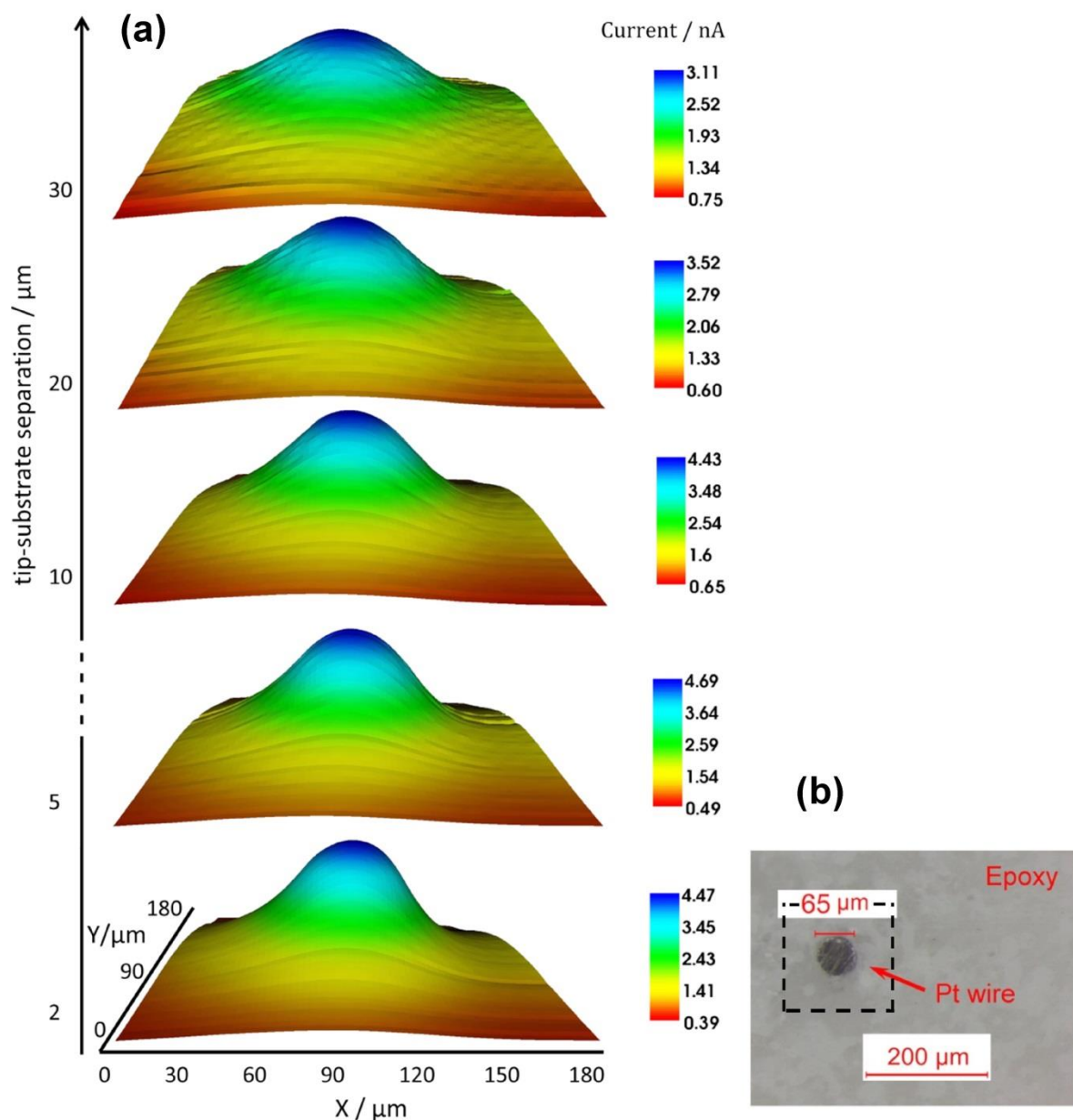


Figure 4 (a) Distribution of H_2 concentration versus distance from a $65\mu\text{m}$ diameter Pt disk substrate biased at -1.0 V (Ag/AgCl). (b) Optical micrograph of the Pt micro-substrate. SECM probe was a $10\mu\text{m}$ Pt UME biased at 0.0 V (Ag/AgCl). The tip/substrate separations were $2\mu\text{m}$, $5\mu\text{m}$, $10\mu\text{m}$, $20\mu\text{m}$ and $30\mu\text{m}$. Dashed box in (b) shows the scanned area.

Due to the contribution of other phenomena (i.e. multi-directional diffusion of H_2 and feedback effect of H_2/H^+) it is very difficult (if not impossible) to isolate the H_2 collection from a certain spot directly underneath the SECM tip and independently measure its current. It should also be noted that the feedback effect of H_2/H^+ between two Pt surfaces (a Pt substrate and a Pt UME) studied here is different from the feedback effect between a Pt and

another material such as Mg. This is due to different catalytic properties of surfaces for H₂ reduction reaction. Therefore, H₂ detection using SECM in SG/TC mode cannot be utilized as a quantitative measure of H₂ evolution from a given surface. However, as a qualitative and comparative tool it introduces new opportunities for studying and understanding the mechanism of H₂ evolution with a high resolution local approach. Future work in this area may involve theoretical modelling of chemical and physical process to obtain a better understanding of the effect and contribution by each individual factor (i.e. H₂/H⁺ regeneration, diffusion and pH). Numerical modelling based on finite element method using Comsol package has been implemented by Trinh *et al* [22, 23] and shown to provide valuable insight into the mechanism of adsorption kinetic and diffusion of H₂ on the surface of Au and Pt in acidic media.

Conclusion

SECM in SG/TC mode was utilized to sense H₂ evolution on the surface of a Pt substrate. Redox properties of H₂/H⁺ within a thin layer gap between SECM tip and substrate was examined and it was showed that H₂/H⁺ regeneration plays a significant role in the electro-oxidative current sensed by SECM tip. This could be due to the increased concentration of H₂ and also maintaining the neutral pH by the reversible reaction. H₂ diffusion profile was illustrated by performing several lateral H₂ imaging and showed to be in radiant multi-directional after generated at the substrate. Therefore it was postulated that, when sensing H₂ at a certain domain, the H₂ generated from the surrounding area also contributes in the electro-oxidative current sensed by the SECM tip. This and the redox regeneration of H₂/H⁺ adds to the complexity of the quantitative correlation between electro-oxidative current measured by tip and the rate of H₂ generation.

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