Imaging hydrogen oxidation activity of catalyst-coated perfluoro sulfonic acid-polymer electrolyte membranes using Scanning Electrochemical Microscopy[†]

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Abstract. Scanning Electrochemical Microscopy (SECM) is a unique technique for studying fast heterogeneous kinetics and to map reactivity gradients along the surface of an electrocatalyst, especially when it involves multiple surface sites of varying reactivity. It combines the dual advantages offered by ultramicroelectrode (UME) voltammetry in terms of reduced ohmic drop and insignificant double layer charging contribution with the advantages of imaging by rastering the UME across an electro-active surface. In this work, we demonstrate these distinctive features of SECM in evaluating reactivity gradients on catalyst (Pt/C) coated Nafion® films towards hydrogen oxidation activity, a reaction of immense technological relevance. Imaging has been performed in the feedback mode by allowing H_2 evolution at the tip (25 μm Pt UME), which is reoxidized at the substrate electrode containing Pt/C-Nafion film. Interesting distribution in H_2 oxidation activity has been observed as a function of potential applied to the Pt/C-Nafion film. In addition, a plot of normalized tip current versus the substrate electrode potential indicates the effect of potential-induced reactivity change in the catalyst-coated membranes. The results of the present investigation are believed to be useful to H_2/O_2 PEM fuel cells with respect to evaluating reactivity gradients of catalyst-coated polymer electrolyte membranes, which is important to rectify problems related to catalyst utilization.

Keywords. SECM; Nafion; platinum; hydrogen oxidation; imaging.

1. Introduction

Polymer electrolyte fuel cell (PEFC) is one of the major options for achieving clean energy conversion for portable, stationary and automobile applications.[1] Despite the enormous progress achieved during the past few decades in fuel cell components and engineering aspects, their effective commercialization is far from complete owing to several issues. One such important issue is the high cost of the PEFCs mainly due to the use of expensive materials like Pt as the catalyst.[2] Consequently, there have been several attempts to replace Pt as a whole with cheaper non-noble metal catalysts. More recently, a promising breakthrough has been illustrated by using a functional conducting polymer (PEDOT) as a possible electrocatalyst for oxygen reduction.[3] However, the current density accomplished is low and hence more extensive effort is needed to overcome this and also other problems related to the scale-up and life time issues. An alternative approach to make the PEFCs affordable is to reduce Pt loading by improving its utilization in the catalyst layer.[4] Several attempts have been focused on the improvement of catalyst utilization at fuel cell electrodes, including pore engineering of the carbon support,[5] introduction of ionomer molecules in the catalyst layer[2] and coating the catalyst directly on the electrolyte membrane.[6] Nevertheless, the common aspect of all the approaches toward improving catalyst utilization has been to improve the three-phase boundary between the catalyst, polymer electrolyte and the reactant gases.

Owing to the pressing needs of this issue, it is equally important to develop efficient non-destructive techniques, which can provide precise information about the distribution of catalyst particles and their three-phase interface with ionomer molecules and reactant gases. For instance, we have found in our earlier investigations that the catalytic activity is a strong function of the morphology and crystallographic orientation of the Pt electrocatalyst particles

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[†]Dedicated to the memory of the late Professor S K Rangarajan
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for both fuel oxidation and oxygen reduction reactions in a PEMFC.[7] The morphology, disposition and surface structure of the catalyst play a more crucial role in the real fuel cell environment when the three-phase interface of ionomer/catalyst and reactant gases comes into picture. This is particularly significant when the pores are filled at a faster rate with the product (i.e. water) during high current density operations as dynamic electrolyte management with its attendant thermal effects continue to pose significant challenges for PEMFC stack design. The electrocatalyst dispersed on high surface area carbon like Vulcan XC and the membrane undergoes deterioration and the detailed mechanistic aspects (carbon corrosion, diffusion of Pt species across the membrane followed by electro-dissolution, adsorption, redeposition on the other electrode) on porous carbon electrodes have not been completely understood. The effect of surface adsorption on the electrocatalytic activity has long been appreciated since the pioneering efforts put forward by Rangarajan *et al*, who provided a deep insight into the effect of surface roughness on the diffusion of reactant species to the electrode surface.[8,9] Thus, a molecular level description of all associated phenomena including effects of adsorption is essential to design affordable, high performance PEFCs. Normally, catalyst utilization is evaluated using cyclic voltammetry in H_2SO_4, by calculating the area under the H_2 oxidation peak, assuming a charge of 210 μC/cm^2 of a polycrystalline Pt surface.[10] In addition, there are spectro-electrochemical methods like *in situ* Infrared spectroscopy (IR) and Surface Enhanced Raman Spectroscopy (SERS) to study the fuel cell electrodes in many unique aspects during the operation as well as open circuit conditions. Though these techniques provide an overall estimate of catalyst utilization, it is difficult to extract microscopic information about the local reactivity of the catalyst particles at different sites of the carbon support. Further, it is more difficult to understand the three-phase boundary by simple cyclic voltammetry since many of the phenomena like configuration of adsorbed molecule and coverage are strongly sweep rate dependent. In this connection, Scanning Electrochemical Microscopy (SECM) has been demonstrated recently as an efficient tool to interrogate reactivity gradients on catalyst surfaces.[11,12] More specifically, the importance of the technique to study fast heterogeneous kinetics has been realized in many investigations. For example, H_2 oxidation,

an important reaction in electrochemical energy conversion, was commonly studied using cyclic voltammetry,[13-15] rotating disk voltammetry (RDE)[16,17] and steady state voltammetry with intensive bubbling of H_2.[18] While cyclic voltammetry at a macroelectrode suffers from limitations arising from ohmic drop and high charging currents, rotating the electrodes in the RDE at speeds in excess of 10,000 rpm creates turbulence in the solution causing unknown contributions of migration and cavitations effects. On the other hand, SECM combines the dual advantages of ultramicroelectrode voltammetry viz. low charging currents and ohmic drop[19,20] with the ability to raster the UME tip over a substrate electrode to obtain electrochemical images. Thus, SECM has been successfully demonstrated to investigate electrocatalysts with respect to critical reactions of interest to fuel cells such as hydrogen oxidation and oxygen reduction.[21-23] In our earlier investigations, we have demonstrated the importance of functionalized carbon nanotubes and ionomer membranes in enhancing the performance of PEFCs and the effect of catalyst morphology on their fuel cell activity.[7,24] In continuation with our efforts in interrogating and improving the performance of PEFCs, we proceed here by mapping the heterogeneities in the hydrogen oxidation activity of catalyst-coated perfluoro sulfonic acid membrane (viz. Nafion®). Specifically, we report here our SECM investigations of Nafion membranes containing Pt/C catalyst based on H_2 oxidation reactivity. The efficacy of SECM in revealing reactivity gradients has also been demonstrated in our earlier report on electrochemical imaging of stomatal physiology in peanut leaves.[25] The present work is not only of relevance to fuel cells, but also to understand the proton transport properties of hybrid polymer electrolyte membranes like carbon nanotube composites of Nafion®. Analysis of hydrogen oxidation reactivity could be also useful to understand many aspects of hydrogen adsorption on nanoparticles of Pt, Ir and Rh since this is widely used for determining the electrochemical surface area of platinum, iridium and rhodium electrodes.

2. Experimental section

2.1 *Materials*

Nafion (5 wt% solution in a mixture of lower aliphatic alcohols and water (eq. wt. 1000) and Lithium

perchlorate were procured from Aldrich chemicals. Perchloric acid (70 vol% in water) was obtained from Loba chemicals, India. The 25 μm (diameter) Pt UME and all other electrodes were purchased from CH Instruments. Pt catalyst (~100 nm size, 20 wt%) supported on Vulcan XC-72 carbon was procured from Arora Matthey Ltd. All solutions were prepared using de-ionized water (18 MΩ cm).

2.2 *SECM measurements*

All the electrochemical measurements were performed using a CHI900B bipotentiostat and a CHI900B Scanning Electrochemical Microscope. A 1·5 mm dia Pt disk was used as the substrate electrode, a 25 μm Pt UME was used as the SECM tip, Ag/AgCl, sat. KCl as the reference electrode and a Pt wire (0·5 mm diameter) as the counter electrode. The substrate electrode was polished with a 0·3 μm alumina slurry and the tip electrode with a 0·05 μm alumina slurry. A solution of 0·1 M LiClO$_4$ in 10 mM HClO$_4$ was used as the electrolyte and the experiments were performed at room temperature. A

5 μl dispersion of Pt/C in 5 wt% Nafion solution was drop coated on the substrate electrode. Prior to imaging, the UME was standardized using ferrocenemethanol by a procedure reported elsewhere.[25] The separation between the tip and the substrate was determined using few preliminary probe approach experiments, when the tip biased to a potential of −0·7 V corresponding to steady state H$_2$ evolution approached the catalyst film. Subsequently a region of 100×500 μm^2 area of the catalyst coated films was imaged by setting the tip at a distance of 10 μm above the substrate and rastering it at a speed of 0·3 μm/s over the film surface. To discriminate the images from artifacts, the same area was scanned repeatedly at least twice after performing independent probe approach experiments and also with another SECM tip with same dimensions.

3. Results and discussion

Figure 1a shows a typical cyclic voltammogram of Pt/C catalyst (of similar composition used in fuel
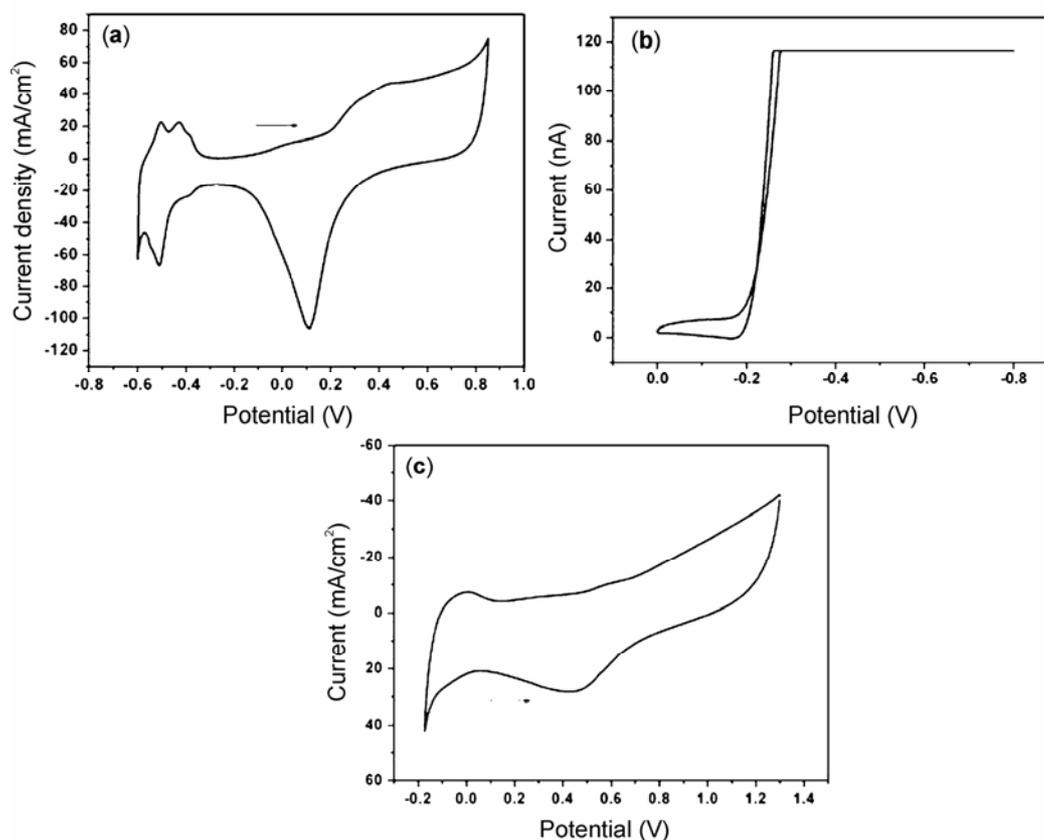
Figure 1. Cyclic voltammograms of Pt/C in 0·5 M H$_2$SO$_4$ (**a**), Pt disk UME, (**b**) and Pt/C-Nafion film-coated substrate electrode, (**c**) in 0·1 M LiClO$_4$ containing 10 mM HClO$_4$ at a scan rate of 25 mV/s.

cells anodes) coated on a glassy carbon disk electrode in 0.5 M H_2SO_4. It is instructive to compare this with typical voltammograms obtained for polycrystalline Pt in the same medium where well-understood characteristics of reversible hydrogen adsorption are evident in the region of -0.6 to 0 V. A simple calculation based on the area under the hydrogen adsorption peaks and further comparison with the theoretically expected area based on the area of Pt/C, indicates that only 50% (approx.) of the catalyst in the slurry is utilized effectively for the fuel cell reaction. Figures 1b and 1c show the cyclic voltammograms of 25 μm Pt UME used as the SECM tip and the Pt disk substrate electrode (1.5 mm diameter) coated with Pt/C-Nafion film, after cycling the potential between 0.8 and -0.8 V (vs Ag/AgCl ref) to obtain reproducible behaviour. Figure 1a indicates that H_2 is evolved after revealing characteristic adsorption desorption peaks at the UME tip at potentials more negative than -0.6 V, from the reduction of protons present in the electrolyte.

$$2H^+ + 2e^- \rightarrow H_2.$$
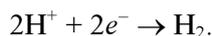
The steady state current at the UME is given by the expression,

$$i_{T,\infty} = 4nFDCa,$$

where n is the number of electrons transferred, F is the Faraday constant, D is the diffusion coefficient, C is the concentration of the electroactive species and a is the radius of the UME. $i_{T,\infty}$ refers to the stationary tip current when it is far away from the substrate electrode, where it will be independent of processes occurring at the latter. The tip current measured at shorter tip-substrate separation is always expressed as a normalized quantity, $i_T/i_{T,\infty}$. On the other hand, potentials corresponding to hydrogen oxidation at the Pt/C-Nafion film are obtained from figure 1b.

The basic instrumentation of SECM and the principle of feedback imaging used in this work along with the configuration of working, counter and references electrodes are depicted in scheme 1. The imaging experiments involve the H $+$ /H_2 couple as the mediator to establish feedback currents by re-oxidizing H_2 evolved at the tip by the substrate electrode.[23]

The low acid concentration in the electrolyte (10 mM) particularly avoids the formation of H_2 bubbles which may otherwise disrupt the steady state response, by creating fluctuations in current.[23]

The separation between the tip and the substrate is determined by monitoring the tip current at H_2 evolution potential as a function of the distance normal to the substrate electrode in a typical experiment, called the probe approach. Accordingly, figure 2 shows the probe approach curve of the UME tip biased to a potential of -0.7 V. Although a positive feedback and hence an increase in tip current as it approaches the Pt/C film surface is expected, the negative feedback in the present case is attributed to the effect of the polymer film on the surface of the
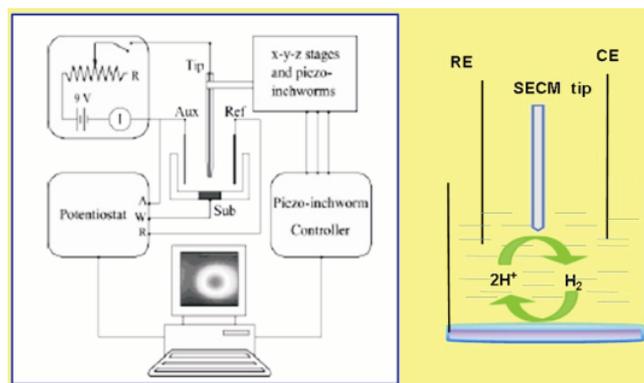
Scheme 1. Schematic representation of SECM (left) and the feedback imaging principle used in this investigation. The SECM probe is a 25 μm Pt disk electrode embedded in an insulating glass sheath, so that the ratio of the diameter of the sheath to that of the electrode (RG) is 7. RE and CE refer to the reference (Ag/AgCl sat. KCl) and counter electrodes respectively.
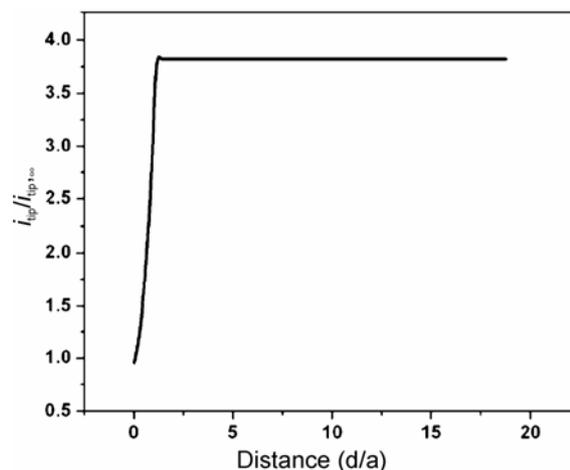
Figure 2. Probe approach curve showing the variation of dimensionless tip current ($i_T/i_{T,\infty}$) versus normalized tip substrate distance (d/a, where d is the actual tip-substrate separation and a is the tip radius) as the SECM tip, biased to a potential of -0.6 V approaches the film surface at a speed of 50 μm/s.
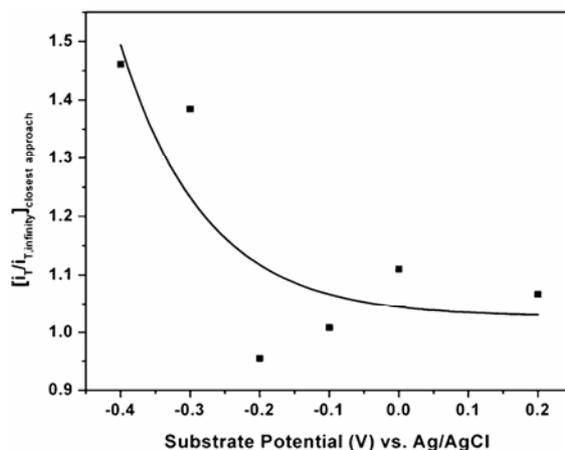
Figure 3. Variation of dimensionless tip current at the closest tip-substrate separation with substrate potential: the decrease in tip current at more positive substrate potentials indicates the effect of Pt oxide formation on its catalytic activity.

catalyst. This could be compared with similar observations in polymer film-coated substrate electrodes reported earlier.[26,27] More interesting information about the effect of Pt oxide formation on the catalytic activity is obtained by plotting the ratio of tip currents at closest tip-substrate separation to those at infinity as a function of the substrate potential (figure 3). As the substrate potential is made more and more positive, the tip current ratio decreases probably due to the oxide formation on Pt surface. X-ray Photoelectron studies have undoubtedly established the presence of PtO, PtO_2, and similar other species on Pt surface depending on the potential and pH by estimating binding energies of O signal. Nevertheless, the possibility of poisoning of the UME surface by ions present in the electrolyte medium has been ruled out by cycling the tip between potentials corresponding to water oxidation and hydrogen evolution after each probe approach experiment.

Having analysed the electrochemical activity of the Pt UME and the Pt/C-Nafion film, the next step is to map the local reactivity gradients along the surface of the catalyst-coated film, which is one of the principal objectives of the work. After determining the tip-substrate separation from the probe approach experiments, the tip is positioned at a constant distance of 10 μm above the film and rastered in the XY plane while monitoring the tip current as a function of distance. Accordingly, figure 4 shows the electrochemical images of a catalyst-coated film as a function of hydrogen oxidation reactivity of the Pt catalyst. More specifically, the images representing the same area of the film, indicate that the whole

area seems to be homogeneous when there is no hydrogen evolution at the tip. Interestingly, the moment the tip is biased to a potential appropriate for H_2 evolution (−0·7 V), regions of varying reactivity can be observed for the same area of the film. Further, more images are recorded by making the substrate potential more and more positive, which indicate critical variations in reactivity profile as the catalyst surface gets oxidized.

One of the major limitations of this study is the inability to access quantitative information due to the negative current feedback behaviour at the metal/polymer electrolyte interface. Despite being semi-quantitative, the results presented are important since this illustrates the efficacy of SECM in understanding gradients in electrochemical activity of fuel cell catalysts in contact with a polymer electrolyte membrane. These results are also valid for analysing many other polymer-modified electrodes since a similar approach could be effectively used for understanding electrocatalytic behaviour for other applications like biosensors.

4. Conclusions

The present investigation demonstrates the applicability of SECM for evaluating reactivity gradients in catalyst coatings, which is of interest to a number of fields including fuel cells. The results obtained here by imaging catalyst particles embedded in polymer electrolyte membranes relate to the real situation present in the catalyst layer of PEM fuel cells. Hence this is a straightforward approach to analyse
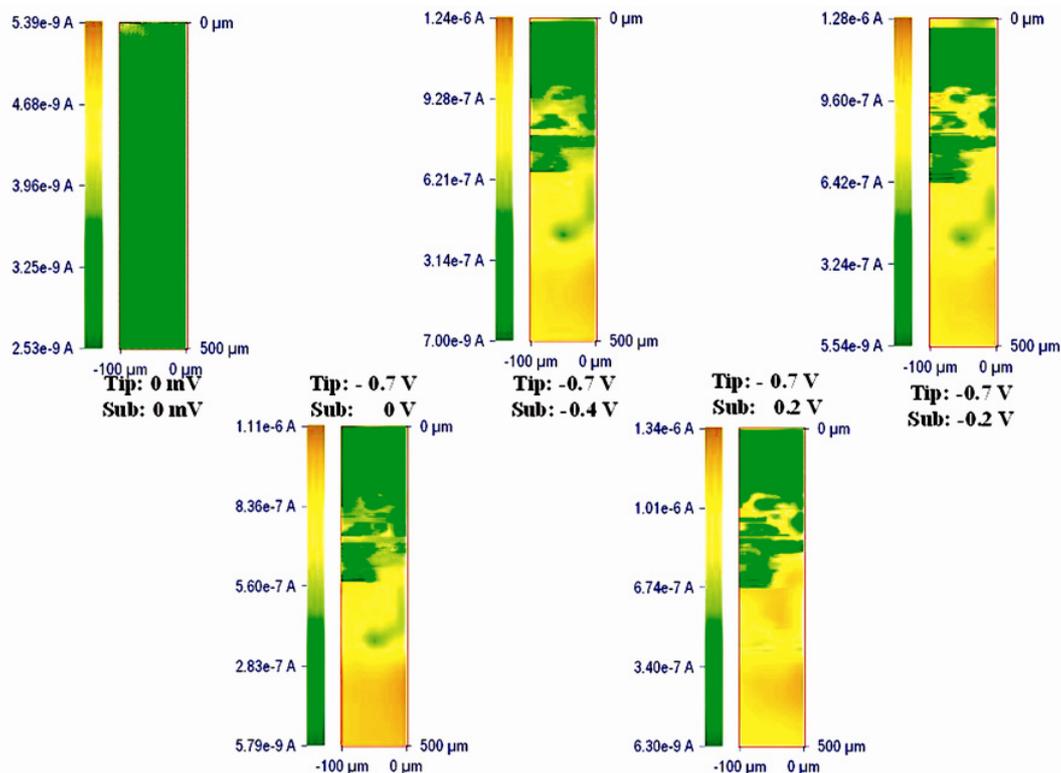
Figure 4. SECM images of the same area ($100 \times 500~\mu$m) of a Pt/C-Nafion film as a function of tip and substrate potentials. The colour changes correspond to changes in current arising in turn from changes in the hydrogen oxidation activity of the catalyst film. The effect of Pt oxide formation is manifested in the relative current intensities with more positive substrate potentials.

critical factors like catalyst utilization in fuel cell electrodes especially when porous electrodes are used using a polymeric binder. Though we have used H_2 oxidation reaction for imaging, the studies could be extended to for other reactions also. If the electron transfer reaction is not reversible, then imaging could be done in the generation/collection mode instead of the feedback mode used here.

Acknowledgement

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