



Mini review

Scanning electrochemical microscopy for combinatorial screening applications: A mini-review



Andrew J. Wain*

National Physical Laboratory, Hampton Road, Teddington TW11 0LW, UK

ARTICLE INFO

Article history:

Received 20 May 2014

Received in revised form 20 May 2014

Accepted 22 May 2014

Available online 2 June 2014

Keywords:

SECM

Electrochemical imaging

Array

Electrocatalysis

Photoelectrochemistry

Biosensing

ABSTRACT

Scanning electrochemical microscopy (SECM) provides a unique approach to combinatorial screening, and this technique has found a wide variety of applications in recent years. This mini-review provides a brief summary of progress in this field, highlighting some of the most significant developments in SECM screening for electrocatalysis, photoelectrochemistry and biosensing applications.

Crown Copyright © 2014 Published by Elsevier B.V. All rights reserved.

Contents

1. Introduction	9
2. Experimental methods	10
3. Applications	10
3.1. Electrocatalysis	10
3.2. Photoelectrochemistry	11
3.3. Biosensing	11
4. Conclusion	11
References	12

1. Introduction

High-throughput and combinatorial methodologies find a wide range of applications in material screening and in (bio)chemical analysis, enabling the rapid and cost-effective assessment of multiple targets or receptors within a single experiment [1]. The fabrication of a readable surface via the immobilization of such elements onto a patterned array or other multi-component platform facilitates their efficient assessment either in parallel, or rapidly in series. Optical readout techniques, such as fluorescence microscopy, are a popular choice of spatially-resolved signal detection, typically coupled with optically responsive chemical

probes or molecular labelling techniques [2]. Early exploitation of such methodologies were in drug discovery, but their application to addressing broader challenges such as genetic sequencing and advanced materials development are now well-established [3–5].

An alternative means to reading combinatorial arrays is to employ scanning electrochemical microscopy (SECM), in which the sample is immersed into an electrolyte solution and a microelectrode is scanned within a few tens of microns of the surface and used to induce or monitor electrochemical processes [6]. This technique provides a unique approach to spatially-resolved interfacial analysis, and can offer potential advantages to high-throughput and combinatorial screening such as no intrinsic requirement for labelling and the ability to directly interrogate redox processes. Various examples of combinatorial SECM have emerged and this mini-review aims to present an overview of the most prominent trends, focusing on three common applications:

* Tel.: +44 20 8943 6243.

E-mail address: andy.wain@npl.co.uk.

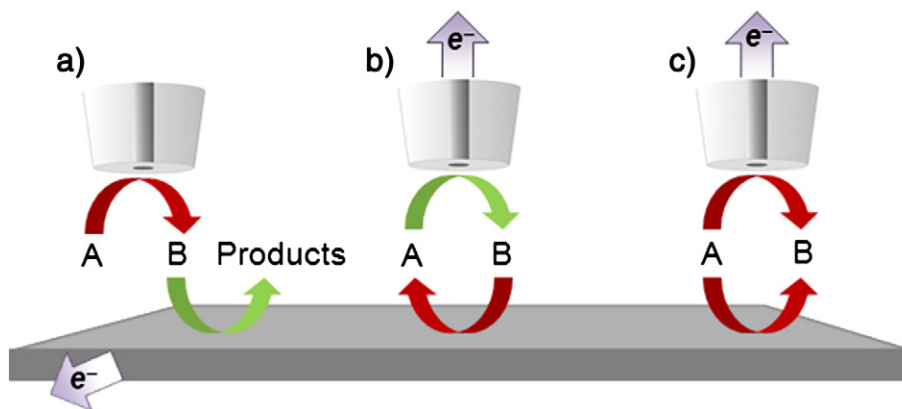


Fig. 1. Modes of SECM employed: (a) Tip-generation substrate-collection, (b) feedback, and (c) redox competition.

electrocatalysis, photoelectrochemistry and biosensing. The review begins with a brief account of experimental methods adopted.

2. Experimental methods

SECM screening strategies can be divided into two categories; substrate-collection and tip-collection mode, depicted schematically in Fig. 1. In substrate-collection mode (Fig. 1a), the microelectrode tip is used to perturb the surface locally, typically via the electro-generation of an analyte of interest, which induces electrochemical processes that are monitored by collecting the associated current at the substrate. Conversely, in tip-collection mode, the microelectrode tip itself acts as a sensor that detects local changes in concentration of the analyte due to reactions driven at the surface. If the reaction of interest is a reversible redox process it is common to exploit feedback mode (Fig. 1b); a special case of the tip-collection approach in which the microelectrode tip acts as both a generator and collector. An alternative tip-collection approach is to use redox competition mode, in which the tip and substrate compete for a common analyte in solution, such that substrate activity is indicated by a decrease in current at the tip (Fig. 1c). These different approaches have their own merits. Feedback mode is typically more sensitive to tip-surface separation than substrate-collection, and is consequently more experimentally challenging, and may also suffer from the effects of microelectrode passivation processes over the experimental timescale. However, tip-collection does benefit, for example, from low background currents associated with microelectrode detection and the potential for screening unbiased surfaces.

Substrate fabrication is an important element of SECM array or combinatorial library screening and this is often achieved by dispensing picolitre volume droplets of a suspension onto a flat and inert electrode surface in an ordered format. The suspension may contain the target material itself or instead a precursor such as a metal salt that is subsequently treated by chemical reduction. Common deposition methods are either based on contact-capillarity or piezo-controlled jetting devices [7,8], although magnetron co-sputtering [9] and various inkjet approaches have also been discussed [10,11].

3. Applications

3.1. Electrocatalysis

The search for new electrocatalyst materials for energy conversion applications has benefitted considerably from high-throughput combinatorial screening methods [4,12,13]. SECM in particular has found numerous applications in the assessment of oxygen reduction reaction (ORR) and hydrogen oxidation reaction (HOR) electrocatalysts for proton exchange membrane fuel cell (PEMFC) electrodes. A number of the most common screening modes are summarised in Table 1.

One of the most common approaches to SECM screening of ORR electrocatalysts is to generate O_2 at the tip via water electrolysis and collect local ORR current at the substrate. This approach has been used extensively by Bard's group to compare the ORR activity of various electrocatalysts including pure Pt and Ru [7], as well as binary and ternary combinations of elements such as Pd, Au, Ag, Co, W and Cu immobilized on glassy carbon by depositing precursor salt solutions in an array format [8,14,15]. Notably, these authors found that the ORR activity of Pd electrocatalysts could be enhanced by the presence of a small (<30%) amount of Co [8,16] or W [17], whilst the addition of Au can lead to improved stability [8]. Tip-collection can also be used for such electrocatalysts as a means to detect electrogenerated H_2O_2 , and determine the predominant mechanism of ORR [14]. In a related substrate-collection approach, Pd-Co electrocatalysts have also been screened for formic acid oxidation (FAO) activity via the generation of formic acid at a Hg/Au microelectrode [18]. The same group also applied SECM combinatorial screening to compare the oxygen evolution reaction (OER) activity of $Sn_{1-x}Ir_xO_2$ combinatorial mixtures, employing an additional gold shield electrode on the outer wall of the SECM tip to minimise lateral interference from neighbouring spots [19].

An alternative methodology for ORR screening has been developed by the Schuhmann group, who used the redox competition mode wherein both tip and substrate compete for dissolved O_2 , which can be electrogenerated by the tip as part of a voltammetric pulse profile. This approach addresses the problem of high background currents at

Table 1
Reported modes of SECM used for electrocatalyst and photocatalyst screening.

Application	Tip reaction	Substrate reaction	Mode	Ref.
ORR	$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	$O_2 + ne^- \rightarrow xH_2O + yH_2O_2$	Substrate collection	[7,8,15,16]
ORR	$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$	$O_2 + ne^- \rightarrow xH_2O + yH_2O_2$	Tip collection	[14]
FAO	$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$	$HCOOH \rightarrow CO_2 + 2H^+ + 2e^-$	Substrate collection	[18]
OER	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	Tip collection	[19]
ORR	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	$O_2 + ne^- \rightarrow xH_2O + yH_2O_2$	Tip collection (competition)	[20,21,28]
HOR	$2H^+ + 2e^- \rightarrow H_2$	$H_2 \rightarrow 2H^+ + 2e^-$	Tip collection (feedback)	[22–25]
Photocatalysis	Optical fibre $\rightarrow hu$	$H_2O + SO_3^{2-} + hu \rightarrow 2e^- + SO_4^{2-} + H_2$	Substrate collection	[30–35]
DSSCs	$I_3^- + 2e^- \rightarrow 3I^-$	$D + hu \rightarrow D^+ + e^-; 3I^- \rightarrow I_3^- + 2e^-$	Tip collection (feedback)	[37]

Download English Version:

<https://daneshyari.com/en/article/179142>

Download Persian Version:

<https://daneshyari.com/article/179142>

[Daneshyari.com](https://daneshyari.com)