Catalysis Today 159 (2011) 108–119

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Rapid optical screening technology for direct methanol fuel cell (DMFC) anode and related electrocatalysts

F.G. Welsch, K. Stöwe, W.F. Maier*

Lehrstuhl für Technische Chemie, Universität des Saarlandes, Gebäude C4 2, 66123 Saarbrücken, Germany

ARTICLE INFO

Article history:
Available online 13 April 2010

Keywords:
Optical screening
High-throughput
DMFC catalysts
Acid stability
Electrocatalyst

ABSTRACT

We describe here the development of an optical high-throughput screening method for direct methanol fuel cell catalysts based on the fluorescence of protonated quinine generated during electro-oxidation of methanol. The design of the working electrode allows the parallel quantification of the fluorescence development for up to 60 materials. For the preparation of the working electrode a coating routine has been developed, which allows the use of sol–gel derived materials. Due to the required stability of the electrode catalysts towards the acidic polymer membrane, a fast optical pre-screening method for acid stable materials has been developed. The electrochemical high-throughput system has been validated with Pt-Ru catalysts. Automation of data acquisition and data processing led to a fast and reliable high-throughput screening setup.

1. Introduction

The direct methanol fuel cell (DMFC) is an alternative for a decentralized power supply. The high power density of methanol in combination with a low operating temperature and the possibility to incorporate compact membrane electrode assemblies (MEAs) in the DMFC makes this type of fuel cell applicable for a variety of technical areas, especially mobile devices such as mobile phones, PDAs, laptops or even for electric vehicles. Compared to hydrogen-based fuel cells no reforming unit or high pressure storage tank is needed. In addition, the compatibility of methanol with the existing petrol distributions system may become a key aspect for potential future applications of the DMFC.

A DMFC MEA consists of a cathode and an anode divided by a proton conducting polymer electrolyte membrane (PEM). Nafion, a copolymer of a tetrafluoroethylene and perfluorinated vinyl-ether comonomer [1], is commonly used as PEM. Due to its sulfonic-acid groups, Nafion determines the milieu of the catalyst/polymer membrane interface (pH ~ 1) [2]. Therefore, the corrosion resistance of the electrodes is absolutely required. Flow field plates, positioned next to the electrodes, provide the oxygen and the aqueous solution of methanol. Oxygen is reduced to water (Eq. (1)) at the cathode while methanol is oxidized to carbon dioxide at the anode by its electrode catalyst (Eq. (2)).

$$1.5O_2 + 6H^+ + 6e^- \leftrightarrows 3H_2O \quad (1)$$

$$CH_3OH + H_2O \leftrightarrows CO_2 + 6H^+ + 6e^- \quad (2)$$

$$1.5O_2 + CH_3OH \leftrightarrows CO_2 + 2H_2O$$

Among pure metals, platinum shows the best activity for the electro-oxidation of methanol at temperatures below 80 °C [3,4]. In the course of methanol electro-oxidation, platinum is poisoned by carbon monoxide (CO), an intermediate product adsorbed on the catalyst surface (Eq. (3)). Hydroxyl groups (OH), originated by water activation, oxidatively remove the adsorbed CO. Water activation on the platinum surface is responsible for a high over potential for the electro-oxidation of methanol on pure platinum [5].

$$Pt + CH_3OH \rightarrow Pt\text{-}CO_{ads} + 4H^+ + 4e^- \quad (3)$$

$$Ru + H_2O \rightarrow Ru\text{-}OH_{ads} + H^+ + e^- \quad (4)$$

$$Ru\text{-}OH_{ads} + Pt\text{-}CO_{ads} \rightarrow CO_2 + Pt + Ru + H^+ + e^- \quad (5)$$

In order to decrease the over potential due to the water activation platinum was alloyed with oxophilic metals. Among them, binary platinum-ruthenium (PtRu) alloys show the best activity for the electro-oxidation of methanol [5], but still methanol-oxidation kinetics is sluggish because ruthenium does not adequately activate water (Eq. (4)) [6]. Eqs. (3)–(5) illustrate the bi-functional mechanism of the electro-oxidation of methanol.

The high noble metal contents of the DMFC cathode and the PtRu-anode in combination with the slow reaction kinetics of electrode reactions [7] exhibit the economic weakness of the DMFC as a ubiquitous decentralized mobile power source. Present research activity concentrates on the optimization of the PtRu catalyst system through composition, surface area, particle size, morphology,

* Corresponding author. Tel.: +49 6 81 302 2422.
E-mail address: w.f.maier@mx.uni-saarland.de (W.F. Maier).

0920-5861/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2010.03.006

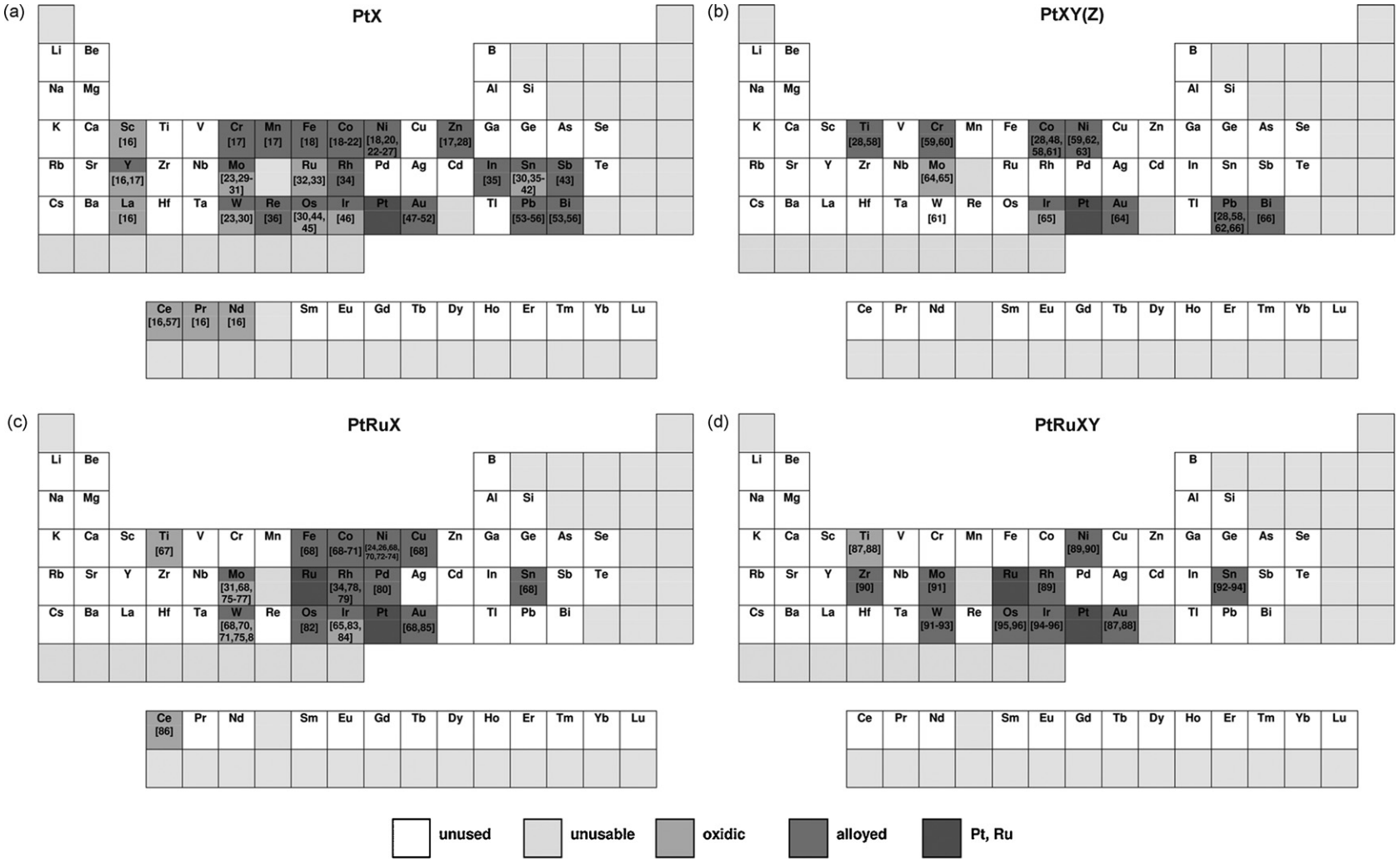

Fig. 1. Overview over the existing elemental compositions of DMFC anode catalysts of (a) PtX, (b) PtXY(Z), (c) PtRuX and (d) PtRuXY. Elements are labelled whether reported as oxidic phase or alloyed with the Pt, Ru; unused and unusable. Associated literature is referenced [16–27,29,30–52,54–57,60–65,67,68,70,72–78,80,81–86,88,89,92–94,96].