

Understanding underlying processes in formic acid fuel cells

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A basic understanding of electrode structure and the characteristics of its components can be powerfully utilized in fuel cell applications such as direct formic acid fuel cell (DFAFC) system integration and HCOOH concentration controlled systems. There have been, thus, tremendous efforts made to elucidate theoretical aspects of electrochemical processes involving new anode catalysts and put them into practical effect on formic acid fuel cells. Herein, we highlight recent studies for better understanding of the underlying processes in DFAFC: (i) a systematic approach for developing cost-effective and stable anode catalysts and electrode structures that incorporate mass transport characteristics of HCOOH; (ii) a clear evaluation of the HCOOH crossover rate based on its physicochemical properties; and (iii) a theoretical assessment process of individual electrodes and related components during DFAFC operation using electrochemical impedance spectroscopy and a reversible hydrogen reference electrode, which can potentially detect subtle changes in the DFAFC mechanism and provide useful information pertaining to rate-limiting processes.

1. Introduction

With the high energy density and fast oxidation kinetics inherent in liquid fuels, convenient usage and simplicity of power system integration, direct liquid fuel cells (DLFCs) are a promising power source for portable device applications.^{1–7}

This potential, combined with the considerable progress in DLFC research and engineering aspects achieved in recent years, has enabled DLFC technology to be implemented in actual devices. However, large-scale commercialization has been limited by challenging issues such as high anode and cathode overpotential, excessive fuel and water crossover rate through the polymer electrolyte membrane, unusual energy dissipation and the questionable long-term stability of each fuel cell component.

Among various liquid fuels, formic acid has emerged as a promising source due to its better oxidation kinetics, high theoretical thermodynamic cell potential and less fuel crossover problems associated in fuel cell systems. Fig. 1

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Sunghyun Uhm studied chemical engineering at the Inha University, Incheon, South Korea and earned his PhD there in 2008. During his PhD research, he worked on the development of anode catalysts in formic acid fuel cells with Prof. Sung Taik Chung and relevant electrochemical processes at ERTL led by Prof. Dr Jaeyoung Lee. He has now moved to the German Aerospace Center (DLR), Stuttgart to take up a

post-doctoral position in Prof. Dr Andreas Friedrich's group and has been researching various fundamental topics in direct methanol fuel cells (DMFCs) as well as alkaline fuel cells (AFCs). His interests include effective electrode structure for fuel cells, new carbon materials and impedance spectroscopy.



Hye Jin Lee is an Assistant Professor in the Department of Chemistry at Kyungpook National University, South Korea. She obtained a PhD in 1999 from the Ecole Polytechnique Federale de Lausanne, Switzerland, with Prof. Hubert H. Girault creating novel microfabricated liquid-liquid interfaces for use as ion selective sensors. Following postdoctoral research at the University of Wisconsin-Madison, Dr Lee undertook

an Associate Researcher position at the University of California, Irvine where she developed a series of novel surface enzymatic amplification methodologies that enable the direct detection of biomolecules down to femtomolar concentrations. Her primary research focus is the design and application of highly sensitive and selective biological and chemical sensors integrating emerging micro- and nanotechnologies.

Formic Acid in Electrochemistry

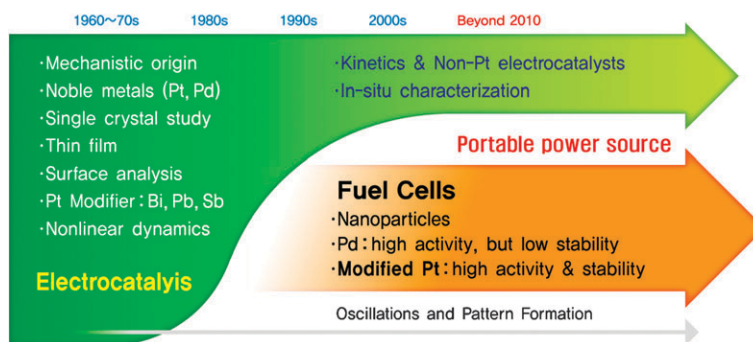


Fig. 1 An overview of formic acid research in electrochemistry, from understanding the mechanistic origin of electro-oxidation to applications in fuel cells.

shows a brief timeline for formic acid in electrochemistry research and their applications in particular to fuel cell developments. Initial efforts were made in developing electrocatalysts for formic acid oxidation, and investigation of the reaction mechanism and kinetics on the single crystal catalyst surface has been widely carried out.^{2,4} However, research has not fully addressed why various materials show differences in activity or performance under fuel cell operation. On the other hand, extensive research efforts on reducing poisoning materials such as CO have been made by modifying noble metal catalyst surfaces and developing non-Pt based electrocatalysts, whereas others have focused on the study of oscillations and pattern formation in an electrooxidation of formic acid.⁴ There is still a great demand for understanding how the structural, morphological, and physicochemical properties of an electrode could affect fuel cell performance due largely to a lack of related research.^{8–10} More efforts have been made recently in order to improve the activity and stability of the

electrocatalyst used in fuel cells by the use of nanomaterials, Pd-based catalysts and modification of Pt catalysts.^{2,11} Nonetheless it should be noted that issues related to the mass transport characteristics of formic acid, as well as kinetics and mechanisms of formic acid oxidation in practical fuel cell configurations still remain to be resolved further.

Herein, we demonstrate a rational strategy for developing a more stable and effective anode structure in direct formic acid fuel cells (DFAFC), encompassing a broad research area that includes new material (*i.e.* electrocatalyst) design, electrochemical synthesis and characterization of the material, development of diagnostic tools for fuel cell evaluation, as well as desirable design concepts for membrane electrode assembly and DFAFC systems. Among these topics, the effective installation of a reference electrode inside a fuel cell unit as a diagnostic tool is more extensively addressed, along with electrochemical impedance spectroscopy (EIS), which can potentially detect subtle changes in fuel cell structure and provide useful information pertaining to rate-limiting processes.



Jaeyoung Lee is a Vice Director in the Ertl Center for Electrochemistry and Catalysis at GIST, South Korea. He received his doctoral degree in 2001 from Fritz-Haber-Institut der MPG and FU Berlin, Germany, with Prof. Dr Gerhard Ertl (Nobel Laureate 2007) studying "Spatiotemporal pattern formation of small organic molecules". He was a senior scientist at Research Institute of Industrial Science and

Technology (RIST, 2002–2004) and at Korea Institute of Science and Technology (KIST, 2004–2007) where he developed a stable and cost-effective electrocatalyst for fuel cells and water treatment. He is trying to apply his experience to the development and optimization of a number of processes involving electrocatalysis for (a) hydrogen generation; (b) oxygen & CO₂ reduction; (c) liquid fuel oxidation and electrochemical power production, in particular for construction of biocompatible fuel cells for micro medical devices.

2. Reaction mechanism of formic acid oxidation

The reversible potential of formic acid can be thermodynamically calculated to a close approximation based on the change of Gibbs free energy, ΔG° , of reaction (1)



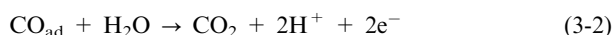
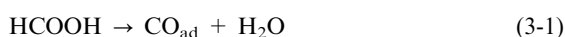
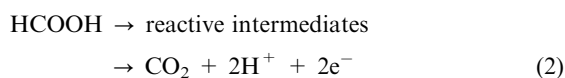
in relation to the theoretical oxygen reduction potential in the same electrolyte. From $\Delta G^\circ = -68.2 \text{ kcal mol}^{-1}$, it follows that $E^\circ = 1480 \text{ mV}$ is the theoretical electromotive force (EMF) of the formic acid–oxygen cell at 25 °C. The corresponding data for methanol, formaldehyde, and hydrogen are presented in Table 1.^{3,4} In the Table, the direct formic acid fuel cell has a higher EMF than that of either the hydrogen or direct methanol fuel cells. In addition, a faster kinetics aspect enables formic acid fuel cells to have a much wider range of operating conditions, in particular operating at lower temperatures. The regulated and low crossover rate as well as the corresponding higher fuel cell efficiency are additional advantages. These could compensate its lower energy density (2104 Wh L⁻¹) comparing to that of methanol (4900 Wh L⁻¹) and ethanol (6280 Wh L⁻¹), which has been one of the major

Table 1 Theoretical EMF values at 25 °C

Fuel	Reaction	$\Delta G^\circ/\text{kcal mol}^{-1}$	E°/mV	Potential vs. RHE/mV
Formic acid	$\text{HCOOH} + 1/2\text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$	-68.2	1480	-250
Methanol	$\text{CH}_3\text{OH} + 3/2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$	-166.77	1210	20
Formaldehyde	$\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$	-124.7	1350	-120
Hydrogen	$\text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O}$	-56.69	1230	0

disadvantage of using formic acid as a fuel. Energy density of small organic molecules (SOM) represents the maximum value of energy from each mol of SOM that can be completely oxidized.

It is generally accepted that the electrocatalytic oxidation of HCOOH to carbon dioxide (CO₂) on a metal surface proceeds *via* a dual path mechanism,^{2,11–14} the direct oxidation (reaction 2) of reactive weakly-adsorbed intermediates to form CO₂ in parallel with an indirect oxidation (reactions 3-1 and 3-2) pathway involving formic acid dehydration and subsequent electrooxidation of the resultant strongly-adsorbed carbon monoxide (CO) to CO₂.



In addition to the dual path mechanism, Behm *et al.* recently proposed a new scheme describing the mechanism of formic acid oxidation on Pt, a so-called “triple pathway”, involving bridge-bonded formate formation and subsequent oxidation of formate to CO₂.^{15,16}

3. More effective anode catalysts

Developing new catalysts in the research area of anode electrocatalysts is necessary in order to improve catalytic performance and resistance against poisoning. Owing to their high catalytic activity in various reactions, Pt and Pd have been the most vigorously studied metals which are the main metal components in a great majority of bimetallic alloys. It is, however, well-known that the interaction of formic acid molecules with Pt and Pd atoms is completely different.¹⁷ Pd has a propensity to break only the O–H bonds of the HCOOH molecule in the entire potential region, while Pt seems to have a propensity to break the C–O and/or C–H bond (at low overpotential) and the O–H bond (at high overpotential). Consequently, formic acid oxidation on Pd surfaces proceeds exclusively through the dehydrogenation reaction step, whereas on Pt surfaces the dehydration pathway is predominant at low potentials. It should be noted that one of the major problems in formic acid oxidation is that the intermediary species formed during the electro-oxidation of HCOOH cause catalyst poisoning. These intermediary species could be mostly CO, which strongly interacts with the active sites on the electrode surface and requires a higher overpotential for oxidation; many combinations for overcoming this poisoning problem have been investigated, some of which are summarized in Table 2.

The use of pure Pd catalyst as an anode catalyst has been recently demonstrated by Masel *et al.* to possess superior

oxidation performance of ultra-pure formic acid DFAFCs compared to Pt-based catalysts, due to its great initial activity even at low temperature (see Fig. 2(a)).^{9,10,18–21} However, pure Pd has a significant drawback (see Fig. 2(b)) in that its high performance is not sustained for extended periods of time, largely due to vulnerability with respect to the generation of unrevealed intermediate species^{22–24} and the probability of Pd dissolution in acidic solutions.^{25,26}

Formic acid oxidation is believed to be a reaction in which the ensemble effect plays an important role,^{27,28} thus, controlling the surface composition when exploring new systems is of great importance. According to the ensemble effect associated with particular arrangements of the active constituents, one of the requirements for the second metal would be an ability to suppress the formation of poisoning species adsorbed on more than one surface active site. Among the groups categorized in Table 2, Group I, platinum group metals (PGMs), have been recently studied in terms of their enhancement of the Pt (or Pd) surface and replacement of Pt. Moreover, PGM alloys are expected to show superior durability compared to transition metal alloys. Specifically, the combination of Pt and Pd can potentially provide a synergistic effect in Pt and enhance activity as both metals possess a similar property such as the electronegativity representing their ability to oxidize CO and various other hydrocarbons.^{23,28–32} However, the performance obtained from the combined Pt and Pd is much lower than that of even pure Pd, although the degradation rate is somewhat alleviated.

Alternatively, Ru alloy catalysts, mostly with Pt, have been reported as one of the best electrocatalysts for small organic molecules due to their bifunctional mechanism, involving the adsorption of OH species on Ru, which then promote the complete oxidation of CO to CO₂.^{8,33,34} However, since formic acid oxidation proceeds *via* different reaction mechanisms compared to the alcohol oxidation, Ru(Pt or Pd) alloys are not as effective as even pure Pd or Pt catalyst. Likewise, Au^{8,9,21,28,35,36} or Ir^{37,38} have been suggested as promising PGM alloys for the enhancement of formic acid oxidation by reducing poison formation due to the so-called “third body effect”, which is based on the role of second metal (or adatoms) in blocking the surface sites for a side reaction that generates poisonous species, or in blocking the adsorption of the inhibiting species, which requires more than one surface site for adsorption. However, formic acid oxidation activity investigations of such alloys are very limited, probably because PGM alloys have no clear inherent advantage for lowering the catalyst cost. Accordingly, from a traditional catalytic point of view, Pt- or Pd-based alloys containing early d-metal elements have attracted attention due to their interesting thermodynamic properties, as shown in Group II (see Table 2).^{35,39–42} However, from an electrochemical viewpoint special care must

Table 2 Classification of secondary metals paired with Pt or Pd for formic acid fuel cell anode catalysts

	Elements	Remarks
Group I	Au, Ir, Pd, Pt, Ru	Precious metals
Group II	Cr, Cu, Fe, Mo, Nb, V	Transition metals apart from precious metals
Group III	Bi, Pb, Sb, Sn	Post-transition metals

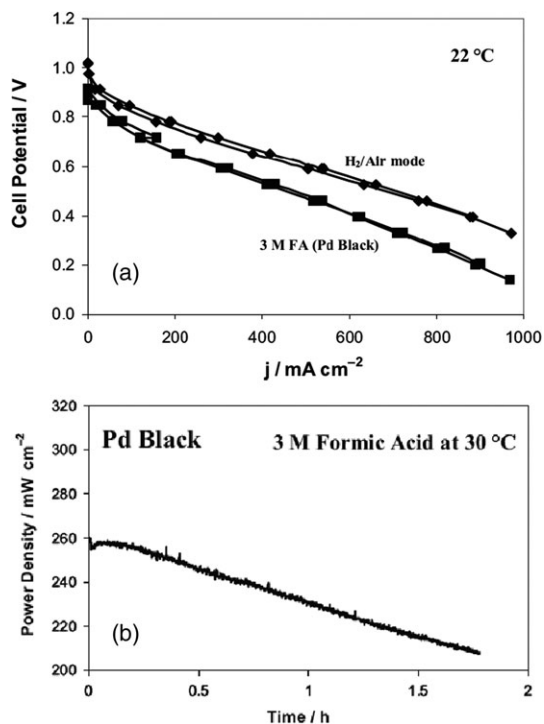


Fig. 2 Current–voltage polarization plots of formic acid–air and hydrogen–air modes at 22 °C. (a) The formic acid and hydrogen flow rate to the anode were 3.5 ml min^{-1} and 200 sccm , respectively, and (b) constant voltage tests at a cell potential of 0.4 V in 3 M formic acid at 30 °C. Dry air was supplied to the cathode at a flow rate of 390 sccm without backpressure. Pd black and Pt black were used for the anode and cathode electrode, respectively.²¹ The reference 21 was reproduced with permission.

be taken to avoid the inevitable dissociation of the secondary elements over the potential window of interest in fuel cell operation.

Since stability (or durability) and efficiency issues are key problems in the development of fuel cell catalysts, in addition to the cost reduction, post-transition metals or poor metals such as Bi, Pb, Sb, Sn (Group III)^{43–52} could be excellent candidates for anode catalyst materials. These elements possess a unique characteristic such as under-potential deposition (UPD) property, in which the electrodeposition of an adsorbate material on the electrode surface occurs at potentials more positive than those require for the bulk deposition of the metal. Thus, Pt-UPD metal systems show a reasonable stability similar to that of Pt at relatively high potentials, depending on the surface coverage of the elements. Of these elements, Bi is one of the most promising elements in that it not only has a higher tolerance to CO poisoning and corresponding superior electrocatalytic activity toward formic acid oxidation,^{46–48} but also has better stability over a wider range of potential

windows.^{53,54} As an example, Fig. 3 presents a typical current–voltage polarization curves and voltage variation acquired as a function of time when using Bi-modified Pt catalyst for a DFAFC anode.⁴⁶ The performance of the Bi-modified catalyst was also compared to that of commercial Pd and PtRu catalysts. PtBi catalyst shows a lower catalytic performance than that of the Pd catalyst (Fig. 3a). However, PtBi catalyst outperforms the Pd black catalyst if the currents are normalized by the total weight of the precious metal (Fig. 3b), and the performance of the Pd catalyst decreases gradually not only during polarization measurements but also during constant

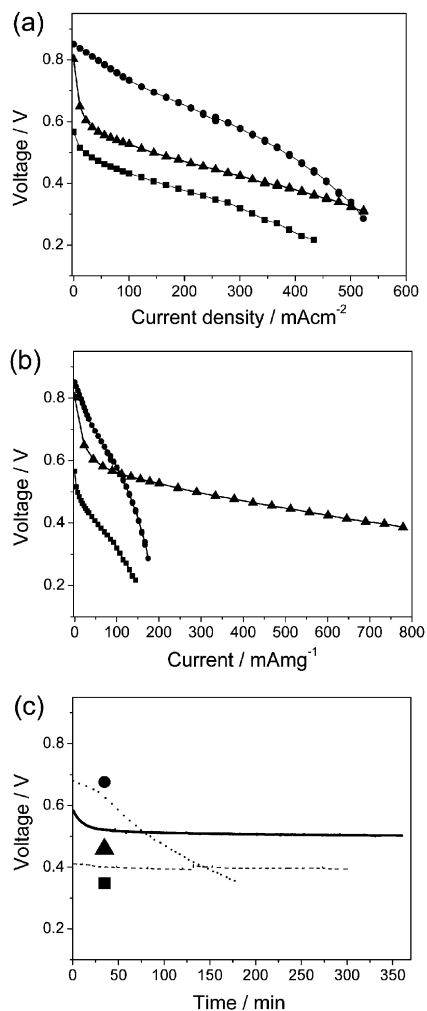


Fig. 3 Current–voltage polarization measurements for direct formic acid fuel cells with different anode catalysts (▲ PtBi, ● Pd, ■ PtRu). Currents are normalized by geometric area (a) and total weight of the respective precious metals (b). Voltage variation as a function of time at a constant current density of 150 mA cm^{-2} (c). The fuel cell was operated at 60 °C with formic acid (6 M) as the fuel and dry air as an oxidant.⁴⁶ The reference 46 was reproduced with permission.

current measurements (Fig. 3c). Although the catalytic activity of Bi-modified Pt catalyst theoretically increases with an increasing UPD Bi surface coverage of up to 80%, practical fuel cell performance does not improve as much, due primarily to overly-covered Bi adatoms and/or their oxidized forms giving rise to the suppression of proton conductivity in the catalyst layer. Nevertheless, owing to the irreversibility of UPD Bi adatoms Pt–Bi systems can indeed be effective catalysts as a DFAFC anode.⁵⁴ Surface modification of noble metal catalyst by UPD can be also applicable to Pd.^{43,49} However, the feasibility of the Pd-UPD system and the stability of UPD metals have not been clearly validated yet, therefore requiring further studies.

4. Mass transfer and fuel crossover rate in fuel cell structures

Other important components of membrane electrode assembly (MEA) are diffusion media (DM), especially anode diffusion media, which may be easily ignored in direct liquid fuel cell (DLFC) studies even if Kulikovskiy *et al.* introduced the mass transfer models in DMFC.⁵⁵ DM play important roles in the passage of reactants toward the catalyst layer and water/heat/gas product removal towards the flow field channels. Additionally, DM also provide a path for electrons to flow between bipolar plates and catalyst layers, and also behave as a mechanical support to protect the catalyst layer from corrosion or the flushing out caused by flow or other factors.

Previous studies have mostly focused on highly concentrated formic acid operation because of its advantages in water management for system integration.^{6,10,20,21} In addition, highly concentrated formic acid is generally used in direct formic acid fuel cell (DFAFC) systems due to its hydrophilic properties, though formic acid suffers from significant mass transfer limitations compared to alcohol fuels such as methanol.^{56–58} As such, hydrophilic formic acid cannot penetrate through anode diffusion media as easily as methanol; most DM such as carbon paper or carbon cloth is made exclusively for favorable gas diffusion and/or water removal in hydrogen fuelled polymer electrolyte membrane fuel cell (PEMFC) systems. However, in the case of DLFCs, DM represents adjustable impedance to reactant supply; hence, the wettability characteristics of DM are of great importance in its function in overall fuel cell performance as well as in the practical estimation of formic acid crossover rate in the fuel cell operating conditions.

The degree of formic acid crossover rate has usually been estimated *via* measuring the crossover current of formic acid in comparison to that of methanol under given fuel cell operating conditions.^{34,58–60} According to these studies, the formic acid crossover rate is typically five to ten times lower than that of methanol due largely to the electrostatic repulsion of formate anions and their lack of affinity with the Teflon backbone in a Nafion membrane. However, when a formic acid fuel cell adopts the identical conventional anode components of a methanol fuel cell, significantly different initial conditions between the two fuel cells exist, even if the same molar concentration of a fuel is used. Since formic acid cannot penetrate both the hydrophobic DM and catalyst layer as easily as methanol can, there is a much steeper concentration

gradient occurred through the anode (diffusion media and catalyst layer) than that in methanol. This indicates that a more diluted concentration could have anticipated between the anode catalyst layer and the membrane.⁵⁸ Moreover, special care must be taken to select the anode components because the diffusion of formic acid can be affected by the physical properties of anode components other than hydrophobicity—for example, the thickness or density of the diffusion media and catalyst layer. Fig. 4(a) shows the relationship between the crossover current and the methanol (or formic acid) concentration with different anode diffusion media and catalyst layers. It can be clearly seen that formic acid diffusion is significantly affected by anode component properties while methanol diffusion is rarely influenced by them.

It is also noteworthy that fuel cell operation with highly concentrated formic acid can potentially deteriorate membrane electrode assembly (MEA) components, particularly the polymer electrolyte membrane.^{58,61} However, such a probability has been largely underestimated since long-term stability and power performance has only been evaluated with respect to electrocatalysts and their deactivation due to poisoning.

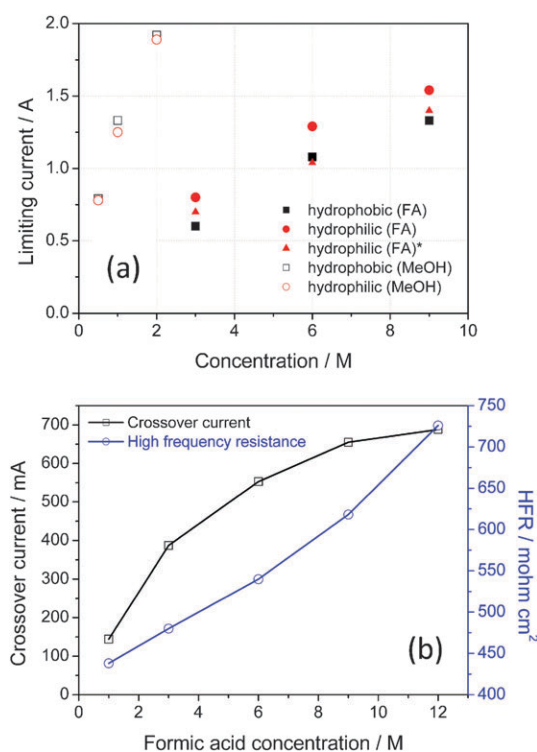


Fig. 4 (a) The effects of fuel concentration and catalyst layer properties on limiting the crossover current through the Nafion 115 membrane. Cell temperature is 70 °C. Anode is 5 ml min⁻¹ formic acid or methanol, and cathode is 100% RH, 200 sccm N₂ under ambient conditions. Asterisk (*) indicates the use of a supported catalyst (0.3 mg cm⁻² PtRu/C) having a similar thickness to 3 mg cm⁻² black catalysts.⁵⁶ (b) Crossover current through Nafion 115 and high frequency resistance as a function of formic acid concentration. The measurement is conducted at room temperature, where 5 ml min⁻¹ formic acid is supplied to the anode and 100% RH, 200 sccm N₂ is supplied to the cathode under ambient pressure.⁵⁸ Potential ranges from 0 V to 1.0 V (*vs.* RHE), and the scan rate is 1 mV s⁻¹.

Fig. 4(b) shows another representative plot showing the crossover current as a function of formic acid concentrations under formic acid fuel cell operating conditions with much hydrophilic anode diffusion media by pretreatment. This experimental setup can alleviate the mass transport limitation through the anode components of formic acid, resulting in a more reasonable estimation of the crossover current. It should also be emphasized that the crossover current (or rate) increases with an increase of formic acid concentration, but the rate of increase becomes negligible beyond a 10 M concentration of formic acid; there is also a tremendous increase of high frequency resistance along with an increase in formic acid concentrations. Highly concentrated formic acid near the polymer electrolyte membrane can dehydrate the interface between the membrane and catalyst layer because of its hygroscopic properties, especially between the membrane and the cathode catalyst layer, leading to a decrease in the proton conductivity and an increase in the cell resistance.

The use of highly concentrated formic acid could be effective for system integration; however, it may both reduce fuel efficiency by increasing fuel crossover and induce membrane dehydration due to its hygroscopic properties. A recent study also reported that there is an optimal concentration showing the maximum of dissociation of formic acid and water mixture,⁶² thereby indicating that *ca.* 6 M (≈ 25 wt%) formic acid is sufficiently dissociated that adequate acidity levels for improving proton conducting media can be maintained.

In summary, the formic acid crossover rate must be taken into account in a different way compared to previous studies. Since both the anode components and the membrane itself play important roles in crossover rate, properties of the anode components are as important as operating variables such as temperature and formic acid concentration.

Furthermore, regulating formic acid crossover can improve the performance of anode catalysts. Fig. 5 presents the current–voltage polarization curves with two different anode components and two different molar concentrations of formic acid, where it is obvious that 3 M formic acid operation is more sustainable, over 300 min, on both the unsupported (black) and supported catalysts. Conversely, 6 M formic acid operation showed a gradual decrease of voltage in line with a sharp increase of high frequency resistance. Because higher concentrations of formic acid are more uncontrollable under given operating temperatures, membrane dehydration due to overly penetrated formic acid becomes prevalent, resulting in performance decays by way of changing membrane properties accompanied with a rise of cell resistance, regardless of the catalyst layer properties. However, by regulating the formic acid diffusion with both a thicker hydrophobic catalyst layer (carbon supported catalyst) and a lower concentration of formic acid, much higher catalyst utilization (1 mg cm^{-1} PtRu/C vs. 3 mg cm^{-1} PtRu) could be obtained. Furthermore, high temperature operation does not as markedly enhance formic acid diffusion and proton conductivity; rather, the conductivity of the formic acid and water mixture decreases with increasing temperature due to the formation of more complex molecular chains by hydrogen bonds.⁶¹ Moreover several studies regarding formic acid tolerant cathodes have been recently conducted since the crossover of formic acid is

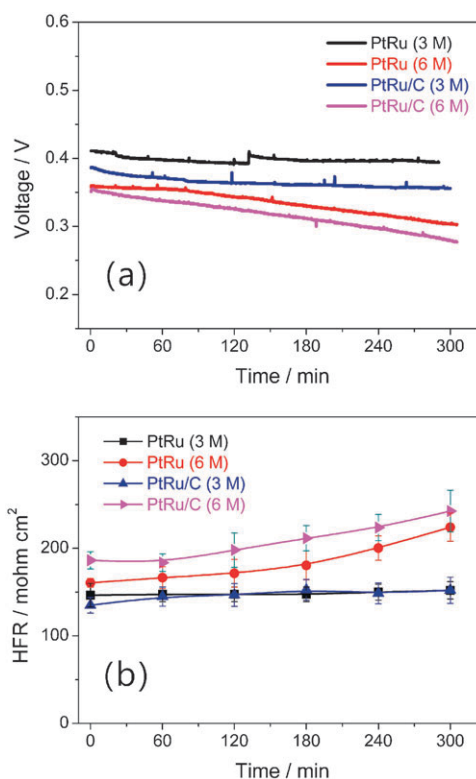


Fig. 5 Variation of (a) cell voltage and (b) high frequency resistance at a constant current density of 150 mA cm^{-2} as a function of time at 70°C . The flow rate of formic acid and dry air is 5 ml min^{-1} and 200 sccm , respectively at the ambient pressure.⁵⁸

inevitable, and not negligible, and as such is still a critical issue limiting the performance of formic acid fuel cells.^{63,64}

5. Effective diagnostic tools for direct formic acid fuel cells

To date, diagnostic tools for direct liquid fuel cells (DLFCs) are generally limited to the use of various dc electrochemical techniques; these techniques provide only the sum of various cell polarizations, which are difficult to break down into individual polarization contributions. In contrast to dc techniques, electrochemical impedance spectroscopy (EIS) has long been used to probe interfacial processes and species in electrochemical systems. Specifically, EIS has proved to be very useful in distinguishing processes with different time constants, and with this method it might be possible to separate different elementary steps of the reaction (see Fig. 6).⁶⁵

Numerous studies have used EIS to investigate methanol oxidation and methanol tolerant cathodes in DMFCs;^{66–75} relatively fewer reports have focused on formic acid oxidation and related studies in DFAFCs.^{57,60,76} Thus, further EIS analysis of electrochemical processes in real electrode environments is important for not only obtaining a clearer discrimination of the different fundamental processes occurring in fuel cells, such as charge transfer kinetics or double layer charging, but also avoiding the generation of artifacts arising from the difference of components or environments. Furthermore, it is essential to measure individual electrode potentials and

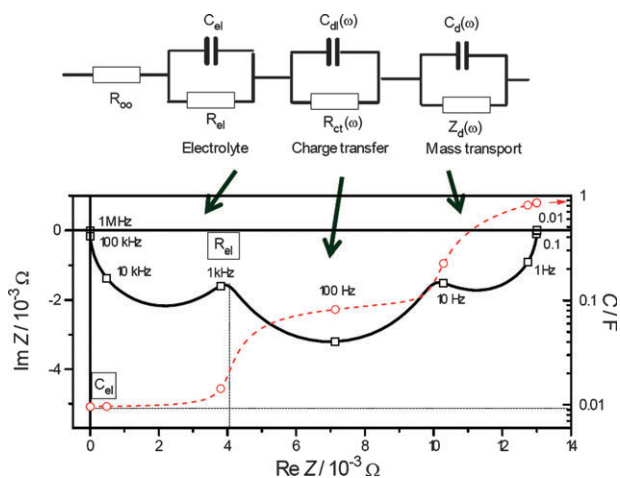


Fig. 6 (a) A general equivalent circuit of an electrochemical system, and (b) simplified frequency response of impedance and capacitance. Note the mathematical convention of impedance.⁶⁵

impedance spectra in order to understand the distribution of voltage losses and polarization contributions of individual electrodes. There have been a number of attempts to investigate these electrode effects by separately introducing a reference electrode. However, due to the constraints of cell construction and the requirement of physical contact with the electrolyte, it has proven rather difficult to place a reference electrode in the cell; instead, a dynamic hydrogen counter/pseudo-reference electrode is commonly used as the reference electrode (see Fig. 7).^{65,71–74,76} In this case, the cathode simultaneously acts as both the reference electrode and the counter electrode by supplying the cathode compartment with either hydrogen or an inert gas such as nitrogen or argon. Under these conditions, it is assumed that the cathode hydrogen evolution reaction experiences only a small overvoltage

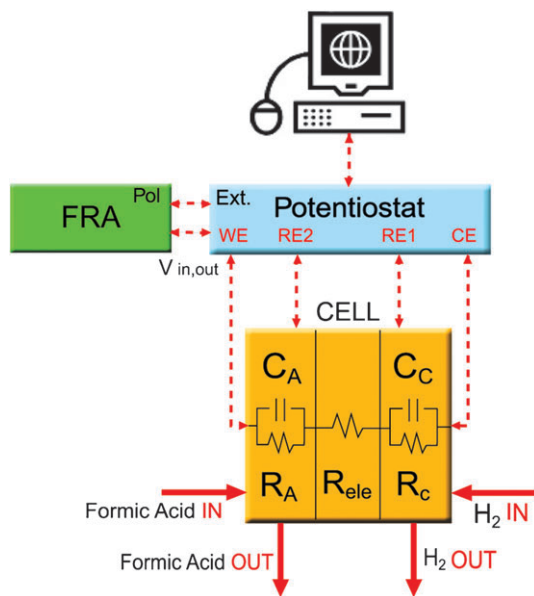


Fig. 7 Experimental setup for measuring anode impedance spectra of DFAFCs under dynamic hydrogen counter/pseudo-reference electrode mode.⁷⁶

compared to the large anode overvoltage of the liquid fuel oxidation reaction. Cathode impedance of the oxygen reduction reaction can also be obtained by subtracting anode impedance from the single cell impedance.

The use of reference electrode in practical fuel cell configuration is a well-known approach for PEM fuel cells applying hydrogen, but not easy to achieve, especially in direct liquid fuel cell system.^{77–91} A dynamic hydrogen electrode (DHE) is a reference electrode used for fuel cells, as shown in the digital image of Fig. 8, which uses the potential of the hydrogen evolution reaction (HER). Although the DHE potential contains a slight overvoltage caused by the reaction, it is only minimally influenced by environmental factors such as some organic impurities; therefore, it has been used in DMFC and DEFC studies.^{68,77–82} However, DHE construction is relatively more complicated due to geometric restrictions and the high contact resistance between reference electrodes and polymer electrolytes.

More often a reversible hydrogen electrode (RHE) is used as the reference electrode in PEMFCs,^{83,84} where hydrogen gas is usually supplied to the separated channel as a reference electrode to avoid possible poisoning from impurities. Fig. 9 shows the RHE structure of which both DMFC and the DFAFC cathode in the RHE configuration have been previously evaluated.^{57,69,85} The end of the reference electrode with the catalyzed carbon paper was placed on the same substrate in a controlled atmosphere to establish a steady reference voltage signal. A constant gas passage for a hydrogen reference electrode was constructed in this cell because hydrogen is potentially an ideal gas for the reference electrode, due to its high reversibility and well-defined electrode potential. Unlike DHE, no polarization losses occurred in this cell as no current was drawn from the reference electrode.

One major obstacle in using a reference cell on a very thin substrate is the potential for misalignment of the electrodes,^{86–91} as there can be a significant amount of induced

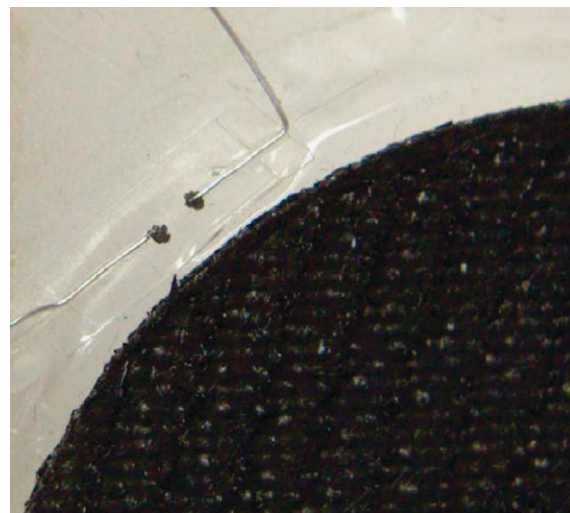


Fig. 8 Photograph of an MEA with the DHE unit attached just outside the gas diffusion electrodes. The gap between the ends of the two Pt wires is ca. 1 mm.⁸¹

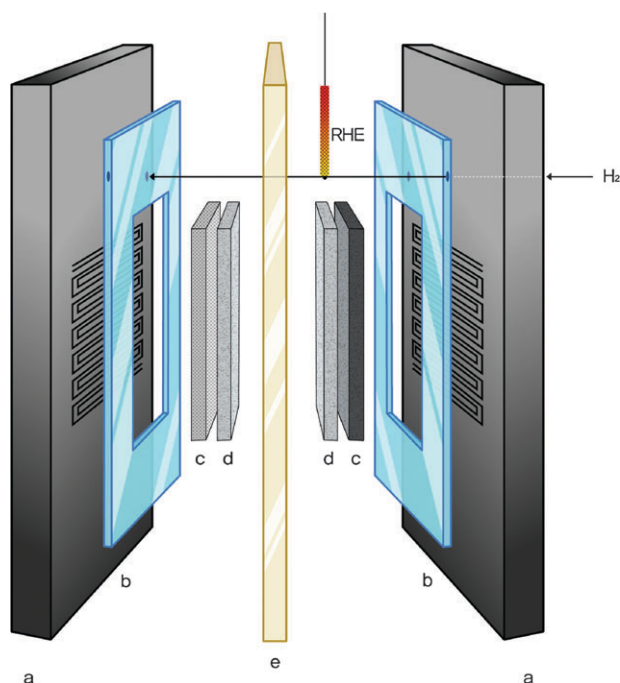


Fig. 9 Internal structure of a single cell unit with a reversible hydrogen electrode. (a) flow field plate (FFP); (b) gasket; (c) diffusion layer (DL); (d) catalyst layer (CL); and (e) polymer electrolyte membrane (PEM). RHE: reversible hydrogen electrode.

error and asymmetrical potential distribution inside the membrane. Thus, great care must be exercised when interpreting single electrode overpotentials as they may not be the representative of the whole cell, and may indeed be misleading. For example, the edge of the active area will often carry a lower current density than that of the bulk and the measured overpotentials will also be the representative of this non-typical performance. Since it is inevitable that a single potential measurement error can occur over a typical range of current densities, a multi-reference electrodes approach can be used to minimize measurement errors. However, for EIS measurements this can be neglected as the amplitude and phase shift of the ac signal is solely important.^{68,89} Thus, the stability of the reference electrode during measurement is only crucial for the determination of impedance spectrum. Based on this design, we subsequently measured the half-cell impedance spectra of the anode and cathode, respectively, as working electrodes; the sum of the two half-cell measurements was subsequently found to be equal to the impedance spectra of the entire cell.⁵⁷

Fig. 10 shows a set of typical experimental results consisting of (a) current–voltage polarization curves, (b) anode/cathode potential variation, and (c) anode/cathode impedance as a function of current density using the built-in RHE fuel cell unit.⁵⁷ From the Figure, the anode and cathode potential variations along with the cell voltage verify the individual contribution of voltage loss. In particular, depending upon the formic acid concentration, the mass transfer limitation of the anode and the mixed potential effect of cathode side can be clearly observed. It should also be emphasized that in individual impedance spectra, high frequency resistance and

charge transfer resistance can be separated,^{57,68} enabling us to ascertain which factors are dominant in performance loss or degradation as a function of time. The intersection distance of the high frequency part is due to the ohmic resistance of the cell. Considering that the resistance for electron transport is negligible, this resistance can be assigned to the proton transport in the electrolyte and interfaces, *i.e.* the membrane itself and membrane/electrode interfaces. It is worthwhile to mention that the high frequency resistance is an important parameter obtained with EIS and is used to optimize fuel cell operating conditions. The value can also be used to correct iR drop in the polarization curve. Here, the anode and cathode impedance contributions are of the same order of magnitude to the entire cell impedance, although the anode impedance is relatively larger, due to both the sluggish kinetics of formic acid oxidation and the dominating effect of mass transport limitations. Other points of interest are that the charge transfer resistance out of cathode impedance spectra decreases with an increase in the methanol crossover rate and an inductive behavior is apparent in all cases; similar to the anode, which becomes less pronounced with an increase in current density.^{57,71}

It is understood that the slow kinetics of formic acid oxidation and inductive behavior in anode impedance spectra is caused by the poisoning of reaction intermediate (mostly CO_{ads}) which is strongly adsorbed on Pt sites and blocks continuous adsorption and dehydrogenation of formic acid.^{66–72} With an increase of current, the diameter of arc decreases slowly, indicating that charge-transfer resistance for the formic acid becomes smaller whereas mass transfer limitation becomes predominant. However, a totally different behavior has also been observed in the Pd^{76} and Pt-Pb^{92} catalyst system. In addition to the reduced diameter of semicircle, the inductive behavior at a low frequency regime disappeared, thereby clarifying that such system has a totally different reaction mechanism without strong reaction intermediates. (reaction 2 in section 2).

Both the cathode potential variations and unexpected trends of charge transfer resistance with formic acid concentration are characteristic phenomena of direct liquid fuel cells. This can be explained by an equivalent circuit model, with which a further understanding of the potential state of cathode should be accompanied.^{57,71,80} Moreover, the dehydration effect due to the hygroscopic property of formic acid was clearly addressed in cathode impedance as described in section 4. As such, a higher concentration of formic acid gives rise to a linear increase of high frequency resistance, regardless of the current density applied. Therefore, more sophisticated approaches are required not only to minimize the formic acid diffusion through anode catalyst layer but also to maintain appropriate water content in the cathode.⁵⁸

6. Nonlinear electro-oxidation and its possible application in fuel cells

From another point of view, the variation of the phase shift between fluxes (current) and forces (potential) through appropriate periodic perturbations under autonomous and/or externally driven oscillatory operating conditions could enhance the efficiency compared to that of stationary states.^{53,93} It has

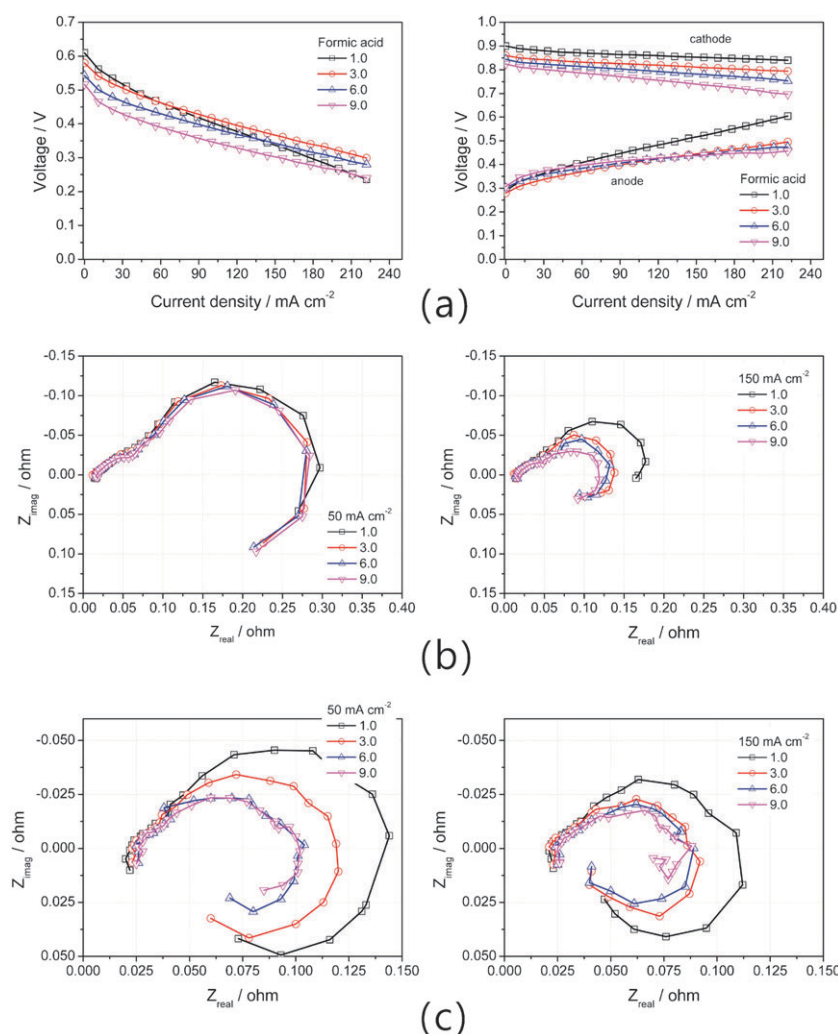


Fig. 10 (a) Current–voltage polarization curves and individual potentials variation of DFAFC using diffusion media of SGL 35AA. Nyquist plots for a direct formic acid fuel cell at (b) anode and (c) cathode with an increase of current density and formic acid concentration. Cell temperature is 60 °C, cathode air flow is 200 scm, and liquid fuel flow is 5 ml min⁻².⁵⁷

recently attracted renewed interest in the context of electrochemical energy conversion devices, *i.e.*, direct hydrogen and liquid fuel cells.^{94–96} Aside from temporal aspects, the control of spatial coupling across electrified interfaces may provide interesting applications. For example, electrochemical devices are conceivable where local activation of a poisoned electrocatalytic surface is sufficient to restore complete activity, if the interface can support the propagation of active fronts; the three-electrodes setup with the counter electrode sufficiently far away from the working electrode could be used in previous studies.^{53,93,97–99} However, there is no reference electrode in real fuel cells, and working and counter electrodes are often very close together in order to minimise ohmic losses in the electrolyte. In such cases, the coupling relevant for one electrode will not only depend on the potential distribution along itself, but also on the distribution at the other electrode. Thus, two types of migration coupling have to be considered, one along the electrode in question, the other between the electrodes. In this respect, further experiments and theoretical studies should be conducted.

7. Summary and outlook

In the past, researchers used to only compete over increasing power performance, but now the hottest trend is to improve stability with lower catalyst loading for use in practical fuel cell applications. In order to achieve this milestone, a clear understanding of the underlying processes of the entire system should be established before developing individual components. Otherwise, it remains impossible to determine whether or not fuel cells will be a good solution for portable power source in the future.

In-depth investigations of the physical and chemical properties of key components in practical formic acid fuel cells should reach a comparable level to that of synthetic research of electrocatalysts and their basic mechanistic principles studied extensively during the last decade. In our opinion, research efforts into the synthesis and design of new electrocatalysts or membranes should be motivated by the search for more general concepts, where the enhanced study of the underlying processes in related components would be a key

step on the way to a faster implementation of technological applications. Further developments in fundamental research in this field are expected to flourish in the coming years, and the increased use of fuel cells will probably lead to a decrease in their price. Indeed, from an industrial point of view, the most cost effective and competitive variants of fuel cell applications will establish themselves in the market. To this end, formic acid fuel cells are definitely one of the most promising candidates with ethanol.

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