

# Formic Acid as a Hydrogen Carrier for Fuel Cells Toward a Sustainable Energy System

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#### Abstract

Formic acid is considered as one of the promising organic liquid hydrogen carriers for the next generation; it can offer a viable method for safe hydrogen transport. In this chapter, we introduce the potential of formic acid in terms of thermodynamics and mechanism as described in earlier work in this area, as well as homogeneous catalysts providing a viable method for the production of molecular hydrogen as a sustainable fuel source through dehydrogenation. In addition, pentamethylcyclopentadienyl iridium (Cp\*Ir) catalysts are also focused upon for this reaction and shown as a strategy to improve catalyst activity by introducing hydroxyl groups to increase turnover numbers. One of the major advantages of using formic acid as a hydrogen source is the regeneration of formic acid through the interaction with carbon dioxide, thus maintaining a continuous cycle, and offers a possibility for high energy output applications. The developed catalyst, Cp\*Ir has potential to produce hydrogen gas with very high pressure, 120 MPa, without facing the problem of decomposition. The generated gas pressure is sufficient for feeding a fuel cell vehicle, which requires 75 MPa, according to the present standard of a hydrogen gas station. Furthermore, even though the generated gas consists of hydrogen and carbon dioxide with the ratio of 1:1, hydrogen can be separated easily and purified from the generated gas under supercritical conditions, by simply cooling to change the gas–liquid state of the system while maintaining the pressure. Finally, we introduce some applications of this gas generation system in fuel cells, and also for the production of electric power. It is worth mentioning that commercialization of the developed process for hydrogen generation via transformation of formic acid may be achievable in the near future.

## **1. INTRODUCTION**

The increasing demand of energy especially in the transportation sector is diminishing fossil fuel supplies, and there are escalating environmental concerns such as global warming (1). Recently renewable energy resources, such as solar and wind power, geothermal energy, biomass energy, and ocean energy, are receiving considerable attention in order to develop a sustainable system (2). However, many researchers are focusing on these renewable energy systems as there is not yet any widely applicable, practical resolution. Nowadays, hydrogen gas (H<sub>2</sub>) can be considered as one of the promising alternative clean fuels to replace conventional fossil fuels, and it can be produced from any primary energy source. As a fuel, H<sub>2</sub> can be used either through direct introduction to an internal combustion engine or to a fuel cell, and produces only water as a by-product (3, 4). Thus, hydrogen can be considered as one contender for zero-emission technology, which would improve air quality especially of urbanized areas (5).

In Europe, a Strategic Research Agenda by the European Hydrogen and Fuel Cell Technology Platform was published in 2004 for the development of the necessity of hydrogen technologies in production, storage, transport, and application in stationary and mobile systems (6). A development strategy was also reported in 2004 for the technical, socioeconomic, and political challenges of deploying world-class, competitive hydrogen technology and fuel cell applications, and recommended courses of action (7).

In the United States, the Department of Energy published a hydrogen and fuel cell program plan in September, 2011 (8), and clear technology development targets are set, and progress is frequently assessed. In California, demonstration fleets of fuel cell vehicles are in use on the roads, and state legislation on emissions represents a strong driving force for clean vehicles. In Japan, after the Great East Japan Earthquake and the accident at the Tokyo Electric Power Company (TEPCO)'s Fukushima Daiichi Nuclear Power Plants in 2011, the energy situation changed drastically, both domestically and abroad. Then in 2014, METI (the Ministry of Economy, Trade and Industry, Japan) produced the fourth Strategic Energy Plan for Japan's new direction of energy policy. Within the plan a strategic road map for hydrogen and fuel cells was published in June, 2014. This was to enable the rapid expansion of hydrogen utilization such as hydrogen power generation, establishment of a large-scale hydrogen supply system, and a totally carbon dioxide-free hydrogen supply system to form a "hydrogen society."

# 2. LIQUID ORGANIC HYDROGEN CARRIERS

Every year, 60 million tons of hydrogen are produced in chemical industry which mainly comes from natural gas (48% of total hydrogen production), 30% from heavy oil and naphtha, 18% from coal, and 4% through electrolysis (3,9). Steam reforming of natural gas and light hydrocarbons (methane, ethane, etc.) is a commonly used technique of hydrogen production. Basic reactions of steam reforming to produce hydrogen are shown as Eqs. (1) and (2)

$$C_n H_m + n H_2 O \rightarrow n CO + (n + m/2) H_2$$
(1)

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{2}$$

Generally, the reaction was carried out at very high temperatures of 700–850°C using a nickel catalyst. The disadvantages associated with this process are the formation of large amounts of  $CO_2$  and the use of fossil fuels for heating.

Similarly, the production of hydrogen from coal gasification (reaction scheme shown in Eq. 3) also generates  $CO_2$  along with small amounts of CO and methane

$$C + 0.2H_2 + 0.6O_2 + 0.8H_2O \rightarrow CO_2 + H_2$$
 (3)

Therefore, to remove  $CO_2$  from  $H_2$  an additional step was required, which involves washing with monoethanolamine or potassium hydroxide to obtain 97%–98% of  $H_2$ . Recently, technological development on the production of hydrogen as a long-term energy fuel with little or no pollution is receiving considerable attention, especially for safe and cost-effective storage and transportation. However, application of  $H_2$  as an alternative fuel is still in its infancy because of the associated difficulties, particularly, its low volumetric energy density and gaseous properties (10, 11). To overcome these difficulties, several methods were developed considering: (1) hydrogen compression under high-pressure conditions, (2) hydrogen liquefaction at low temperature, (3) hydrogen adsorption in metal hydrides, (4) cryogenic storage with hydrogen adsorbing materials, and (5) hydrogen storage in liquid organic hydrides.

Among these methods, hydrogen storage in liquid organic hydrides has several beneficial aspects in terms of environmental, economical, technical, and social usage. The concept of using liquid organic hydrides is preferred because of the advantage of the capability of catalytic hydrogenation and dehydrogenation in a cyclic manner. This concept has been investigated in the Euro-Quebec Hydro Hydrogen Project regarding liquid hydrogen and methyl cyclohexane; in addition various other liquid organic hydrides were developed (12-14).

# 3. RECENT ORGANIC MATERIALS FOR LOHC

Various reagents such as ammonia borane, N-ethylhydrocarbazole, methyl cyclohexane, hydrazine, decalin, methanol, formic acid, and ammonia have also become attractive, gradually as Liquid Organic Hydrogen Carrier (LOHC) as they provide significant advantages in terms of availability, recharging, and safety (Table 1) (10,11,15,16). Wellknown LOHC candidates are cyclic aliphatic hydrocarbons, such as methylcyclohexane (MCH), cyclohexane, decalin, and bicyclohexane, which have a gravimetric hydrogen capacity in the range of 6-8 wt% and a volumetric hydrogen density of  $60-62 \text{ g L}^{-1}$  (17–29). MCH, which can generate H<sub>2</sub>, then transforms to toluene (MTH cycle), is one of the most important candidate as a LOHC. Many reports were published about the cyclohexane, cyclohexane–benzene–hydrogen (CBH) cycle. Although, better reversibility and selectivity than that of the MTH cycle were obtained, CBH cannot be considered as a preferred material as an LOHC because it is a carcinogenic system. Recently, benzyltoluene (HOBT)/ perhydrobenzyltoluene (H12-BT) and dibenzyltoluene (HODBT)/ perhydrodibenzyltoluene (H18-DBT) LOHC systems have been investigated and demonstrated; they exhibit higher volumetric storage density, easier hydrogen purification and reduced toxicity, properties that yield a significant advantage over the TOL/MCH system (30).

Liquid Organic Hydrogen Carrier	Boiling Point (°C)	Density (g mL <sup>-1</sup> )	Energy (kJ molH <sub>2</sub> <sup>-1</sup> )	Gravimetric Content (wt%)	Volumetric Content (kgH <sub>2</sub> m <sup>-3</sup> )	Reaction Temperature (°C)
Liquid H <sub>2</sub>	-252.8	0.071	0.9	100	70	
Water	100	1.00	286	11.2	111	ca. 1000
Methyl cyclohexane	100.4	0.77	68	6.2	47	>350
Cyclohexane	80.7	0.78	65.3	7.2	56	>300
Decaline	193/185 (cis/trans)	0.90/0.87 (cis/trans)	63.2/66.1 (cis/trans)	7.3/7.3 (cis/ trans)	32.4/32.4 (cis/trans)	>200
Bicyclohexane	227	0.86	66.6	7.3	32	
Ammonia	-33.4	0.73	31	17.8	121	>400
Methanol	64.6	0.79	44	12.1	100	>250
Formic acid	100.8	1.22	31	4.3	53	<100

#### Table 1Hydrogen Storage Properties of Various LOHC Including $H_2$ and Water

The simplest alcohol, methanol (MeOH), can also be applicable as an LOHC. Methanol can be stored and handled very easily at ambient conditions. Industrially, methanol can be produced from various sources such as low-cost biomass on a large scale, or by the reduction of  $CO_2$  with  $H_2$  in the presence of an appropriate catalyst, which in turn is converted to hydrogen via steam reforming. The general process of hydrogen production from methanol reforming, in the presence of a heterogeneous catalyst, involves high temperature (200–300°C), high pressure (2.5–3 MPa), and steam (H<sub>2</sub>O) as shown in Eq. (4)

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \tag{4}$$

$$CH_3OH \rightarrow CO + 2H_2$$
 (5)

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{6}$$

A disadvantageous aspect is the generation of impurities within CO through methanol decomposition as described in Eq. (5); this poisons the fuel cell catalysts and should be minimized below 10 ppm. For example, in the case of a successful commercialized fuel cell system, the ElectraGen<sup>TM</sup> power generator, CO is transformed by the water-gas shift reaction (Eq. 6) to CO<sub>2</sub>, then purified H<sub>2</sub> can be obtained (31–33).

Dehydrogenation at low temperature, catalyzed by organometallic catalysts, can only promote the liberation of hydrogen from alcohol along with the corresponding aldehydes, ketones, and esters including polyesters.

$$\begin{array}{c} OH \\ R_1 \end{array} \longrightarrow \begin{array}{c} O \\ R_1 \end{array} + H_2 \end{array}$$
(7)

$$\begin{array}{c} OH \\ R_1 \\ H_2 \end{array} \longrightarrow \begin{array}{c} O \\ R_1 \\ H_2 \end{array} + H_2 \qquad (8)$$

$$\begin{array}{c} OH \\ R_1 \end{array} \longrightarrow \begin{array}{c} O \\ R_1 \end{array} \begin{array}{c} O \\ R_1 \end{array} \begin{array}{c} O \\ R_1 \end{array} \begin{array}{c} H \\ R_2 \end{array} \begin{array}{c} (9) \end{array}$$

$$\begin{array}{c} OH \\ \downarrow \\ R_1 \end{array} + \begin{array}{c} OH \\ R_2 \end{array} + \begin{array}{c} OH \\ R_3 \end{array} + \begin{array}{c} OH \\ R_1 \end{array} + \begin{array}{c} OH \\ R_1 \end{array} + \begin{array}{c} OH \\ R_2 \end{array} + \begin{array}{c} 2H_2 \end{array} (10)$$

$$HO \longrightarrow OH \longrightarrow H_2 \qquad (11)$$

$$HO_{n} ( ) HO_{n} ($$

An early example of dehydrogenation without acceptors was reported by Robinson et al. They used perfluorocarboxylate complexes (M(OCO- $R_{F}_{2}(CO)(PPh_{3})_{2}$ : M=Ru, Os;  $R_{F}=CF_{3}$ ,  $C_{2}F_{5}$ , or  $C_{6}F_{5}$ ) and achieved an initial turnover frequency (TOF) of 8172  $h^{-1}$  for the dehydrogenation of benzyl alcohol (34,35). Although the catalyst shows high TOFs, methanol cannot be dehydrogenated, and the result is attributed to the slightly stronger  $\alpha$ -CH bond in methyl groups compared to larger alkyl groups. Recently, hydrogen production from methanol at low temperature in the presence of a homogeneous catalyst was extensively investigated and the process promoted (36-39). One of the examples is the aqueous phase dehydrogenation of methanol developed by Beller and coworkers in 2013 at low temperature  $(<100^{\circ}C)$  and ambient pressure in the presence of [Ru(H)(Cl)(CO)(HN)] $(C_2H_4PiPr_2)_2$  (iPr = CH(CH<sub>3</sub>)<sub>2</sub>) as the precatalyst and under strongly alkaline conditions (8.0 M KOH) (40). Due to the limited availability and high cost of precious metals, Fe complexes with pincer ligands were investigated for participation in the reaction. With the catalyst that was studied, a high-TOF of over 700  $h^{-1}$  in the first hour and a good TON of almost 10,000 in 46 h were achieved (41). Furthermore, a manganese complex that largely resembles the Fe complex with the pincer ligands was also developed for the dehydrogenation of methanol, whereupon the TON was reduced to 68 during the same time. Interestingly, this manganese catalyst can be applicable for the dehydrogenation of different substrates, such as ethanol, paraformaldehyde, and formic acid (42). By using various organometallic catalysts, the hydrothermal dehydration of primary alcohols was also reported to accelerate the dehydration of alcohols into their corresponding aldehydes (41-43). Nevertheless, the TOF and TON obtained were still too low for large-scale production and the requirement of a strongly basic condition for activation is still a concern.

# 4. FORMIC ACID FOR LOHC

Formic acid can be utilized commercially in various fields, such as in industry, grass silage, leather tanning, antiicing, textile dyeing, finishing, food additives, natural rubber, drilling fluids, and various chemical processes.

The worldwide production of formic acid was about 621,000 t/a in 2012. One of the main industrial routes is the carbonylation of methanol (Eq. 12) and subsequent hydrolysis of methyl formate (Eq. 13). BASF (Germany, BASF process), Kemira (Finland, Kemira-Leonard Process), Feicheng Acid Chemicals (China), and Luxi Chemical Group (China) produce formic acid by this route

$$CH_3OH + CO \rightarrow HCOOMe$$
 (12)

$$HCOOMe + H_2O \rightarrow HCOOH + CH_3OH$$
(13)

Formic acid can also be produced by other methods such as (i) from formates (usually sulfuric acid); (ii) by-products from pentaerythritol, trimethylolpropane, and 2,2-dimethyl-1,3-propanediol; and (iii) from biomass (Eq. 14)



The hydrogenation reaction of carbon dioxide to formic acid is receiving much attention again, and there are many published reports. The early technology of formic acid production from  $CO_2$  in the presence of catalysts (especially soluble Ru complexes are preferred) was first introduced by BP Chemicals in 1980s and then developed by BASF. In their method the reaction takes place in a mixture of  $CO_2$ , tertiary amine, and hydrogen in alcohol at 10–12 MPa to form a formic acid–amine complex, followed by thermal dissociation at 150–185°C. This process faces issues involving the use of an expensive catalyst, the desirability of maintaining its activity, and therefore its reuse, and further, whether the catalyst can be separated from formic acid to avoid its decomposition.

The physical properties of formic acid are also favorable for the use as an LOHC. Formic acid is a low flammable, biodegradable, and stable liquid under ambient conditions, with a boiling point of 101°C and a freezing point of 8.3°C. It is a colorless, clear, and corrosive liquid with a pungent odor (44). Even though its acidity is  $pK_a$  3.74, which is the strongest among



Fig. 1 A photo of a plastic bottle for formic acid, commercially available in Japan.

unsubstituted alkyl carboxylic acids, formic acid is extremely stable. Thus, transportation, handling, and storage of formic acid are feasible under typical infrastructure conditions. Furthermore, dilute formic acid (less than 78%) is not designated as a hazardous material under Fire Defense Laws in Japan (Fig. 1) and is listed on the US Food and Drug Administration's list of food additives in the United States.

Ready availability of formic acid through large-scale production, in combination with unique properties, makes it a most promising material among the LOHCs. Considering the criteria for LOHC, formic acid has a 4.4 wt% of hydrogen content, corresponding to a volumetric capacity of 53 g L<sup>-1</sup>; these values are not so high as water (11.2 wt%, 111 kg m<sup>-3</sup>), liquid NH<sub>3</sub> (17.8 wt%, 0.1 kg m<sup>-3</sup>), and methanol (12.6 wt%, 100 kg m<sup>-3</sup>), but almost equal with 100 MPa of compressed H<sub>2</sub> or MCH (6.2 wt% of hydrogen content and 47 kg m<sup>-3</sup> of volumetric capacity) (Fig. 2) (45).

Dehydrogenation of formic acid has a low-reaction enthalpy among those of the other H<sub>2</sub> storage chemicals as shown in Table 2 (46–50); thus, H<sub>2</sub> can be produced from formic acid at moderate temperatures (lower than 100°C) that match with targets for releasing chemically stored H<sub>2</sub>, according to the DOE (Department of Energy) (51). Therefore, less

![](_page_9_Figure_1.jpeg)

Fig. 2 Volumetric vs gravimetric hydrogen densities.

energy is required for H<sub>2</sub> production from formic acid and could, therefore, be a more attractive H<sub>2</sub> storage material. Moreover, carbon dioxide (CO<sub>2</sub>), which is the coproduct of formic acid dehydrogenation, can be allowed to hydrogenate back to formic acid in water or organic solvents on the catalyst surface or in the presence of specific homogenous catalysts (52–55). Therefore, formic acid can be shown to be a renewable chemical for H<sub>2</sub> storage (56–65) (Fig. 3).

#### 5. HOMOGENEOUS CATALYTIC DEHYDROGENATION OF FORMIC ACID

Formic acid has a potential to be used as a valuable LOHC as outlined earlier. Beside the dehydrogenation process, there is also a possibility of the formation of water and carbon monoxide from dehydration of formic acid. The generation of CO is fatal to fuel cells, because of facile catalyst poisoning (51). In the presence of water, formic acid undergoes dehydration and dehydrogenation reactions (56, 59), but both of the reactions remain unselective in the aqueous phase because the difference between the enthalpies of formation of CO and CO<sub>2</sub> (Eqs. 14 and 15) is very small. Thus, to avoid the dehydration reaction, it is necessary to use an effective catalyst to dehydrogenate formic acid selectively under moderate temperatures (lower than  $100^{\circ}$ C)

				, <u>g</u>					$\Delta_r H^0/(kJ \cdot mol^{-1})$	$\Delta_r G^0 / (kJ \cdot mol^{-1})$
HCO <sub>2</sub> H(I)			$\rightarrow$	$H_2(g)$	+	$CO_2(g)$			+31.2	-33.0
HCO <sub>2</sub> H(I)			$\rightarrow$	$H_2O(I)$	+	CO(g)			+28.4	-13.0
HCO <sub>2</sub> H (aq)			$\rightarrow$	$H_2(g)$	+	$CO_2(g)$			+32.0	-43.2
HCO <sub>2</sub> NH <sub>4</sub> (aq)			$\rightarrow$	$H_2(g)$	+	$CO_2(g)$	+	NH <sub>3</sub> (g)	+84.3	+9.5
CH <sub>4</sub> (g)	+	$H_2O(g)$	$\rightarrow$	3H <sub>2</sub> (g)	+	CO(g)			+206.1	+140.9
CO(g)	+	$H_2O(g)$	$\rightarrow$	$H_2(g)$	+	$CO_2(g)$			-41.2	-28.6
H <sub>2</sub> O(I)			$\rightarrow$	$H_2(g)$	+	1/2O <sub>2</sub> (g)			+285.8	+238.2
NH <sub>3</sub> (g)			$\rightarrow$	3/2H <sub>2</sub> (g)	+	1/2N <sub>2</sub> (g)			+46.1	+16.5
C <sub>6</sub> H <sub>11</sub> CH <sub>3</sub> (I)			$\rightarrow$	3H <sub>2</sub> (g)	+	$C_6H_5CH_3(I)$			+202.2	+93.3
CH <sub>3</sub> OH(I)	+	$H_2O(I)$	$\rightarrow$	3H <sub>2</sub> (g)	+	$CO_2(g)$			+131.0	+9.0

#### Table 2 Thermodynamic properties of the dehydrogenation reactions

(I), (aq) and (g) are represented as liquid phase, aqueous solution phase and gas phase of substances, respectively.

![](_page_11_Figure_1.jpeg)

Fig. 3 Schematic of a cycle for sustainable hydrogen generation and storage with formic acid.

$$\begin{aligned} HCO_{2}H(l) \rightarrow H_{2}(g) + CO_{2}(g) & \Delta G = -32.9 \text{kJ/mol}, \\ \Delta H = 31.2 \text{kJ/mol} \end{aligned} \tag{15} \\ HCO_{2}H(l) \rightarrow H_{2}O(g) + CO(g) & \Delta G = -12.4 \text{ kJ/mol}, \\ \Delta H = 28.7 \text{kJ/mol} \end{aligned} \tag{16}$$

Early studies of the decomposition and dehydrogenation from formic acid in the presence of a homogeneous catalyst were reported in the 1960s by Coffey (66), Otsuka (67), Strauss (68), focusing on Pt- (69), Rh-, Ir-, and Pd-based molecular catalysts (70–73). Among these catalysts,  $[IrH_3(PPh_3)_3]$  was the most rapid, with the initial TOF of 8890 at 118°C, under refluxing conditions. Even though no CO was detected by this reaction, a metal carbonyl species was formed. Then, further studies progressed gradually, and since then many catalysts have been applied in attempts to generate H<sub>2</sub> with high efficiency from the decomposition of formic acid (57, 58, 60-64). Among the different metals used, the catalytic activity of a Rh complex has been studied by Beller and Laurenczy and coworkers. They independently screened the catalytic activity with various types of Ru complexes. Moreover, homogeneous catalysts containing nonnoble metals such as Fe were also tested in efforts to develop a cost-effective method (62, 74-78). Beller and coworkers reported a high activity of  $Fe(BF_4)_2 \cdot 6 H_2O$  with the  $P(CH_2CH_2PPh_2)_3$  ligand (abbreviated as  $PP_3$  in Table 3). Recently, Hazari and Schneider and coworkers obtained the highest TOF of 196,728 h<sup>-1</sup> and turnover numbers up to 983,642 within 9.5 h. Studies on the dehydrogenation of formic acid using homogeneous catalysts are summarized in Table 3.

No.	Catalyst	Solvent	Temp. (°C)	TON	TOF $(h^{-1})$	Conversion	Remarks	References
1	$[IrH_3(Ph_3)_3]$	Acetic acid	118	>11,000	8890		No CO	(66)
2	$[Pt(2-Pr_3P)_3]$	Acetone/water	20	25	100	100		(67)
3	Rhl/Nal	Water	100	_	4.4	—	Significant amount of CO	(73)
4	RhCI <sub>3</sub> 3H <sub>2</sub> O/NaNO <sub>2</sub>	Water	90		126	12.5		(70)
5	[Fe <sub>3</sub> (CO) <sub>12</sub> ]/PPh <sub>3</sub> /tpy	DMF	40	200			With NEt <sub>3</sub>	(74)
6	[Fe <sub>3</sub> (CO) <sub>12</sub> ]/PBn <sub>3</sub> /tpy	DMF	40	1266			With NEt <sub>3</sub>	(75)
7	$[Fe(BF_4)_2]6H_2O/PP_3$	Propylene carbonate	80	92,417	9425	—		(62)
9	FeCl <sub>2</sub> /PP <sub>3</sub> TS	Water	80	1000	133	100		(76)
10	[(tBu-PNP)Fe(H) <sub>2</sub> (CO)]	Dioxane	40	>999	653		With NEt <sub>3</sub>	(77)
11	[(PNP)Fe(CO)H(HCO <sub>2</sub> )]/LiBF <sub>4</sub>	Dioxane	80	983,642	196,728			(78)

#### Table 3 Homogeneous Catalysts for the Dehydrogenation of Formic Acid

## 6. CP\* WITH IRIDIUM COMPLEX FOR H<sub>2</sub> GENERATION FROM FORMIC ACID

Himeda *et al.* studied a series of iridium catalysts containing pentamethyl cyclopentadienyl (Cp<sup>\*</sup>) iridium with various bipyridine and azol ligands, without any phosphine derivatives. At first, they investigated the dehydrogenation in the presence of SO<sub>4</sub> salts of the Cp<sup>\*</sup>Ir complex with the 4,4'-dihydroxy-2,2'-bipyridine (4DHBP) ligand for solvation into the aqueous formic acid solution (79). In 2 M aqueous formic acid (FA) solution, a gas mixture of H<sub>2</sub>+CO<sub>2</sub> was evolved with high TOF values at 40–90°C, and the maximum of 14,000 h<sup>-1</sup> was achieved at 90°C (Fig. 4). Almost all the FA was decomposed after the reaction, and no CO formation was detected by a GC-FID equipped mechanizer. An Arrhenius plot permitted calculation of the activation energy for the decomposition of FA to be 76 kJ mol<sup>-1</sup> in the case of the Cp<sup>\*</sup>Ir complex catalyst, whereas the activation energy was 87 kJ mol<sup>-1</sup> when [Cp<sup>\*</sup>Rh(bpy) (H<sub>2</sub>O)]<sup>2+</sup> was used.

![](_page_13_Figure_3.jpeg)

Fig. 4 Time course of evolved gas volume from the catalysis of formic acid conversion.

![](_page_14_Figure_1.jpeg)

Fig. 5 The dependence of the dehydration of FA at various pH values.

An important experimental parameter with respect to the catalytic process is the pH (Fig. 5). When the pH is adjusted by the addition of sodium formate (SF) from 1.8 to 7.3, an increasing pH value caused a decrease of the initial TOF values as well as the conversion of FA. Once above pH 4.5, the reaction does not proceed and no gas evolution was detected. According to the results, the structure of the iridium catalyst would be changed under the various pH conditions. When the 4DHBP ligand is dissolved in an aqueous solution of formic acid, it assumes the bipyridinol form (A) in the lower pH range. At higher pH conditions, hydroxyl groups are reversibly deprotonated to generate an oxyanion group  $(O^{-})$ , which is a Lewis base with a stronger electron donating ability than that of its conjugate acid. The deprotonation of hydroxy groups can also cause significant changes in the electronic properties and water solubility of the complex (80, 81). Consequently, the ligand changes to the bipyridinolate form (B and C, Scheme 1) (82). It prevails that an important factor in improvement of the activity of the Ir catalyst is functionalization of the bipyridine ligand.

Previously Himeda *et al.* also studied the effects of substitution on the bipyridine ligand on the catalytic activity by using the hydrogenation of 2-cyclohexene-1-one as a substrate. They evaluated its activity in terms of a Hammett type correlation with a substituent constant ( $\sigma_p^+$ ) at pH 2.6 and 7.3, respectively (83). A similar tendency was also observed in the

![](_page_15_Figure_1.jpeg)

Scheme 1 The acid—base equilibrium between the hydroxy and oxyanion forms, and the resonance structures of the oxyanion form.

![](_page_15_Figure_3.jpeg)

**Fig. 6** Hammett type plot of  $\log(TOF_R/TOF_H)$  vs  $\sigma_p^+$  values of substituent (R) in the catalyst at 60°C in 1 M aqueous formic acid solution (10 mL).

dehydrogenation of formic acid in the presence of the Cp\*Ir catalyst (54, 79, 84). The substitution effect was prominent on the initial TOF of dehydrogenation. In the acidic conditions, the initial TOF of the hydroxyl catalyst was approximately 90 times and 2 times higher than that of the unsubstituted bipyridine and methoxy catalysts, respectively (Fig. 6).

![](_page_16_Figure_1.jpeg)

Fig. 7 Cp\*Ir complex with 4,7-dihydroxy-1,10-phenanthroline ligand.

![](_page_16_Figure_3.jpeg)

**Fig. 8** The pH dependence of the solubility of Cp\* catalyst with PHDP ligand and 4DHBP ligand. Solid squares represent DHBP and open circles represent PHDP.

An interesting phenomenon regarding the solubility of the Cp\*Ir catalyst with 4,7-dihydroxy-1,10-phenanthroline (DHPH; Fig. 7) can be seen in Fig. 8. The catalyst solubility changed drastically with pH, and the complex easily precipitates. In the pH range from 4.5 to 5, the DHPH Ir catalyst has very low solubility, around 0.1 ppm (85). The dehydrogenation of formic acid is processed following the change in the pH of the system, which increased from acidic to neutral (around 7) and eventually, the catalyst started to precipitate and stopped functioning as a catalyst. Thus, it can be separated easily without any decomposition and ready for recycling (86).

The effect of the position of the substituent on the catalytic activity was also investigated (Fig. 9) (87). The catalytic activity was evaluated using

![](_page_17_Figure_1.jpeg)

Fig. 9 Structure of the Cp\*Ir complex with BPY ligands.

		Concentration	Initial TOF		, [op(=)(o: .2/]oo4		
	L	of Catalyst [mM]	[h <sup>-1</sup> ]	TON	References		
1	bpy	1.5	18	280	(87)		
2	3DHBP	0.2	440	780	(87)		
3	4DHBP	0.2	1800	5000	(87)		
4	4DHBP	0.2	2400	5000	(54)		
5	5DHBP	1.0	32	280	(87)		
6	6DHBP	0.2	2200	5000	(87)		
7	6DHBP	1.0	2450	10,000	(88)		

Table 4 Results of Dehydrogenation of HCO<sub>2</sub>H Catalyzed by [Cp\*lr(L)(OH<sub>2</sub>)]SO<sub>4</sub>

transfer hydrogenation, dehydrogenation, and hydrogenation of CO<sub>2</sub>. The Cp\*Ir complex having diols at 4,4'-(4DHBP) and 6,6'-positions (6DHBP) exhibited high catalytic activity which is attributed to the electron donating capability of the hydroxy groups at *ortho*- (6-) and *para*-(4-) position (Table 4) (54,87,88).

The reaction mechanism of the dehydrogenation of formic acid catalyzed by various catalysts can be explained, as shown in Fig. 10. It is considered to consist of three steps: (step I) formation of the formato complex B with formic acid, then (step II) release of  $CO_2$  by  $\beta$ -hydrogen elimination to generate the iridium hydride complex C (89), and (step III) production of H<sub>2</sub> from the reaction of [Ir]-H and H<sup>+</sup>.

The principal difference between complexes containing 4DHBP and 6DHBP groups is the *ortho* and *para* positions of the OH groups. Experimental and computational methods reveal that hydroxyl groups at *ortho* positions lead to a proton relay incorporating a molecule of H<sub>2</sub>O by a "pendant base"

![](_page_18_Figure_1.jpeg)

Fig. 10 Reaction mechanism for the dehydrogenation of formic acid catalyzed by Cp\*Ir catalyst.

![](_page_18_Figure_3.jpeg)

Scheme 2  $H_2$  generation from formic acid enhanced by the pendant base effect through a proton relay (proton transfer) in step (B).

effect that facilitates the heterolysis of  $H_2$  in CO<sub>2</sub> hydrogenation (90). According to the calculations, however,  $H_2$  addition through heterolytic cleavage is rate-limiting,  $H_2$  heterolysis with the "proton relay" by the pendant base is preferred as shown in Scheme 2 (88). Thus, in the reverse reaction, the enhancement by the 6DHBP ligand hydroxyl groups at the *ortho* position was also observed in the case of formic acid formation from CO<sub>2</sub> and  $H_2$ . Namely, when the reaction condition is acidic, a water molecule in the form of a hydronium ion, and a hydroxyl group at the *ortho* position can also form a proton relay and assist the reaction of [Ir]-H with a proton (Scheme 2). The proton relay stabilizes the [Ir]-H<sub>2</sub> transition state and lowers the energy barrier for generating H<sub>2</sub>.

To understand the rate-determining step of the dehydrogenation of formic acid, deuterium kinetic isotope effect (KIE) studies were performed in the presence of Cp\*Ir-4DHBP and -6DHBP. The results are summarized in Table 5.

		4DHBP		6DHBP		6DHBP		
S	ubstrate /Solvent	TOF $(h^{-1})$	KIE	TOF $(h^{-1})$	KIE	TOF $(h^{-1})$	KIE	References
1	HCOOH/H <sub>2</sub> O	2400	_	2160	—	5400	—	(88)
2	HCOOH/D <sub>2</sub> O	1140	2.1	1610	1.3	1130	1.2	(88)
3	DCOOD/H <sub>2</sub> O	1660	1.4	1100	2.0	1340	1.8	(89)
4	DCOOD/D <sub>2</sub> O	940	2.6	905	2.4	2560	2.1	(88)

Table 5 Deuterium Kinetic Isotope Effect (KIE)

When the substrates or solvents were replaced with deuterated materials, the reaction rate decreased considerably. In the case of 6DHBP, TOF values were similar for reactions at the different pH values of 1.8 (1 M HCO<sub>2</sub>H) and 3.5 (1 M HCO<sub>2</sub>H/HCO<sub>2</sub>Na (1:1)), and the result indicates that the rate-determining step remained unaffected by pH values. Then, when D<sub>2</sub>O was used instead of H<sub>2</sub>O, the KIE of the 4DHBP complex was 2.1, whereas that of the 6DHBP complex was 1.2 (Table 5, entry 2), and when the substrate (HCO<sub>2</sub>H) was replaced by DCO<sub>2</sub>D, the KIE values in the case of the 4DHBP and 6DHBP complexes were obtained as 1.4 and 2.0, respectively (Table 5, entry 3). These KIE experiments suggest that the deuterated solvent  $(D_2O)$  influences the reaction rate to a greater extent than the deuterated substrate (DCO<sub>2</sub>D) in the case of the 4DHBP complex. Accordingly, when 4HHBP was used, the H<sub>2</sub> (HD) release step for the reaction of [Ir]-H and H<sup>+</sup> (D<sup>+</sup>) (step III, Fig. 10) is the rate-determining step rather than the formation of [Ir]-H from the formato complex. Thus, a high proton concentration (low pH) will lead to high reaction rates, whereas the reaction rate will decrease with increasing pH of the reaction solution, which is consistent with the pH dependence in the case of the 4DHBP complex (Fig. 5). On the other hand, in the case of the 6DHBP complex, KIE values were 1.3 and 2.0 with deuterated solvent ( $D_2O$ ) and substrate ( $DCO_2D$ ), respectively (Table 5, entries 2 and 3). Accordingly, when 6DHBP was used as a ligand, the generation of [Ir]-H from the formato complex (step II, Fig. 10) should be the rate-determining step rather than H<sub>2</sub> release from the reaction of [Ir]-H with H<sup>+</sup>. This is consistent with the DFT calculations previously reported (90).

According to these results, the more favorable ligand for the Cp\*Ir complex was developed by extending the number of OH groups, and the pendant base effect. The examples of developed catalysts (THBP, TH4BPM, THBPM) are shown in Fig. 11, and their corresponding catalytic activities

![](_page_20_Figure_1.jpeg)

Fig. 11 Structure of the Cp\*Ir complex with THBP, TH4BPM, and THBPM ligands.

	L	Concentration of Catalyst [mM]	Initial TOF [h <sup>-1</sup> ]	TON	References
1	4DHBP	0.2	2400	5000	(79)
2	THBP	0.2	3890	7650	(88)
3	TH4BPM	0.05	39,500	11,000	(88)
4	THBPM	0.0015	158,000	308,000	(54)
5	THBPM	0.0031	228,000	165,000	(54)

**Table 6** Results of Dehydrogenation of  $HCO_2H$  Catalyzed by Cp\*Ir Catalysts

are shown in Table 6. Introducing four hydroxy groups at *ortho* and *para* positions, the catalytic activity of THBP was improved with the high TOF (3890 h<sup>-1</sup>) and TON (7650) values compared to these of 4DHBP and 6DHBP containing species (Table 6, entry 2). Interestingly, when a pyrimidine-based ligand was introduced, cited as TH4BPM in Fig. 11, TOF and TON were drastically improved over 10 times (39,500 h<sup>-1</sup>) and 2 times, respectively, than the values for the 4DHBP complex. In addition, a dinuclear complex, (Cp\*Ir)<sub>2</sub>(THBPM), showed further higher activity with the TOF of 228,000 h<sup>-1</sup> at 90°C and TON of 308,000 at 80°C under the optimal reaction conditions (*54*).

The Cp\*Ir(THBPM) catalyst has four OH groups at the *ortho* and *para* positions to activate the catalyst. When THBPM was used as a ligand, much faster gas generation compared to the case for 4DHBP as ligand was observed, as shown in Fig. 12. For the optimization of the catalyst, the pH dependence of the reaction was investigated, and the maximum can be seen at pH 3.5 with TOF of 31,600 h<sup>-1</sup> (Fig. 13), which is close to the p $K_a$  of the catalyst (p $K_a$  3.8) and to the p $K_a$  of formic acid (p $K_a$  3.75). These data suggest the OH groups on the THBPM ligand play not only the "pendant base" role, but also other critical roles in the dehydrogenation.

![](_page_21_Figure_1.jpeg)

Fig. 12 Time course of the gas evolution from formic acid.

![](_page_21_Figure_3.jpeg)

Fig. 13 Optimization of pH conditions for the dehydrogenation of formic acid.

## 7. HIGH-PRESSURE H<sub>2</sub> GENERATION

Formic acid dehydrogenation is thermodynamically favorable, so that high-pressure  $H_2$  is generated easily from formic acid rather than other  $H_2$ storage chemicals. Thus, there is the possibility of high-pressure gas generation by the decomposition of formic acid to the mixture of gas with H<sub>2</sub> and CO<sub>2</sub>. The first example was demonstrated by Laurenczy et al., in aqueous solution using hydrophilic ruthenium-based catalysts, generated from the highly water-soluble ligand meta-trisulfonated triphenylphosphine with either  $[Ru(H_2O)_6]^{2+}$  or, more conveniently, commercially available RuCl<sub>3</sub>. The generated  $H_2/CO_2$  pressure was typically between 1 and 220 bar, but no inhibition of catalytic activity was observed up to a pressure of 75 MPa (Fig. 14). The total conversion did not reach 100% because 10% of SF added for the activation of the catalyst remained unconverted; however, all the formic acid was consumed. Notably, the decomposition of formic acid under high-pressure conditions prevents the generation of CO and  $H_2O$ as confirmed by the analysis of a gas sample using FTIR spectroscopy (detection limit of 3 ppm). The continuous evolution of gases from formic acid was also evaluated under high-pressure conditions (typically 5-25 MPa), which was systematically verified after prolonged addition of formic acid. The maximum gas out flow produced was nearly 600 mL min<sup>-1</sup> at 120°C

![](_page_22_Figure_3.jpeg)

Fig. 14 Kinetic trace of formic acid decomposition in a closed system with a pressure increase to 75 MPa.

with  $[Ru(H_2O)_6]^{2+}$  (1.5 mmol) as the precatalyst. The catalyst's life time is over 1 month with the TOF of  $230 \pm 5 \text{ h}^{-1}$ , and the TON exceeded 40,000 cycles without any deactivation (53,57).

Seven years after the first report on high-pressure gas generation from formic acid, Iguchi and Kawanami et al. reported very high-pressure gas generation, over 120 MPa, from the decomposition of formic acid in the presence of a water-soluble iridium catalyst at a moderate temperature of less than 80°C (86,91). They used the Cp\*Ir complex bearing 4DHBP as the catalyst and obtained 123 MPa maximally (Fig. 15), but thermodynamic calculations predicted the possibility of the generation of high-pressure gas at 225 MPa, using the method that had been developed. The TON was 37,000-38,000 in one batch with 92-93 mol% of high conversion at 40 MPa. The TOF value was decreased with the generated pressure from  $9100 \text{ h}^{-1}$  at 0.1 MPa to 5700  $\text{h}^{-1}$  (2/3) at 10 MPa and 2500  $\text{h}^{-1}$  (1/4) at 40 MPa, respectively. Despite the successful generation of high-pressure gas, the Cp\*Ir catalyst was gradually decomposed. The catalyst undergoes partial hydrogenolysis due to the presence of high-pressure H<sub>2</sub> in the system, resulting in an insoluble compound, which then precipitates after the reaction. The deactivation mechanism predicted that the BPY ligand might be

![](_page_23_Figure_3.jpeg)

**Fig. 15** Time course of the pressure generated by the decomposition of FA at various initial concentrations. The initial concentration of FA is as follows: 4 mol L<sup>-1</sup> (*square*), 10 mol L<sup>-1</sup> (*triangle*), 15 mol L<sup>-1</sup> (*cross*), 20 mol L<sup>-1</sup> (*circle*). Reaction conditions: 80°C, aqueous solution of FA (4–20 mol L<sup>-1</sup>, 13 mL), [Cp\*Ir(4DHBP)(H<sub>2</sub>O)][SO<sub>4</sub>] (2.0 mmol L<sup>-1</sup>, 26 mmol).

changing from its chelating conformation to another conformation under the high-pressure  $H_2$  conditions. To resolve this problem, another catalyst was developed; it contained a 1,10-phenantroline skeleton ligand (Fig. 7) to prevent the rotation at the bond between the pyridine moieties of BPY by bridging, and its potential was investigated in terms of catalytic activity, durability, and reusability. The catalyst bearing a 1,10-phenantroline skeleton was successful in generating a much longer life time (more than 3 months) and the TON exceeded 5,000,000. The catalyst was also recyclable after reaction. It could be separated by filtration more than 10 times without any deactivation (Fig. 16).

From the view point of the catalyst cost, a noble metal complex cheaper than iridium, viz. Ru, was employed for the generation of high-pressure gas. Recently, Guan and Huang *et al.* used a Ru complex bearing a 2,2'biimidazoline ligand for the generation of high-pressure gas from formic acid. The Ru catalyst can generate up to 24.0 MPa of high-pressure gas successfully with 1.8 MPa of He (total 25.8 MPa), and no CO formation was detected by GC-TCD (92) (Fig. 17). In the case of the Ru catalyst, the pH of the system was maintained at 3.5. The reaction mixture consisted of formic acid and sodium formate (FA:SF=1:1). The SF was not converted into H<sub>2</sub> and CO<sub>2</sub>; thus, the maximum pressure obtained was lower compared to a comparable reaction with the iridium complex.

A disadvantage of the method of production of  $H_2$  by the decomposition of formic acid is that the generated gas requires purification for the use in FCVs such as cars, buses, and forklifts. In the present system, FCVs equipped PEFC (polymer electrolyte fuel cell), 99.999% of pure  $H_2$  at 35 or 70 MPa is

![](_page_24_Figure_4.jpeg)

**Fig. 16** Images of the reactant (catalyst 2.8 mmol; water, 3 mL; FA (100%), 1 mL) during the reaction at different stages: (A) before the reaction at RT (20°C), pH 6.8; (B) dissolution of the catalyst at the initial stage in aqueous FA solution at 50°C under high pressure (22 MPa), pH 0.9; (C) during reaction at 50°C under high pressure (22 MPa), pH 0.9; (D) after the reaction; and (E) the precipitation of catalyst after cooling down to RT (20°C), pH 1.9.

![](_page_25_Figure_1.jpeg)

**Fig. 17** Time-dependent gas evolution through FA decomposition in the presence of Ru catalyst bearing 2,2<sup>*i*</sup>-biimidazoline ligand. The reaction was carried out at 80°C in an autoclave (internal volume is 7.0 mL) with 2 MPa of He gas, FA aqueous solution (6.5 mol L<sup>-1</sup>, 4.0 mL), and catalyst (8.0 mol, 2.0 mmol L<sup>-1</sup>).

injected at the hydrogen station. For the preparation of high-pressure purified H<sub>2</sub> gas, generally H<sub>2</sub> was purified from the natural gas under atmospheric pressure, then the purified H<sub>2</sub> was compressed to the desired high pressure. Although already in use at a H<sub>2</sub> station, the separation and purification process consumes a large amount of energy resulting in a high cost for high-pressure H<sub>2</sub>, about 1000–1100 Yen kg<sup>-1</sup> in Japan.

One simple purification technique, that of separating H<sub>2</sub> from the generated gas mixture (H<sub>2</sub> and CO<sub>2</sub>), was reported to be via a gas–liquid phase separation method, simply by changing the physical state of the fluid (Fig. 18 and Table 7). The high-pressure gas at >7.4 MPa, which is generated from FA as a mixture of H<sub>2</sub> and CO<sub>2</sub> at 80°C, has a lower critical point than CO<sub>2</sub> itself (31.1°C, 7.4 MPa). Therefore, the generated gas is in the supercritical phase. Thus, to purify H<sub>2</sub> gas from the gas mixture, the gas separator was simply cooled down to a temperature below the critical temperature in order to change the generated gas from the supercritical state to the gas–liquid state without depressurization. When the generated gas entered the gas separator at 80°C and 30 MPa of pressure, the gas separator was set at 35°C, which is the supercritical condition at 30 MPa. The equimolar mixture of H<sub>2</sub> and CO<sub>2</sub> gases was obtained from the back-pressure regulator attached to the separator.

![](_page_26_Picture_1.jpeg)

Fig. 18 View of the phase separation.

Table 7	Gas Contents	of the Separated	Gas Generated	From the De	composition of
FA at Va	rious Tempera	tures of the Sepa	arator at 30 MPa	а	

Entry	Separator Temp. (°C)	X <sub>H2</sub> (mol%)	X <sub>CO</sub> (mol%)	Flow Rate (L h <sup>-1</sup> ) <sup>b</sup>	Production Rate $(h^{-1})^{c}$
1	35	51	n.d. <sup>d</sup>	0.93	2560
2	0	58	n.d.	0.86	2620
3	-15	69	n.d.	0.75	2790
4	-40	80	n.d.	0.73	3030
5	-51	85	n.d.	0.69	3050

<sup>a</sup>Gas generation condition: 80°C, 30 MPa. Gas separation condition: -51°C to 35°C, 30 MPa. Aqueous solution of FA: 8 mol L<sup>-1</sup>, 40 mL, catalyst ([Cp\*lr(4DHBP)(H<sub>2</sub>O)][HSO<sub>4</sub>]): 0.2 mmol L<sup>-1</sup>, 7–8 μmol. <sup>b</sup>Average gas rate for initial 1 h.

<sup>c</sup>Average rate of H<sub>2</sub> gas per mole of the catalyst.

<sup>d</sup>Not detected (less than 6 vol ppm).

## 8. APPLICATION FOR FUEL CELL BATTERIES

Formic acid is one of the promising choices as the hydrogen carrier for fuel cell batteries that may be developed in the near future. There are published reviews on formic acid as a hydrogen carrier, but applications as a fuel cell using a homogeneous catalyst are limited. In order to establish an economically feasible system for initial commercialization, a significant reduction of the cost of the catalyst is required. Furthermore the system must be able to operate under mild conditions and without sacrificing the activity and selectivity of the catalyst for hydrogen generation. In addition there is a need for advances in the formic acid synthesis and  $CO_2$  capture operations. However, the identification of the main technological obstacles on the

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route to efficient use of FA as a hydrogen source and storage material remains to be established. A hydrogen generator based on the decomposition of FA was designed and built in early 2009. An early report of its applications was published by Boddien and Beller *et al.* The system combined the hydrogen generation unit with a  $H_2/O_2$  polymer electrolyte membrane fuel cell (PEMFC) as shown in Fig. 19 *(93)*. They developed the simple power generation (Fig. 20) through the dihydrogen production system, which involves  $HCO_2H/NEt_3$  and a Ru catalyst. The  $H_2$  and  $CO_2$  gas generated was contaminated by a small amount of the volatile organic amine (NEt<sub>3</sub>); charcoal (CarboTex) was used as a gas absorber to remove the contaminant; otherwise, it can deactivate the membrane electrode of the fuel cell. At the initial stage, the cell power was 48 mW and then it decreased to 26 mW for 42 h, and finally 14 mW was obtained after 69 h.

Grasemann and Laurenczy also developed a hydrogen generator based on the decomposition of FA over a homogeneous Ru(II) catalyst (Fig. 21) (94); the general concept had been published earlier. The hydrogen generator successfully met the target power output of 1 kW or roughly  $30 \text{ L min}^{-1}$  of H<sub>2</sub>/CO<sub>2</sub> assuming 50% fuel cell efficiency.

The exact reason for the decreasing cell voltage is unknown, but there are some possibilities for deactivation of the cell. One of the reasons could be contamination by formic acid in  $H_2$  gas. Zhang *et al.* performed long-term (100 h) tests to detect contaminants and showed that 100 ppm

![](_page_27_Figure_4.jpeg)

Fig. 19 The hydrogen generation unit with a polymer electrolyte membrane fuel cell (PEMFC).

![](_page_28_Figure_1.jpeg)

Fig. 20 Power output as a function of time.

![](_page_28_Figure_3.jpeg)

Fig. 21 Industrial prototype for 1 kW power output.

HCOOH in the  $H_2$  stream significantly degrades the electrode performance and can significantly affect the performance of the PEMFC (95).

Recently Czaun *et al.* fed the mixture of  $H_2$  and  $CO_2$  obtained by decomposition of FA, using an  $IrCl_3/1,3$ -bis(2'-pyridyl-imino)-isoindoline (IndH) catalyst, into a hydrogen-air PEMFC (96). At first, they set the cell voltage at a standard current (I=1.0 A) using ultrahigh-purity hydrogen, then introduced  $H_2/CO_2$  from FA into the cell. The cell voltage was stable (0.85 V at I=1.0 A) for the time of the measurement, using either  $O_2$  or air as cathode feed gas. The integrated FA decomposition showed no difference in performance under the given experimental conditions compared with the

![](_page_29_Figure_1.jpeg)

Fig. 22 Fuel cell performance comparison (H<sub>2</sub>/CO<sub>2</sub> from formic acid and H<sub>2</sub>/air).

 $H_2/O_2$  or  $H_2/air$  fuel cell (Fig. 22). The durability of the system was assessed in a longer duration experiment; the fuel cell maintained its voltage (0.85 V) at a current value of 1.0 A, for the entire 14 h.

A group of students in Eindhoven "Team FAST" built successfully a 400 W model car that can carry 45 kg at approximately 8 km  $h^{-1}$ , and further developed buses powered by formic acid. According to their website, they will start to run a bus in the city for test purposes in 2017 (http://www.teamfast.nl/).

## 9. CONCLUSION

In 2014, the Toyota Motor Cooperation started to sell the fuel cell vehicle, Mirai, globally, followed by Honda selling the FCV, Clarity Fuel Cell, in March, 2016. Even though FCVs are available commercially, the overall program is still in its infancy considering the technologies as well as the infrastructure to utilize FCVs; issues relating to the production, transportation, storage, and feeding of hydrogen, especially at high-pressure, over 35 MPa up to 70 MPa, remain to be solved. As described in this chapter, formic acid as a hydrogen storage material has immense potential that offers many benefits to develop a sustainable society. We believe that formic acid will be one of the promising hydrogen carriers for the next generation throughout the world.

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