# 알칼라인 하이드라진 연료전지 운전 안정성을 위한 전극 구조

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# Effective Electrode Structure for the Stability of Alkaline Hydrazine Fuel Cells

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## 초 록

하이드라진 직접 액체 연료전지는 이산화탄소를 배출하지 않으며, 높은 에너지 밀도를 가지고, 귀금속 촉매를 사용하지 않고도 높은 촉매 활성을 보이는 장점으로 유망한 연료전지로써 활발히 연구가 진행되어 왔다. 하지만, 고안전성 연료전지 운전 성능을 위해서는 전극촉매를 비롯한 핵심소재 개발 및 성능 연구를 토대로 연료의 물질전달 특성을 비롯한 하이드라진 연료전지 내에서 진행되고 있는 작동 프로세스를 충분히 이해할 필요성이 있다. 본 논문에서는 최근의 직접 하이드라진 연료전지 연구결과 중에 가격 경쟁력을 확보한 전극촉매 및 연료 확산, 물 관리, 기체 발생 측면에서 전극 구조 개발 동향을 소개하며 향후 개발 방향에 대해서 고찰하고자 한다.

## Abstract

Direct hydrazine fuel cells (DHFCs) have been considered to be one of the promising fuel cells because hydrazine as a liquid fuel possesses several advantages such as no emission of $CO_2$, relatively high energy density and catalytic activity over platinum group metal (PGM)-free anode catalysts. Judging from plenty of research works, however, regarding key components such as electrocatalysts as well as their physicochemical properties, it becomes quite necessary to understand better the underlying processes in DHFCs for the long term stability. Herein, we highlight recent studies of DHFCs in terms of a systematic approach for developing cost-effective and stable anode catalysts and electrode structures that incorporate mass transport characteristics of hydrazine, water and gas bubbles.

*Keywords*: Alkaline hydrazine fuel cells, Hydrazine hydrate, Electrode structure, Gas evolution reaction, Water management

## 1. Introduction

Easy storage and handling, high energy density and wide availability are features that make alcohols attractive fuel for the most promising alternative power sources for transportation, portable electronics and stationary applications[1-4]. Direct methanol fuel cells (DMFCs) are the most studied systems and the closest to commercialization, since methanol is the simplest alcohol among small organic molecules (SOM) and the electrooxidation of methanol is relatively simple compared to other alcohols. However, DMFCs still have a number of drawbacks, including the usage of high amounts of platinum as anode and cathode catalysts, resulting in an extremely high price for the final devices, and methanol crossover from anode to cathode through cation exchange membranes, significantly decreasing the fuel cell performance and durability.

Direct oxidation alkaline fuel cells (DOAFCs), which oxidise fuels directly on the anode in alkaline media, have attracted attention again in recent years because of the potential solutions to overcome the problems associated with the use of platinum group metal (PGM) catalysts and fuel efficiency[1-3]. The increased number of studies in the past few years indicates a growing interest in the research community, driven by the several advantages of the anion exchange membrane fuel cells (AEMFCs) technology over the currently commercialized proton exchange membrane fuel cells (PEMFCs)[5]. Technically, AEMFCs are similar to PEMFCs, with the main difference being that the solid mem-

**Table 1. Characteristics of Direct Hydrazine Fuel Cells in Comparison with Direct Methanol Fuel Cells**

| | | DHFC | DMFC |
|---|---|---|---|
| Reactions | | $N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$<br>(anode) $N_2H_4 + 4OH^- \rightarrow N_2 + 4H_2O + 4e^-$<br>(cathode) $O_2 + \mathbf{2H_2O} + 4e^- \rightarrow 4OH^-$ | $CH_3OH + 1.5O_2 \rightarrow CO_2 + 2H_2O$<br>(anode) $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$<br>(cathode) $O_2 + 4H^+ + 4e^- \rightarrow \mathbf{2H_2O}$ |
| Advantages | | · Non-precious metals for anode and cathode catalysts<br>· High power density due to high concentration fuels | · Technically mature enough for commercialization due to the use of developed technologies in PEMFC |
| Disadvantages | | · Relatively immature in polymer electrolyte and ionomer technology<br>· Relatively thicker electrodes due to the use of non-precious metal catalysts<br>· CO$_2$ poisoning in cathode | · Low cost-effectiveness due to the use of precious metals for both electrodes<br>· Emission of CO$_2$ via anode reaction<br>· Limited power density due to high fuel cross-over |
| Fuel issues | Crossover | · Relatively low cross-over due to the electroosmotic drag toward anode<br>· Readily controlled via chemical decomposition to hydrogen and nitrogen | · Quite helpful from a system control perspective in terms of start-up, heat-up and system reliability when using active cross-over control strategies |
| | Handing & storage | · Equivalent level of safety to gasoline<br>· DMFC cartridges available (polyethylene tank) | · Fulfill the highest applicable consumer safety standards when property packaged in cartriges<br>· Actually much safer than batteries |
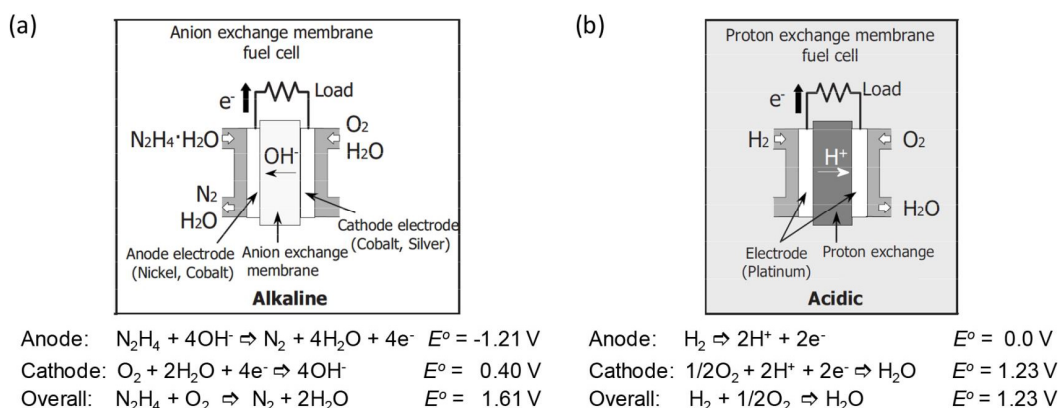


**Figure 1. Comparison of (a) alkaline hydrazine fuel cells and (b) proton exchange membrane (PEM) fuel cells[10].**

brane is an alkaline AEM instead of an acidic PEM. With an AEM in an AEMFC, the OH$^-$ anion is transported from the cathode to the anode, opposite to the H$^+$ conduction direction in a PEMFC as shown in Figure 1. In an AEMFC, water as well as ions are not transported in the same directions as in PEMFCs.

Hydrazine, N$_2$H$_4$ is a strong reducing agent that can be used as a rocket fuel. As it can exist in the form of stable aqueous solutions in concentration of up to 100% hydrazine hydrate (N$_2$H$_4$ · H$_2$O or N$_2$H$_5$OH), it can be transferred easily like alcohols. Therefore, hydrazine as an inorganic fuel for alkaline fuel cells has been studied since the 1970s[6,7]. The main advantages of hydrazine fuel cells are the high hydrogen contents (12.5 wt%) as a hydrogen carrier, high reactivity which leads to higher cell voltages (about 1.61 V) and no emission of any green house gases[3,8-10]. The characteristics of alkaline hydrazine fuel cells are also described and compared with DMFCs in terms of customer benefits in Table 1. Direct hydrazine fuel cells (DHFCs) can be the most promising candidate if the technologies for DMFCs are effectively implemented to avoid potential safety hazards due to high toxicity no of hydrazine.

This paper reviews the recent developments of the catalysts and effective electrode structure affecting the performance and stability of alkaline hydrazine fuel cells. Cathode catalysts and their physico-chemical property, however, are ruled out to better focus on the characteristics of DHFCs rather than entire AEMFCs.

## 2. Anode Catalysts for Hydrazine Oxidation

Platinum (Pt) is considered to be the best electrocatalyst for hydrazine oxidation with the lowest onset potential, but the socioeconomic problem associated with Pt catalysts (cost and scarcity) pose serious challenges for its widespread use in commercial applications. Thus, the need for a cost-effective and efficient electrocatalysts for hydrazine oxidation is essential for the further development of alkaline hydrazine fuel cells.

Since many researches regarding noble metal free catalysts revealed that relatively low cost transition metals and their alloy exhibit higher activities for hydrazine oxidation than Pt, most of the studies on DHFCs have focused on the development and characterization of no-
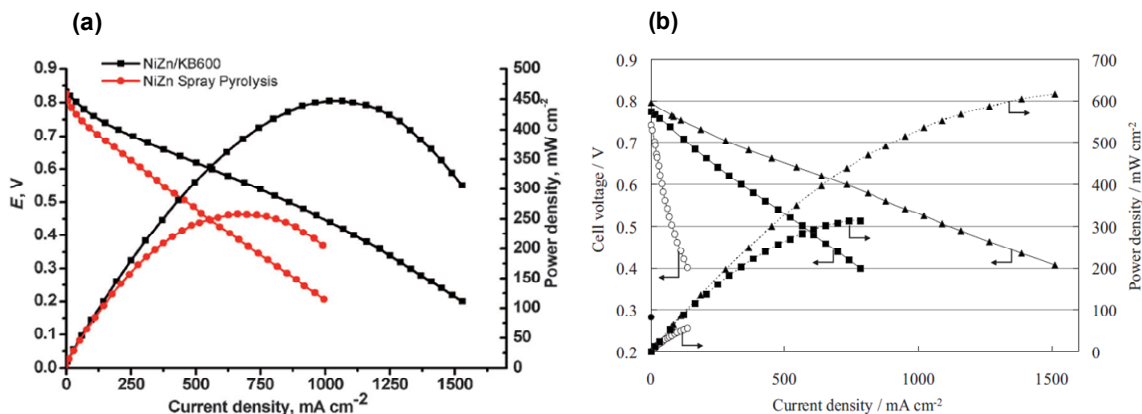
Figure 2. (a) MEA performance of two different Ni-Zn catalysts[11]. Conditions: catalyst loading 2 mg/cm$^2$ (anode), 1 mg/cm$^2$ (cathode); T$_{cell}$ = 80 ℃, HH flow rate = 2 mL/min (20 wt%), air flow rate = 500 cm$^3$. (b) Influence of KOH concentration in fuel on fuel cell performance[10]: (●) without KOH, (○) 0.1 M KOH, and (▲) 1 M and (■) 3 M KOH. The cell temperature was 80 ℃. An aqueous solution of hydrazine and KOH (2 mL/min) was supplied to the anode, and humidified oxygen (55 ℃, RH 27%, 500 mL/min) was supplied to the cathode.

ble-metal-free catalysts over the last few decades[10-20].

Among the promising candidates, Ni-based catalysts for hydrazine oxidation have been extensively explored by various research groups, despite that these catalysts suffer from poor stability due to the formation of inactive oxide layer on the surface during or before the oxidation step of hydrazine[20]. As a representative example, Figure 2(a) presents a typical current-voltage polarization curves when using Ni-Zn catalysts for anode of direct hydrazine fuel cells[12]. It should be noted that peak power density for 60 wt% Ni-Zn/KB (Ketjenblack) of 450 mW/cm$^2$ is the highest ever reported under humidified air supply as an oxidant. The extraordinary power performance is associated with the increased retention time of hydrazine hydrate in contact with the active sites of the catalysts due to the increase of surface area in supported catalysts.
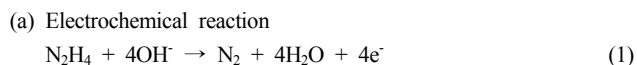
The influence of the KOH concentration on fuel cell performance is also shown in Figure 2(b)[11]. The hydrazine hydrate concentration was set to 4 M. It was found that the addition of KOH improved the cell performance remarkably. The cell performance was very poor in the absence of KOH and for 0.1 M KOH. It is, therefore, considered that the addition of KOH improves the ion conductivity of anion exchange membranes as well as ionomer in the electrodes[21]. However, the cell performance decreases when the KOH concentration is 3 M. This decrease can be attributed to mass transfer limitation due to the specific viscosity of the high concentration of KOH that influences the cathode polarization. The cell performance is also influenced by hydrazine hydrate concentration. The increase in the hydrazine concentration to some extent results in an increase in the reactivity. However, an excess concentration of hydrazine adversely affects the cell performance because of a decrease in ion conductivity.

Carbon-based nanomaterials (graphene, carbon nanotubes and mesoporous carbon, etc.) can be good candidate for anode catalyst partially because of their stability in strongly alkaline and acidic conditions. Moreover, these materials possess high intrinsic electrical conductivity that facilitates the electron transfer processes for hydrazine oxidation along with high surface area[22].

The surface property of the N-doped carbon nanofibers (NDCs) is selectively controlled by poly(methyl methacrylate) (PMMA) and water vapor treatments to tune the pore size, structure and surface morphology as shown in Figure 3[18]. The PMMA and water vapor treatments contribute to the development of both microporous (< 2 nm) and meso/macroporous (>10 nm) structures on the surface of the NDCs coincidentally, resulting in much higher accessibility of KOH electrolyte toward active sites for hydrazine oxidation. However, only the active sites in the mesoporous structures, not those in the microporous structures, mainly contribute to the cell performance as shown in Figure 3(e). This is in good agreement with that the meso/macroporous structures were predominantly utilized as the active catalyst sites in membrane-electrode-assembly (MEA) level performance[23].

## 3. Effective Electrode Structure for Stable Operation

The anodic reaction of hydrazine in an alkaline environment takes place through the following reactions

(a) Electrochemical reaction

$$N_2H_4 + 4OH^- \rightarrow N_2 + 4H_2O + 4e^- \tag{1}$$

(b) Chemical reaction

$$N_2H_4 \rightarrow N_2 + 2H_2 \tag{2}$$

$$3N_2H_4 \rightarrow 4N_2 + NH_3 \tag{3}$$

In the electro-oxidation reaction of hydrazine, the most desirable reaction is the four electron reaction given by Equation 1. However, especially on noble metals, such as Pt, an electroless (nonfaradaic) purely chemical catalytic decomposition pathway takes place. This is due to the fact the thermodynamically hydrazine is unstable. Therefore, like the oxygen electrode, the open circuit potential of a hydrazine electrode deviates from the thermodynamic value and in certain case comes close to that the hydrogen electrode. At temperature above 60 ℃, traces of ammonia are also detected in the gases evolved. This in-
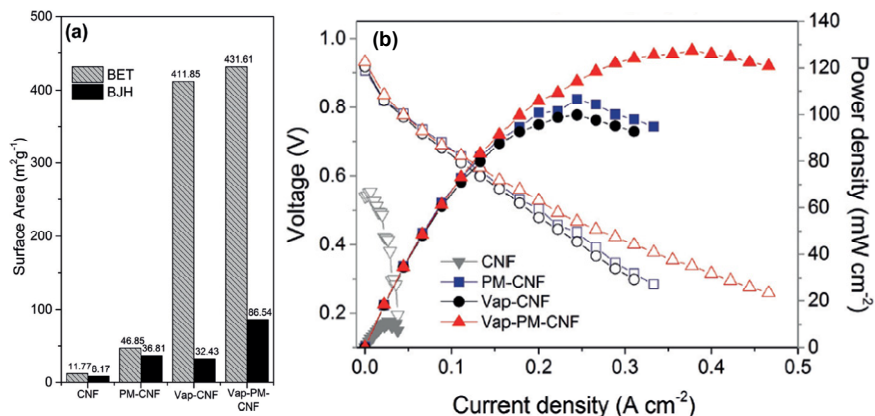
**Figure 3. (a) Bar graphs of the BET and BJH surface areas of the N-doped carbon nanofibers (NDCs), (b) I-V and I-P plots of the NDCs in DHFCs. The cell temperature is 60 ℃. The anodic fuel (5 mL/min) is 4.0 M KOH + 4.0 M hydrazine hydrate, and the cathodic fuel (500 sccm) is oxygen[17].**
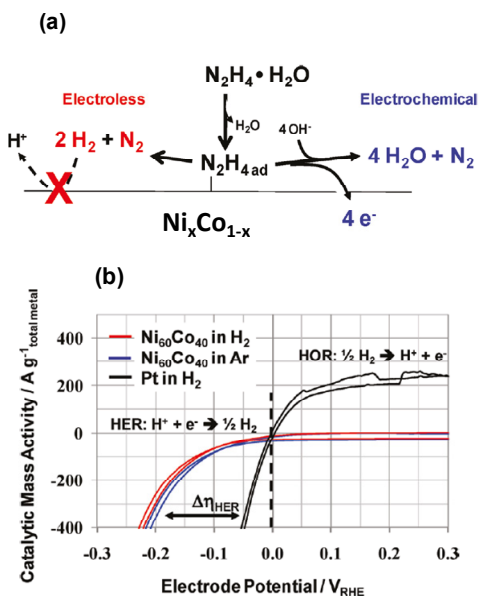


**Figure 4. (a) Proposed competing chemical (red) and electrochemical (blue) HH decomposition pathways. (b) Hydrogen oxidation reaction (HOR) and hydrogen evolution reaction (HER) activity of the NiCo bimetallic catalyst in H₂-saturated (red) and Ar-saturated (blue) 1 M KOH electrolyte. HER and HOR on a Pt in H₂-saturated KOH is shown for comparison (black)[12].**

dicates that a slow catalytic decomposition of hydrazine might occur according to Equation 3.

One of the important issue regarding gas evolution is the catalytic decomposition of hydrazine hydrate by electrochemical promotion of chemical catalysis (EPOC effect) according to Equation 2[13]. Moreover, the applied electrochemical potential and the associated faradaic current appear to promote the purely chemical catalytic decomposition of hydrazine hydrate as shown Figure 4(a). However, the fact that the highly active Ni-Co alloy catalysts does not electrooxidize molecular hydrogen as shown in Figure 4(b) indicates parasitic fuel loss at open circuit voltage (OCV) conditions as well as reduced fuel efficiency under op-

erating conditions, despite the expected significant improvement in fuel cell output power.

A novel approach was proposed to alleviate the undesirable fuel loss of chemical decomposition of hydrazine hydrate and mass transfer limitation by gas bubbles even at OCV conditions[24]. Anode for multi-step reaction (MSR) consists of both hydrazine decomposition catalysts and hydrazine & hydrogen oxidation catalysts as shown in Figure 5(b). In the MSR-DHFCs system, anode catalyst layer is readily filled with gases such as $N_2$ and $H_2$ formed by hydrazine chemical decomposition. Next, generated $H_2$ can be electrooxidized in hydrogen oxidation reaction (HOR) with power generation while unreacted liquid hydrazine is also electrooxidized on the bi-functional electrocatalysts contributing into overall power generation. The durability of DHFC and MSR-DHFC was compared in the AEMFC configuration as shown in Figure 5(c,d). In case of operation with 1 M KOH electrolyte (after 350 h), cell voltage at 5 mA/cm², OCV are significantly improved as well as very stabilized enough, demonstrating the potential advantages of this approach for prevention of fuel loss and crossover.

Gas evolution reactions (GERs), which are processes of converting liquid reactants to gas products accompanied with electron transfer in aqueous media, are of great importance in energy storage and conversion systems[25]. In particular, GER is important in anodic reaction in direct hydrazine fuel cells, which exhibit relatively much higher current density region in comparison with any other direct liquid fuel cells. It is because at especially high reaction rates, the gas slugs accumulated on the electrode surface may not only hinder the liquid fuels transport to the catalyst sites, but also impose a higher pressure in the flow field, thus restraining the liquid fuel supply[26-28].

It was reported that adhesion behavior of gas bubbles could be flexibly tuned by designing the surface architecture of electrodes [19,20,29-31]. Direct construction of electrochemically active materials into micro-/nanostructured film can offer a superaerophobic effect to improve GERs. The discontinuous three phase (solid-liquid-gas) contact line (TPCL) built by creating the high surface porosity would significantly reduce the adhesion force resulting in accelerated gas evolu-
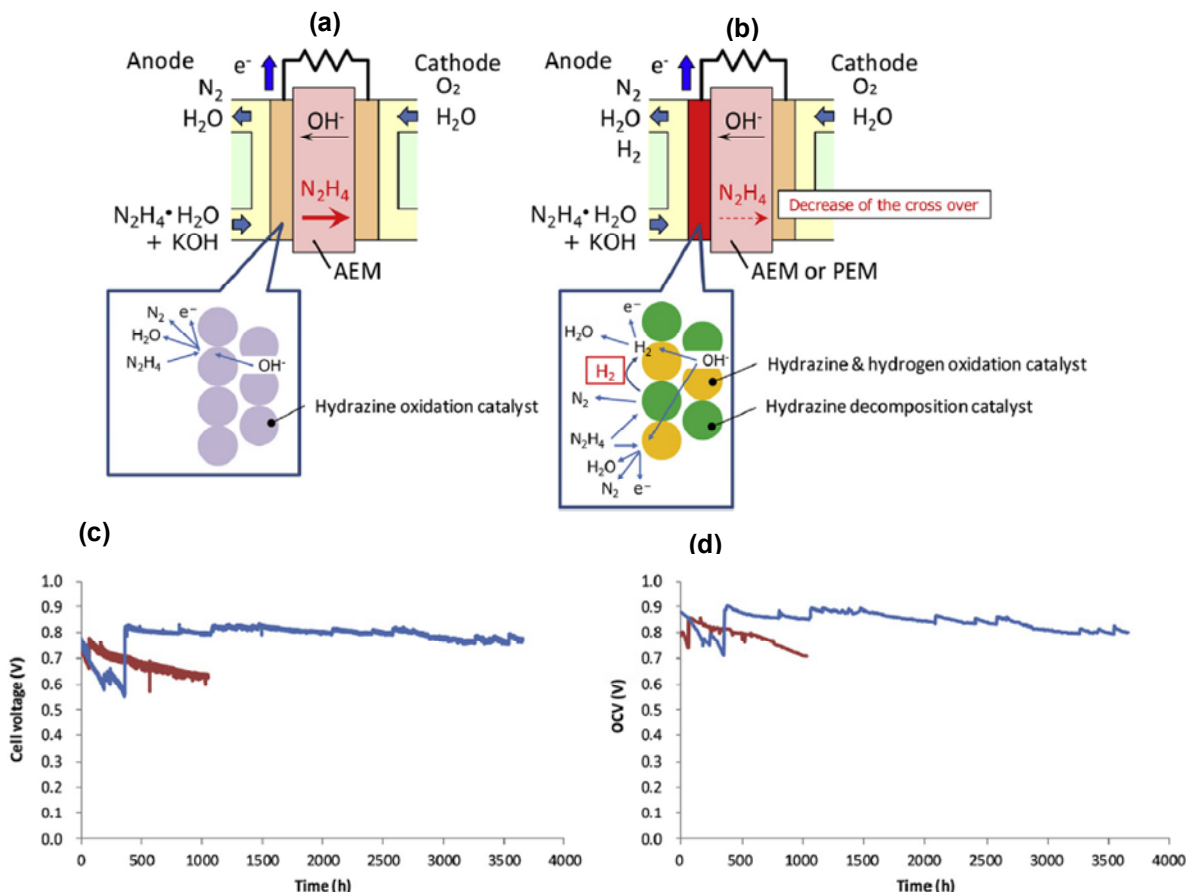
**Figure 5.** Schematic illustration of (a) DHFCs and (b) MSR-DHFCs. Durability of DHFC and MSR-DHFC using AEM at 60 ℃. (a) Voltage variations at 5 mA/cm², (b) OCV variations. Anode; 1 wt% hydrazine hydrate + 1 M KOH, 2 cc/min, Cathode; 20% O₂/N₂, 100 cc/min[23].

tion and eventually much improve electrocatalytic performance even at high reaction rates.

3D nanostructured Cu metal catalyst was fabricated by electrodeposition to obtain a "superaerophobic" surface for diminishing the negative effects induced by the gas bubble adhesion[19]. The highly porous nanostructured Cu showed a negligible adhesion force to the gas bubbles, resulting in much smaller bubble size and fast removal of as-formed nitrogen gas bubbles at high reaction rates, in contrast to the planar counterpart with continuous TPCL as shown in Figure 6(a,b). The practical application was demonstrated by testing a DHFC assembled by the nanostructured Cu film on Cu foam and commercial Pt/C catalyst as the anode and cathode, respectively in Figure 6(c). The open-circuit voltage of the cell was close to 1 V, and the maximum power density of 160 mW/cm² was achieved at 353 K, showing that the value is more than 2 times higher than that of the DHFCs assembled with the commercial Pt/C catalysts (58 mW/cm²). Therefore, the inherent superaerophobic property by ultra-rough, vertical and nano-architectured surface will further facilitate and enhance the electro-oxidation of hydrazine on the electrode surface by swiftly removing the nitrogen bubbles produced on its surface at even higher current density region.

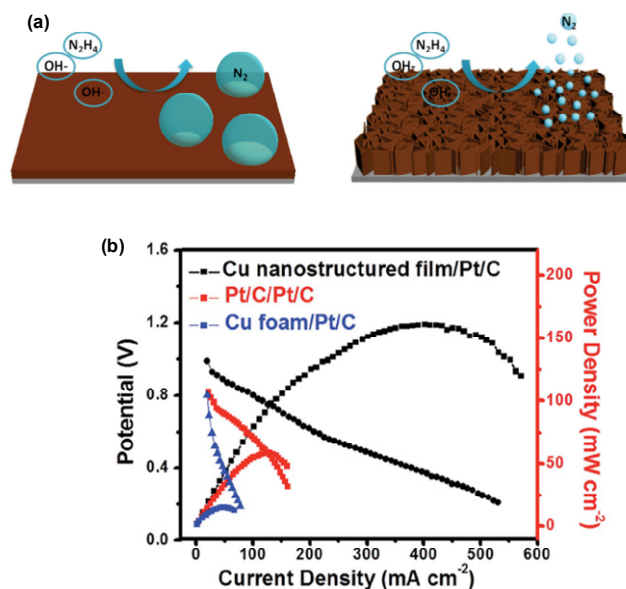Apart from the well-designed catalyst layer, efforts for the ideal con-



**Figure 6.** (a) Schematic illustration of flat and nanostructured Cu films for hydrazine oxidation, the nanostructured Cu film can offer a discontinuous TPCL, result in small releasing size of the N₂ product. (b) DHFC performances containing the anodes of nanostructured Cu film, commercial Pt/C film and Cu foam, respectively[18].
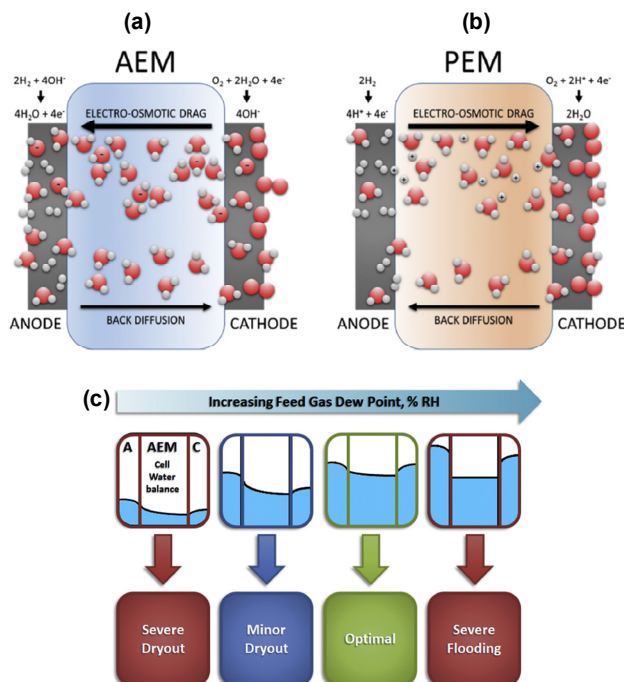
**Figure 7.** Schematic comparison of water consumption, generation, migration, and diffusion in (a) AEMFCs and (b) PEMFCs. (c) Schematic showing the hypothesized distribution of water across the AEM and electrodes in an AEMFC, containing a high conductivity AEM with high water back diffusion, with increasing gas stream relative humidity[32].

figuration within an electrode are also important because electrodes are highly complex systems with many interfaces. The major criteria that need to be considered in electrode structural design include the transport resistance in the networks of various phases[32].

For the stable operation of alkaline hydrazine fuel cells in particular, water balance is of great importance along with gas management[33]. In PEMFCs [Figure 7(b)], water is only generated (at the cathode as a product of the oxygen reduction reaction, ORR) and not electrochemically consumed. Water is also moved to the cathode from the anode by electro-osmotic drag as H$^+$ produced by the hydrogen oxidation reaction (HOR) moves through the PEM. Thus, removing cathode water is the prime concern in the PEMFC to avoid catastrophic electrode flooding. In the AEMFC [Figure 7(a)], water is both electrochemically generated (at the anode from the HOR) and consumed (at the cathode by the ORR) during cell operation. Water is also moved from the cathode to the anode by electro-osmotic drag (in the reverse direction of a PEMFC). This distinctive water transport scenario, together with the high alkaline medium in AEMFCs, represent a unique feature of AEMFCs. Consequently, different approaches are indispensable for the stable operation of alkaline hydrazine fuel cell system to provide adequate water to maintain AEM and electrode hydration, without flooding or drying out the catalyst or gas diffusion layers as shown in Figure 7(c). Furthermore, special care must be taken to select the anode diffusion media because the diffusion of hydrazine hydrate can be affected by the physical properties of anode components.

Hydrophobicity, thickness and density of the diffusion media and catalyst layer should be tuned, because of the use of highly concentrated hydrazine and KOH electrolyte, which is considered to have something to do with ion conductivity as well as cathode polarization[11,34].

## 4. Concluding Remarks

Since the nature of energy conversion system is trade-offs between many parameters, various approaches on reliability, availability, cost, compactness and user operability should be considered with respect to targeted applications and markets. In this regard, 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 alkaline hydrazine fuel cells will be a good solution for portable power source in the future.

Therefore, research efforts into the synthesis and design of new electrocatalysts, diffusion media and membranes should be motivated by the search for more general concepts, where the extensive study of the underlying processes in related components would be a key step on the way to faster implementation of alkaline hydrazine fuel cells.

## Acknowledgement

## References

1. E. H. Yu, U. Krewer, and K. Scott, Principles and materials aspects of direct alkaline alcohol fuel cells, *Energies*, **3**, 1499-1528 (2010).
2. E. Antolini and E. R. Gonzalez, Alkaline direct alcohol fuel cells, *J. Power Sources*, **195**, 3431-3450 (2010).
3. E. H. Yu, X. Wang, U. Krewer, L. Li, and K. Scott, Direct oxidation alkaline fuel cells: From materials to systems, *Energy Environ. Sci.*, **5**, 5668-5670 (2012).
4. S. Uhm, M. Seo, and J. Lee, Competitiveness of formic acid fuel cells: In comparison with methanol, *Appl. Chem. Eng.*, **27**, 123-127 (2016).
5. D. R. Dekel, Review of cell performance in anion exchange membrane fuel cells, *J. Power Sources*, **375**, 158-169 (2018).
6. G. E. Evans and K. V. Kordesch, Hydrazine-air fuel cells. Hydrazine-air fuel cells emerge from the laboratory, *Science*, **158**, 1148-1152 (1967).
7. K. Tamura and T. Kahara, Exhaust gas compositions and fuel efficiencies of hydrazine-air fuel cells, *J. Electrochem. Soc.*, **123**, 776-780 (1976).
8. A. Serov and C. Kwak, Direct hydrazine fuel cells: A review, *Appl. Catal. B*, **98**, 1-9 (2010).
9. K. Yamada, K. Asazawa, K. Yasuda, T. Ioroi, H. Tanaka, Y. Miyazaki, and T. Kobayashi, Investigation of PEM type direct hydrazine fuel cell, *J. Power Sources*, **115**, 236-242 (2003).
10. K. Asazawa, K. Yamada, H. Tanaka, A. Oka, M. Taniguchi, and

T. Kobayashi, A platinum-free zero-carbon-emission easy fueling direct hydrazine fuel cell for vehicles, *Angew. Chem. Int. Ed.*, **46**, 8024-8027 (2007).

11. K. Asazawa, T. Sakamoto, S. Yamaguchi, K. Yamada, H. Fujikawa, H. Tanaka, and K. Oguro, Study of anode catalysts and fuel concentration on direct hydrazine alkaline anion-exchange membrane fuel cells, *J. Electrochem. Soc.*, **156**, B509-B512 (2009).

12. A. Serov, M. Padilla, A. J. Roy, P. Atanassov, T. Sakamoto, K. Asazawa, and H. Tanaka, Anode catalysts for direct hydrazine fuel cells: From laboratory test to an electric vehicle, *Angew. Chem. Int. Ed.*, **53**, 10336-10339 (2014).

13. J. Sanabria-Chinchilla, K. Asazawa, T. Sakamoto, K. Yamada, H. Tanaka, and P. Strasser, Noble metal-free hydrazine fuel cell catalysts: EPOC effect in competing chemical and electrochemical reaction pathways, *J. Am. Chem. Soc.*, **133**, 5425-5431 (2011).

14. T. Sakamoto, D. Matsumura, K. Asazawa, U. Martinez, A. Serov, K. Artyushkova, P. Atanassov, K. Tamura, Y. Nishihata, and H. Tanaka, Operando XAFS study of carbon supported Ni, NiZn, and Co catalysts for hydrazine electrooxidation for use in anion exchange membrane fuel cells, *Electrochim. Acta*, **163**, 116-122 (2015).

15. F. Yang, K. Cheng, G. Wang, and D. Cao, Flower-like Co nano-particles deposited on Ni foam substrate as efficient noble metal-free catalyst for hydrazine oxidation, *J. Electroanal. Chem.*, **756**, 186-192 (2015).

16. T. Asset, A. Roy, T. Sakamoto, M. Padilla, I. Matanovic, K. Artyushkova, A. Serov, F. Maillard, M. Chatenet, K. Asazawa, H. Tanaka, and P. Atanassov, Highly active and selective nickel molybdenum catalysts for direct hydrazine fuel cell, *Electrochim. Acta*, **215**, 420-426 (2016).

17. T. Sakamoto, T. Masud, K. Yoshimoto, H. Kishi, S. Yamaguchi, D. Matsumura, K. Tamura, A. Hori, Y. Horiuchi, A. Serov, K. Artyushkova, P. Atanassov, and H. Tanaka, $NiO/Nb_2O_5/C$ hydrazine electrooxidation catalysts for anion exchange membrane fuel cells, *J. Electrochem. Soc.*, **164**, F22-F234 (2017).

18. J. Jeong, M. Choun, and J. Lee, Tree-bark-shaped N-doped porous carbon anode for hydrazine fuel cells, *Angew. Chem.*, **129**, 13698-13701 (2017).

19. Z. Lu, M. Sun, T. Xu, Y. Li, W. Xu, Z. Chang, Y. Ding, X. Sun, and L. Jiang, Superaerophobic electrodes for direct hydrazine fuel cells, *Adv. Mater.*, **27**, 2361-2366 (2015).

20. K. Akbar, J. H. Kim, Z. Lee, M. Kim, Y. Yi, and S.-H. Chun, Superaerophobic graphene nano-hills for direct hydrazine fuel cells, *NPG Asia Mater.*, **9**, e378 (2017).

21. W. X. Yin, Z. P. Li, J. K. Zhu, and H. Y. Qin, Effects of NaOH addition on performance of the direct hydrazine fuel cell, *J. Power Sources*, **182**, 520-523 (2008).

22. Y. Meng, X. Zou, X. Huang, A. Goswami, Z. Liu, and T. Asefa, Polypyrrole-derived nitrogen and oxygen co-doped mesoporous carbons as efficient metal-free electrocatalyst for hydrazine oxidation, *Adv. Mater.*, **26**, 6510-6516 (2014).

23. S. Lee, M. Choun, Y. Ye, J. Lee, Y. Mun, E. Kang, J. Hwang, Y.-H. Lee, C.-H. Shin, S.-H. Moon, S.-K. Kim, E. Lee, and J. Lee, Designing a highly active metal-free oxygen reduction catalyst in membrane electrode assemblies for alkaline fuel cells: Effects of pore size and doping-site position, *Angew. Chem. Int. Ed.*, **54**, 9230-9234 (2015).

24. T. Sakamoto, A. Serov, T. Masuda, M. Kamakura, K. Yoshimoto, T. Omata, H. Kishi, S. Yamaguchi, A. Hori, Y. Horiuchi, T. Terada, K. Artyushkova, P. Atanassov, and H. Tanaka, Highly durable direct hydrazine hydrate anion exchange membrane fuel cell, *J. Power Sources*, **375**, 291-299 (2018).

25. Z. Lu, Y. Li, X. Lei, J. Liu, and X. Sun, Nanoarray based "super-aerophobic" surfaces for gas evolution reaction electrodes, *Mater. Horiz.*, **2**, 294-298 (2015).

26. P. Argyropoulos, K. Scott, and W. M. Taama, Carbon dioxide evolution patterns in direct methanol fuel cells, *Electrochim. Acta*, **44**, 3575-3584 (1999).

27. H. Yang, T. S. Zhao, and Q. Ye, *In situ* visualization study of $CO_2$ gas bubble behavior in DMFC anode flow fields, *J. Power Sources*, **139**, 79-90 (2005).

28. K. Scott, P. Argyropoulos, P. Yiannopoulos, and W. M. Taama, Electrochemical and gas evolution characteristics of direct methanol fuel cells with stainless steel mesh flow beds, *J. Appl. Electrochem.*, **31**, 823-832 (2001).

29. X. Chen, Y. Wu, B. Su, J. Wang, Y. Song, and L. Jiang, Terminating marine methane bubbles by superhydrophobic sponges, *Adv. Mater.*, **24**, 5884-5889 (2012).

30. J. Wang, Q. Yang, M. Wang, C. Wang, and L. Jiang, Rose petals with a novel and steady air bubble pinning effect in aqueous media, *Soft Matter.*, **8**, 2261-2266 (2012).

31. W. Barthlott, T. Schimmel, S. Wiersch, K. Koch, M. Brede, M. Barczewski, S. Walheim, A. Weis, A. Kaltenmaier, A. Leder, and H. F. Bohn, The Salvinia paradox: Superhydrophobic surfaces with hydrophilic pins for air retention under water, *Adv. Mater*, **22**, 2325-2328 (2010).

32. B. Jeong, J. D. Ocon, and J. Lee, Electrode architecture in galvanic and electrolytic energy cells, *Angew. Chem. Int. Ed.*, **55**, 4870-4880 (2016).

33. T. J. Omasta, L. Wang, X. Peng, C. A. Lewis, J. R. Varcoe, and W. E. Mustain, Importance of balancing membrane and electrode water in anion exchange membrane fuel cells, *J. Power Sources*, **375**, 205-213 (2018).

34. S. Uhm, H. J. Lee, and J. Lee, Understanding underlying processes in formic acid fuel cells, *Phys. Chem. Chem. Phys.*, **11**, 9326-9336 (2009).