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Hot topics in alkaline exchange membrane fuel cells

1. Platinum group metal-free electrocatalysts for oxygen reduction reaction

The tremendous progress from the first discovery of fuel cell principles by Sir William Robert Grove in 1839 [1] and independent observation of electricity generated in electrochemical reaction of hydrogen and air by a Swiss scientist Christian F. Shoenbein [2] to the recent breakthroughs in the fuel cell field resulted in the appearance of this clean energy technology around us. Indeed, fuel cell technology undoubtedly has entered into our life with the first introduction of Toyota Mirai Fuel Cell Vehicle (FCV) by Toyota Motor Co. in December of 2014 [3,4]. This FCV is commercially available and can be purchased in several countries. However, its sticker price of $57,500 substantially limits the number of customers that can purchase it. There are numerous factors that contribute to the high cost of fuel cell stack, however the price of platinum and platinum alloys is the main contributor [5].

As it was mentioned above, intrinsically non-corrosive environment of AEMFC allows to use less noble than platinum electrocatalysts for oxygen reduction on the cathode side of MEA. Initially, the utilization on non-platinum catalysts included palladium and ruthenium compounds (alloys, selenides, phosphides etc) [6–11]. This direction originated from earlier works on exceptional methanol tolerance of mentioned above materials which was studied in proton exchange types of DMFCs [8,9]. Despite the fact that both palladium and ruthenium are cheaper that platinum, selenides and phosphides did not find a wide application as ORR catalysts in AEMFC, mainly due to lower stability of pnictogenides and chalcogenides in alkaline media in contrast to acidic one.

Among truly PGM-free oxygen reduction electrocatalysts materials from families of base metal oxides (MnO_x, mixed oxides, spinels etc) [12–24], M-N-Cs (M = Fe, Co, Mn etc) [25–28] and silver-based [29–32] were extensively studied.

Due to the fact that oxygen reduction reaction in alkaline media is much faster that in acidic some classes of materials showed performance either similar to Pt/C or even exciding these values and the highest activity achieved in alkaline media was reported for Fe-N-C ORR electrocatalysts [33–35]. These electrocatalysts can be synthesized by thermal decomposition of different N-C organic precursors (N-C source) with transition metals precursors (metal source) [36]. For the last several years multiple organic molecules were used for preparation of M-N-C types of materials for application in alkaline media: phthalocyanines [37–39], ethylenediamine [40], aminoantipyrine [41] and other nitrogen rich organic precursors [36]. The synthesis of M-N-C electrocatalysts for oxygen reduction reaction can be distinctly separated into two divisions: usage of different carbon supports in order to maintain high surface area and using templates, which is removed after high temperature pyrolysis. There is a substantial number of publications where metal free N-C materials were used as catalysts for oxygen reduction in alkaline media [35,42–44].

Majority of earlier works presented only data on catalytic activity of M-N-C types of catalysts obtained only in Rotating Ring Disc Electrode (RRDE/RDE) configuration [36]. This was related with absence of commercially available alkaline exchange membranes and ionomers.

Recently, after at least two companies can supply AEM materials: FumaTech (Germany) and Tokuyama (Japan) several reports on utilization of M-N-C or N-C materials in the realistic conditions of fuel cells were published [35,37–44]. In general, the reported values are still substantially lower compared to the performances of PGM-free M-N-C/N-C catalysts in PEMFC configurations. Using nitrogen and sulfur co-doped mesoporous carbon as a cathode in MEAs tested in H_2/O_2 at room temperature the peak power density of ~20 mW cm^{-2} was achieved [45]. Taking into account requirements of sufficient humidification on cathode and water removal on anode, the operation of AEMFC at low temperatures is not optimal, which can explain such a low performance. PGM-free catalysts derived from high pressure pyrolysis of iron salt, melamine and carbon support (Fe-N-C) were integrated into MEA with commercial Tokuyama AS4 ionomer and A201 membrane. Fuel cell test with no backpressure at 60 °C produces peak power density of 70 mW cm^{-2} confirming the importance of water management in alkaline type of fuel cells [46]. The temperature effect on the fuel cell performance was studied by Kruusenberg et al. using cobalt–nitrogen co-doped carbon nanotubes electrocatalyst [47]. The performance was increased from ~60 mW cm^{-2} (35 °C) to 115 mW cm^{-2} (50 °C) which was close to the performance of commercial 46 wt% Pt/C electrocatalyst. It should be noticed that AEM MEAs were mainly manufactured by Catalyst Coated Membrane (CCM) and Catalyst Coated Substrate (CCS) methods and whole electrode was assembled inside of testing cell hardware. Such the electrode fabrication omits an important step of hot pressing, which is common for making 7 layers MEAs in PEMFC case. Later is generally originates from low thermal stability of commercial AEM materials. However, in the work performed by Li at al. the authors performed a hot pressing at T = 140 °C during the electrode fabrication (Fe-N-C cathode catalyst, Tokuyama A201 and AS4 materials were used). The performance of this MEA achieved promising result of 177 mW cm^{-2} [40]. The effect of hot pressing was not studied in mentioned above work and hot-pressing time was not reported, so attribution of high performance to hot pressing only is questionable. On the other side, the formation of triple-phase boundary in anodic and cathodic catalysts layer by using hot-pressing can be a subject for separate study. The utilization of Carbon Nanotubes/Heteroatom-Doped Carbon core–sheath nanostructures as a cathode in AEMFC was reported by Sa et al. [48]. The author demonstrated very promising results with power

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density of 221 mW cm^{-2} at 0.6 V using H_2/O_2 configuration. It should be mentioned that cell temperature was 50 °C, which indicates that using of ionomer and membrane with higher thermal stability will result in increase of fuel cell performance. Similar performance of ~220 mW cm^{-2} was obtained with a Fe-N-C catalyst synthesized by Sacrificial Support Method (SSM) [49].

To conclude on a development of PGM-free electrocatalysts (M-N-C types) for oxygen reduction reaction in alkaline media it is clear from open literature that these catalysts were not specifically designed to be used in AEMFC. The general approach on catalyst synthesis was used, when synthetic conditions as well as catalysts formulations were mainly copied from best performing ORR M-N-Cs used in PEMFC. Despite the fact that M-N-C materials are intrinsically active in alkaline electrolyte as it was demonstrated in RDE/RRDE experiments, the hydrophilic/hydrophobic properties of these catalysts should be specifically optimized to operate in the conditions of AEMFC.

2. Water management

For AEMFCs effective water management is critical for high power density operation. Water is produced by HOR in the anode and diffuses to the cathode where it reacts in ORR. Hydroxide ions formed by the ORR transport water via electro-osmosis from the cathode to anode. A combination of water production and electro-osmosis can cause flooding on the anode side, whereas at high current density a dehydration can occur on the cathode side. Furthermore, reactant gasses are humidified and water is brought to the catalyst layer (CL) with the gas-streams. Because of the AEMFC stability concerns these cells typically operate at or below 60 °C, where evaporative transport of water is not high. As recently discussed by Ref. [50] cathode dehydration contributes to two types of polarization losses: a) reaction kinetics (because water is a stoichiometric reactant) and b) Ohmic – due to membrane and ionomer conductivity dependence on water. A delicate water balance is required to provide sufficient water to react in the ORR but not to overflood the anode CL [51]. The following review outlines the most recent (the last two-three years) developments in understanding water management using both experimental and computational tools, and highlights the importance of material selection and corresponding operating conditions to enable effective AEMFC water management at high current densities.

2.1. Material selection

In this section a discussion of material considerations for water management is presented. Membrane and ionomer properties perhaps are the most relevant when it comes to water management. At high power density operations a careful selection of GDLs and MPLs, as well as PTFE content is needed to improve the performance of the AEMFC.

2.1.1. Membrane and CL ionomer

The main properties of the membrane that impact water management are its conductivity (because hydroxide ions transport water via electro-osmosis) and membrane water diffusivity. Radiation-grafted membranes and ionomers developed by Varcoe and coauthors [52–54] have hydroxide conductivity approaching proton conductivity of Nafion, however with higher degree of swelling [55]. Ion and water transport in these membranes is faster compared to Tokuyama-family membranes [56]. Water content in anode and cathode strongly depends on membrane and ionomer water diffusion and thus the AEMFCs with different membranes and ionomers can have varied performance even under the same operating conditions and materials. One has to be careful with the general recommendations, as material sets don't necessarily show similar transport properties. AEMFCs with the radiation-grafted membranes and ionomers in the CL achieved the highest power densities (1.4 Wcm^{-2}) to date [52,57]. The AEMFCs with radiation-grafted ionomers showed extreme sensitivity to operational RH, where the current density increased from 700 mAcm^{-2} to 2200 mAcm^{-2} at 0.4 V as anode dew point was reduced from 60 to 58 °C, with cathode dew point and cell temperatures at 60 °C [52]. Further dependence on operation conditions is discussed in the next section. At low current densities (up to 0.35 Acm^{-2}) increasing ionomer content from 0.07 to 0.5 increased the cell performance at all RHs but this is most likely due to improved ion conductivity and not necessarily water management improvement [58].

2.1.2. GDLs (with and without MPLs)

GDLs are generally wetted with PTFE to ensure water removal into the gas-channel. MPL introduces a high resistance barrier for water removal from the CL via the GDL route, as the MPL is highly hydrophobic with small pores. Water is believed to transport from the CL via large cracks that are present in the MPLs in some GDL materials [59]. Even in a crack-free MPL cracks can be formed during the cell operation. At higher temperatures (80 °C) most of the water is transported from the CL in a vapor form due to phase-change-induced flow. Most importantly, MPL prevents water accumulation at the CL|GDL interface, as GDL generally has large (30 μm) voids [60]. It also allows for a better heat redistribution, lowering the CL temperature. The MPL|GDL design should be tightly coupled to the CL transport properties, as if the CL is hydrophilic and carries low water capacity (thin) then it is more prone to flooding [61], whereas thicker CLs can retain more water without flooding.

Recent studies explored varying GDL wetproofing [52,62,63] and/or inclusion or exclusion of the MPL [63–65]. The operation conditions and materials for these studies are reported in Table 1. Kaspar [62] used GDLs (Toray TGP-H-060) without the MPL, and observed that significant wetproofing (50 wt% PTFE) in the anode GDL can result in cell flooding, whereas cathode GDL wetproofing did not change the performance significantly compared to 0 wt% PTFE. Wetproofing (especially at medium-range temperatures, here at 60 °C and fully humidified feeds) changes the local wettability and introduces barriers for water removal from the CL because of higher capillary pressure needed to invade hydrophobic pores. With anode wetproofing it is more difficult to remove water from the anode CL resulting in performance drop and flooding [59,66]. On the other hand, if there is not enough water in the cathode to start with, wetproofing cathode GDL will not influence water balance on the cathode side. Generally, MPL has similar effects to retaining water in the CL as wetproofing the GDL, and Kaspar [62] observed a reduced current density when anode or both anode and cathode MPLs were included. Deng et al. [64] have shown that anode MPL increased water retention in the anode CL by more than 50% at low temperatures and low current densities. Furthermore, including cathode MPL to retain more water in the cathode improved performance slightly. Huo et al. [65] with the modeling study also confirmed a current density increase at fully humidified gas feeds with anode MPL but found that cathode MPL decreases transport of vapor from cathode gas stream to the cathode CL, causing drop in performance. Deng et al. [58] found that inclusion of the MPL into Freudenberg GDL increased the cell's current density and with the modeling study they identified higher liquid water saturation levels in both of the CL when MPL was included. Jia et al. [63] found power density improvement (from 60 to 110 mW cm^{-2}) for the ionomer-free thin-film cathodes when removing MPL from the cathode side, which also increased high-frequency

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