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Anion exchange membrane fuel cells: Current status and remaining challenges

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HIGHLIGHTS

- Reviewed technology progress over the last decade on alkaline membrane fuel cells.
- Demonstrated the H₂/CO₂-free air performance that reaches 0.8 W cm⁻² at 0.6 V.
- Discussed key research challenges of fuel cell materials and system components.

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ABSTRACT

The anion exchange membrane fuel cell (AEMFC) is an attractive alternative to acidic proton exchange membrane fuel cells, which to date have required platinum-based catalysts, as well as acid-tolerant stack hardware. The AEMFC could use non-platinum-group metal catalysts and less expensive metal hardware thanks to the high pH of the electrolyte. Over the last decade, substantial progress has been made in improving the performance and durability of the AEMFC through the development of new materials and the optimization of system design and operation conditions. In this perspective article, we describe the current status of AEMFCs as having reached beginning of life performance very close to that of PEMFCs when using ultra-low loadings of Pt, while advancing towards operation on non-platinum-group metal catalysts alone. In the latter sections, we identify the remaining technical challenges, which require further research and development, focusing on the materials and operational factors that critically impact AEMFC performance and/or durability. These perspectives may provide useful insights for the development of next-generation of AEMFCs.

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1. Introduction

This paper combines contributions made in talks at the US Department of Energy (DOE) Alkaline Membrane Fuel Cell Workshop (Phoenix, Arizona, April 2016) [1]. It has been edited by S. Gottesfeld and Y. S. Kim, highlighting insights and conclusions derived from the process and adding proposed future actions.

The reports and discussion in this paper cover the developments in the science and technology of the anion exchange membrane fuel cell (AEMFC) over the last ten years. The activity in this technical area has increased substantially since the workshop called by the US Army Research Office and organized by Bryan Pivovar (then of Los Alamos National Laboratory) late in 2006; that workshop looked into AEMFC technology as a possible drastic move towards cost-effective membrane fuel cells [2].

The basis for the low-cost projections was, first and foremost, the possible use of non-platinum-group metal (non-PGM) catalysts enabled by an alkaline electrolyte, thereby opening the door for a

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low-cost polymer electrolyte fuel cell. It was clear from the outset (2006) that one key requisite for reduction to practice would be a viable hydroxide exchange membrane: the hydroxide ion version of anion exchange membranes (AEMs) was documented at that time to be chemically and mechanically unstable. There were also questions about the impact of a lower hydroxide ion conductivity versus proton conductivity and consequently, concern about the performance penalty expected from operating the AEMFC with a hydrated AEM as the only electrolyte, i.e., with no added liquid electrolyte. The possible impact of atmospheric CO₂ on the performance of an AEMFC, was unclear at the time and, the challenge of water management in a cell with water generated at the anode and consumed at the cathode, had not yet been addressed. As for catalysts, non-PGM cathode catalysts, including silver and some metal oxides, were already quite well studied at the time and confirmed to be viable in alkaline media. Also, viability of nickel anode catalysts for liquid alkaline fuel cells had been reported.

This paper describes the very substantial increase in performance of AEMFCs over the last ten years, focusing first on cells maintaining at least some Pt catalyst, mostly in the anode, and next on cells with non-PGM catalysts. The beginning of life (BOL) performance of the state-of-the-art H₂/(filtered) air AEMFC in lab tests with optimized humidification is already quite similar to that of H₂/air proton exchange membrane fuel cells (PEMFCs) employing membranes of similar thickness: power density of 0.8 W cm⁻² had been reported at 0.6 V and 1.0 W cm⁻² at 0.5 V (see, Section 3.3.2). This has been achieved with currently available AEMs, based on ionomers of good conductivity (≥ 40 mS cm⁻¹ at room temperature) and a thickness of ≤ 30 μ m in the fully hydrated state. High-frequency resistance (HFR) of 0.10 Ω cm² or lower has been measured for AEMFCs under current (with no added KOH), as can be seen in several reports in this paper. This value is not significantly higher than that reported for PEMFCs employing membranes of similar thickness, thus refuting projections of substantially lower conductivity for AEMs versus proton exchange membranes (PEMs).

As for catalysts, the use of silver or silver alloy as an effective low-cost oxygen reduction reaction (ORR) catalyst for the cathode has been demonstrated in AEMFCs. However, as described in this paper, non-PGM catalysts for the hydrogen oxidation reaction (HOR) in alkaline electrolyte turned out to be a significantly harder nut to crack. Consequently, recent efforts have been invested in the study of the HOR process in alkaline electrolytes, focusing first on why the HOR exchange current density at Pt is about 100 times lower in alkaline than it is in acid. Results reported here suggest, be effective in AEMFC anode, a catalyst with both H-bonding and OH-donating surface sites seems to be required, while minimizing catalyst deactivation by excessive surface oxidation and/or by cation hydroxide ion co-adsorption. An active non-PGM anode catalyst for the AEMFC remains a challenge.

As for AEMFC longevity, substantial strides have been made with more stable membrane electrode assembly (MEA) structures and optimized operating conditions. However, as reported here, significant AEMFC longevity challenges remain, possibly originating from the still-limited long-term stability of hydroxide-conducting ionomers, particularly when operating at higher cell temperatures. The mechanisms of ionomer deterioration under AEMFC operating conditions are quite well documented, as described here in some detail, but better remediation strategies are still required. The successful efforts to date, allowing AEMFC stacks to operate over hundreds of hours under limited cell temperature, still call for next-generation AEMs and recast ionomers, which should enable operation at higher temperatures over thousands of hours.

The last section of this paper describes the significant advancements made in addressing the challenges of carbonation by

atmospheric CO₂ and of effective water management in the AEMFC. Solutions provided to date at the system level for cell carbonation are described, including CO₂ sequestration by a solid-state CO₂-binding resin, which can be rejuvenated and reused with thermal swing cycles. As further reported here, decarbonation within the cell can be enhanced significantly by anodic decomposition of the carbonate at high cell current. The latter process is likely to become sufficient by itself at somewhat higher cell temperatures, enabling continuous removal of the carbonate under current without the need for sequestration upstream of the cathode inlet. As for water management, significant advancements reported here have been made towards establishing AEMFC operation with no supply of water from an external source, using a water exchanger on the air side of the cell and facilitating water transport across the cell membrane.

All in all, this paper reports recent advancements that, while still short of making AEMFCs a fully acceptable alternative to PEMFCs, have brought the technology quite close to that status.

2. Technology development 2007–2017 and current status

A significant fraction of the cost of the PEMFC system is the result of the expensive Pt-based catalysts, needed primarily to catalyze the sluggish ORR at the PEMFC cathode. Operating a fuel cell in an alkaline environment allows for the use of a wider variety of inexpensive, Pt-free ORR catalysts. This potential cost benefit, along with the low cost of poly-hydrocarbon AEMs and recast ionomer and the lower cost of metal stack hardware applicable for an alkaline environment, has resulted in significant interest in AEMFCs [3]. This interest has increased over the last few years, following the demonstration of high hydroxide ion conductance in AEMs and a H₂/air AEMFC BOL performance only slightly below that of the PEMFC. The first sections of this paper summarize AEMFC (BOL) performance achieved using materials and cells available at the relevant time and cells operating under a range of conditions.

2.1. AEMFC performance using Pt-based catalysts

In the first stages of AEMFC technology development, the main progress in cell performance was achieved by the development of AEMs of more robust mechanical properties and of higher anion conductivity, as well as the first developments of anion-conducting recast ionomers, enabling better hydroxide ion conduction in the electrodes of the AEMFCs. In 2007, Varcoe et al. reported H₂/O₂ AEMFC performance for a cell using a 51- μ m thick radiation-grafted poly(ethylene-co-tetrafluoroethylene) (ETFE) as AEM and unsupported metal catalysts (4 mg_{metal} cm⁻² Pt-Ru for anode and Pt for cathode) that reached the peak power density of ~ 130 mW cm⁻² at 50 °C [4]. Compared with a previous AEMFC report in 2006 by the same authors [5], the peak power density improved approximately 50%, ascribed to a more mechanically robust AEM. In 2010, Yan et al. reported 260 mW cm⁻² peak power density for an AEMFC using a phosphonium-functionalized polysulfone AEM and carbon-supported catalysts (0.2 mg_{Pt} cm⁻² Pt/C for anode and cathode) [6]. The improved performance was explained by several contributing factors. First, the mechanically stable quaternized polysulfone AEM (50 μ m thick) could accommodate 250 kPa backpressure and operate at 70 °C. Second, the quaternized polysulfone AEM was more conductive than the ETFE radiation-grafted AEM (46 mS cm⁻¹ versus 27 mS cm⁻¹ at 20 °C). Third, a phosphonium-functionalized ionomeric binder was used instead of quaternary ammonium-functionalized ionomers, albeit the effect of different cationic functional groups on fuel cell performance was not too clear.

In 2013, Kim et al. obtained 580 mW cm⁻² peak power density with a H₂/O₂ AEMFC operating at 80 °C under 30 psig backpressure

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