Novel components in Proton Exchange Membrane (PEM) Water Electrolyzers (PEMWE): Status, challenges and future needs. A mini review

Paige Shirvanian*, Frans van Berkel

ECN Part of TNO, Biomass & Energy Efficiency, Westerduinweg 3, PO Box 15, 1755 ZG Petten, The Netherlands

ABSTRACT

This mini-review presents an overall opinion of the technological challenges associated with each component of PEMWE at the cell level. State-of-the-art and a selection of novel advances in PEMWE technology are presented in order to put the performance and limitations of each component in the context followed by our perspective for strategies in the near future (short term) to alleviate the limitations associated with components in order to reduce cost and improve performance and durability.

1. Introduction

The aim towards $<2€/kg\ H_2$ [1] in order to be competitive with other sources of energy, boils down to reductions in cost, higher efficiencies and longer lifetime at the component level. This review identifies cost, function, state-of-the-art PEMWE cell components along with performance/lifetime limitations and presents a selection of promising novel approaches that constitute the NextGen in the developmental phase. In the backdrop of these limitations and based on existing technology, our short term perspective emerges proposing operating strategies and components level fine-tuning/modifications to achieve improved lifetime and performance.

2. Electrocatalysts: oxygen evolution reaction (OER)

The fast kinetics of Hydrogen Evolution Reaction (HER) on commonly used Pt-catalyst in PEMWE cathodes enable loading reduction from 0.3 to 0.025 mg/cm^2 without any impact on the performance [2], so it is not considered a bottleneck within the scope of this article and thus is not discussed further. On the other hand, OER due to its sluggish kinetics is a major contributor to the overall polarization and remains a major research challenge. A link between activity and stability of monometallic oxides for use as catalysts in OER in acidic media has been established [3,4]: the most active oxides (Os ≫ Ru > Ir > Pt ≫ Au) exhibit increased dissolution rates up to orders of magnitude and thus least stable (Au ≫ Pt > Ir > Ru ≫ Os). For this reason, primarily IrO_2 providing a balance of activity and stability is used as the state-of-the-art catalyst in PEMWE systems and constitute a mere ~8% of the stack cost [1]. However, with expensive and scarce

Ir ($<$9000 kg/year [5] production rate ~4.5% of Platinum), a back-of-the-envelope calculation reveals a major roadblock towards scale-up to Giga-Watt (GW) plants: 500 kg Ir required per GW, assuming a typical Ir loading of 2 mg Ir/cm^2 active area and operation at 4 W/cm^2. So, reducing Ir loading while improving OER performance is crucial: Ir-based catalyst is shown to have the intrinsic OER activity to reach the energy density of ~0.01 g$_{Ir}$/kW @ 1.79 V [2] which translates into reducing Ir loading in PEMWE systems by a factor of ~40 (~0.05 mg Ir/cm^2). On the other hand, the sluggish kinetics of OER and instability of OER catalyst materials create a technical barrier towards eventual commercialization of PEMWE technology and thus are the subjects of vigorous research. As of now though, there is no consensus on the mechanism of OER while its degradation in PEMWE environment remains enigmatic [6,7]. In particular, the oxidation mechanism on the catalyst surface could proceed through "solution route" OER and/or "oxide route" LOER (Lattice-OER). In the former case, oxygen evolves without the interaction of the oxide layer with lower activity and also lower dissolution rate whereas in the latter case, the participation of lattice oxygen atoms are inferred, resulting in higher activity but accompanied with more stress on the oxide layer resulting in higher dissolution rate [6]. Three different dissolution routes [7] are suggested that are triggered based on the potential and the surface composition of the catalyst: direct dissolution of metallic Ir at lower potentials, the formation of IrO_3 at higher potentials and oxidation state transition Ir^V-Ir^{III} at intermediate potentials which is the most dominant dissolution route and should be the focus for the development of more stable OER catalysts. Lack of generally accepted "activity descriptors" to help with identification and prediction of activity trends is another impediment to the OER catalyst development. This is due to the constantly evolving

* Corresponding author.
  E-mail address: paige.shirvanian@tno.nl (P. Shirvanian).

surfaces of the catalysts undergoing OER which can lead to formation of a completely different surface from the bulk material [3,6]. In lieu of that, a recent study [8] indicates close correlation of *ex-situ* measured Ir^{III+} and OH concentrations on catalyst surface with OER activity for Ir-based catalysts as evidenced through construction of OER activity versus OH-surface concentration showing a volcano-type behavior thus providing a more facile route to predict OER activity. A judicious combination of *operando* and *ex-situ* characterization techniques [9] has enabled quantitative decoupling of the contributions due to different degradation mechanisms to Ir-based catalysts instability with recommendations to reduce the *operando* oxidation of catalytic surface by operating at lower OER overpotentials. The latter requires: harnessing maximal number of active sites on the catalytic surface or improvements in electrochemical active area (ECA) and enhancements in intrinsic OER-activity. One strategy is to improve ECA by increasing Ir dispersion onto a stable [10] and high surface area support materials [11] with favorable electronic/lattice interactions [12] with Ir to further enhance stability and intrinsic OER. However, even without using a support material a simple colloidal synthesis method [13] yielded ultrahigh dispersions (1.6 nm average diameter) of Ir with up to 160 m^2/g (in contrast to commercial catalysts with 15–60 m^2/g) with remarkable OER activity, yet intrinsic OER activity showed no changes and was insensitive to nanoparticle sizes. Downshifting d-band center from the Fermi level [14] is a measure of the decrease in adsorption energy of the oxygen species as reaction intermediates which in turn leads to enhanced catalytic activity. By dispersing IrO_2 on Titanium Nitride (TiN) [14,15] both intrinsic and mass activities are shown to improve and ascribed to electron transfer from TiN support to IrO_2 catalyst as observed using x-ray photoelectron spectroscopy (XPS) with concomitant downshift in d-band center of Ir. Linear dependence of OER activity on oxygen species binding energies is demonstrated [16] for RuIr doped with transition metals (TM's) (Co, Ni, Fe) with inevitable leaching of TM's that also promoted OER. In particular, Co-RuIr proved to be quite active and durable with small overpotential of 235 mV @ 10 mA/cm^2 in 0.1 M $HClO_4$ in contrast to RuIr which required 344 mV (Table S1). Using a novel liquid atomic layer deposition (L-ALD) method to synthesis core-shell catalysts [17] with indium and fluorine-doped tin oxide (ITO and FTO) cores, researchers were able to vary the Ir-shell thickness and core diameter to maximize Ir utilization. In contrast to nanoparticle-based catalysts, 3 M's nano-structured thin film (NSTF) [18] comprises an ultra-thin continuous film of Ir deposited on arrays of organic nano-whiskers (PR149) with typical dimensions of ~50 nm diameter and 1 μm length with ~5×10^9 whiskers per cm^2. NSTF is shown to be able to operate at 0.25 mg$_{Ir}$/cm^2 and attain high current densities 10 A/cm^2 @ ~2 V, 80 C with thin (50 μm) 3 M PFSA 825EW membrane, although performance sharply declines at loadings <0.25 mg$_{Ir}$/cm^2. Durability tests at 2 A/cm^2 indicate voltage loss of 6.8 μV/hr over 5000 h. Conductive mixed oxides (perovskites), namely Co-Pt bronzes [19] were synthesized and shown to have promising OER activity though inferior to Ir but superior in durability even in comparison to Ir, yet no *in-situ* data is available for PEMWE operation. Early-stage studies of non-precious catalysts have begun. Boride coatings have been used in electrochemical processes to prevent corrosion but such materials have not been studied extensively for OER. Recently titanium diboride (TiB_2) [20] microparticles supported on FTO were explored as OER catalysts in 1.0 M $HClO_4$ with requisite overpotential of 560 mV to generate 10 mA/cm^2 (Table S1) with Faradaic efficiency >96% and the lowest dissolution rate of 0.24 μg/h.cm^2 for an earth-abundant catalyst. As a 3d transition metal oxide, γ-MnO_2 [21] have been reported to catalyze the OER with overpotential of 489 mV in 1.0 M H_2SO_4 at 10 mA/cm^2 (Table S1) with no activity loss over 8000 h. with Faradaic efficiency ~100%, however even a small ~50 mV deviation in the overpotential was sufficiently anodic to generate $(MnO_4)^-$ leading to dissolution and complete deactivation of γ-MnO_2. Operating within the stable potential window as determined using spectroscopic techniques such as UV/Vis, ICP-MS and electrochemical

tests allows utilization of otherwise unstable materials for long term OER applications. Depending on the catalyst, the anodic dissolution currents could be orders of magnitude smaller than the total current [22], and so not detectable using ordinary electrochemical tests alone; thus complementing the tests with spectroscopic techniques (e.g. ICP-MS, UV–Vis, etc.) is crucial.

3. Membranes: perfluoro sulfonic acid (PFSA)-based membranes

Membranes constitute a small cost fraction (~5%) [1] of the PEMWE stack with substantial contributions to the polarization losses [23,24], thus impacting the overall performance of PEMWE significantly. Achieving high protonic conductivity, chemical-mechanical-thermal stability and gas crossover resistance are amongst the challenges facing membrane technology. Historically, PFSA membranes such as long-side-chain LSC-PFSA (e.g. Nafion [25]) and short-side-chain SSC-PFSA (e.g. Aquivion) [25,26] have been used in PEMWE's and constitute the state-of-the-art. PFSA membranes, with a hydrophobic Teflon-like backbone structure for stability, contain sulfonic acid ($SO_3^-H^+$) side chains to provide protonic conductivity. Among others, protonic conductivity is a function of the water content (λ) which is the ratio of the number of water molecules to the number of acid sites. Microscopically, membrane aggregates into interconnected nano-sized pores with walls lined with sulfonic acid groups which upon hydration form hydronium ions (H_3O^+), detach from the acid sites and with sufficient water (typically λ > 12–20) can transport in aqueous media. Protonic conductivity and water content both rely heavily on the concentration of ion conducting units, i.e. sulfonic acid. A typical Nafion 115 has a thickness of 0.005″ (127 μm) and equivalent weight (EW) of 1100 g/mol$_{sulfonic\ acid}$, which is inversely proportional to Ion Exchange Capacity (IEC) [25]. With SSC-PFSA's, it is possible to produce dispersions with lower EW and thereby higher protonic conductivity while achieving better mechanical properties at the same IEC with direct impact on performance. The favorable protonic conductivity and stability in SSC-PFSA membranes are already studied in PEM fuel cells (PEMFCs) [26,27] and using such membranes (e.g. Aquivion) in PEMWE's is also gaining momentum [28–30]. Aquivion membranes with slightly lower gas crossover rate [28], higher crystallinity and glass transition temperature T_g ~150 C compared to Nafion with T_g ~100 C are thermally stable up to 230 C [26] which in turn enable PEMWE operation at higher temperatures (≥90 C) [29,30]. Aquivion positive effects on electrocatalytic properties and formation of better triple-phase boundaries, in addition to larger protonic conductivity, are attributed to its different structure and EW characteristics in contrast to Nafion [28]. A metric of membrane chemical degradation is the fluoride release rate (FRR) [24] which increases by a factor of 15 upon temperature increase from 60 to 90 C. The extruded and re-cast SSC-Aquivion membranes with thicknesses of 90 μm were deemed appropriate to keep the hydrogen cross-over below the requisite safety limit of 4% Vol. when PEMWE operated under a 20 bar differential pressure and at practical current densities (1–4 A/cm^2). The safety issue especially becomes important with thinner membranes and high differential pressures: using membranes impregnated with Pt nanoparticles as a recombination catalyst have recently been proposed [31] in order to reduce hydrogen crossover significantly in very thin (50 μm) Nafion 212. Gas barrier performance of graphene [32,33] sheet in contrast to its facile protonic conductivity [34] has been established. Recently, a sandwich of Nafion|Graphene|Nafion [35] was used in an electrolyzer to demonstrate a reduction of hydrogen crossover rate by 8 times. Spray coating a solution of Nafion, water, isopropanol and graphene [36] on one side of a Fumapem membrane, showed improvements to in-plane protonic conductivity, IEC and water uptake. However, through-plane conductivity figures are yet to be determined and actual PEMWE tests are underway. Apart from safety regulations, gas crossover can impact the chemical stability of the membranes: hydrogen and oxygen crossover may lead to hydrogen peroxide or radical (H·, OH· and OOH·)

formation at the catalysts which in turn can attack and deteriorate the membrane [37]. Incorporation of radical scavengers such as Cerium (Ce) or Manganese (Mn) oxides either in the membrane or catalyst layer have been studied in PEMFCs [38] with promising results but remain largely unexplored in PEMWEs. Composite SSC-membranes (EW: 700–900 g/mol) reinforced with electrospun polysulfone nanofibers showed improved mechanical and dimensional stability [30] and reduced gas crossover. Other composite membranes, such as Nafion XL [39] and Gore-Select™ [40] initially developed for PEMFC applications remain largely unexplored in PEMWE's while Dimensionally Stable Membranes (DSM) with low EW from Giner Inc. [41] are in use for PEMWE's.

4. Bipolar plates (BPPs) and porous transport layers (PTLs)

BPPs and PTLs are multifunctional components with key roles of electric charge, heat and species (reactant/product) transport and constitute the largest fraction of the stack cost: BPP (~50%) and PTL (~18%) [1]. Highly oxidative and corrosive environment especially at the anode necessitates using expensive state-of-the-art Ti-based BPP/ PTL and protective precious metal coatings such as Pt, Au and Ir [42,43] to reduce the interfacial contact resistance (ICR). To reduce the materials costs use of stainless steel (SS) BPPs [42] coated with combined layers of Nb/Ti on SS is reported [44]. The Nb $(1\,\mu m)$|Ti $(50\,\mu m)$|SS anode BPP system indicated an order of magnitude reduction in ICR compared to Ti|SS while Ti layer protected the SS against corrosion. However, cracking and delamination due to H_2 embrittlement rendered Nb coating on cathode BPP ineffective. Among others, laser treated 316L SS, carbon-based and nitride coatings on SS [45–47] as already investigated for PEMFC could be good candidates to study for cathode BPP in PEMWE. Passivation of anode Ti-PTL is among the main contributors to the performance degradation [24,48]. Sputter coating $0.1\,mg/cm^2$ Ir on Ti-PTL felt [43] reduced the contact resistance by 60 $m\Omega.cm^2$ and improved performance significantly. In contrast other precious metal coatings Pt and Au require thicker coatings and form less conductive oxides in PEMWE environment. Apart from materials aspects, fine-tuning the micro-structure of PTL namely pore size/porosity distribution and surface morphology affects the PTL/ CL contact resistance and catalyst utilization: PTL's with large-pore $(60\,\mu m)$ LP-PTL and small-pore $(16\,\mu m)$ SP-PTL showed wide pore and narrow pore distribution, respectively that in turn translated into significant contact resistance reductions for SP-PTL/anode catalyst layer (CL_a) and 200 mV better performance at all current densities in PEMWE [49]. The micro/macro-porous layer (MPL) [50] developed by Ti-thermal spraying on one side of the PTL (PTL/MPL/CL_a) effectively generates finer pores at the PTL/CL_a interface thus reducing ICR by 20 $m\Omega.cm^2$ with associated performance improvements.

5. Conclusions and perspective for short-term PEMWE operation

Research and development (R&D) for novel components will likely yield results in the long-term. In the short-term, however, it is important to be able to produce high performance, cost effective with long lifetime PEMWE systems based on existing technologies. Therefore, our perspective is based on the substantiation as presented in this review article that PEMWE operation at lower temperatures and overpotentials translates into significant lifetime improvements but with a toll on performance. One strategy to improve the latter will be:

(a) Use ultra-thin, low EW, reinforced membranes with good mechanical and H_2 cross-over resistance: thinner membranes compensate for the reduced protonic conductivity (higher ohmic losses) at lower temperatures with simultaneous reduced FRR translating into longer membrane life.
(b) Set the upper limit on OER overpotential to avoid significant catalyst degradation: obviously, higher activation losses (slower OER

kinetics) occurs at lower temperatures but to a lesser extent than ohmic losses in the membrane.
(c) Utilize coatings on PTL to reduce contact resistance and passivation. Also, PTL's morphology/pore-structure should be designed to improve catalyst utilization and provide a smooth support for the ultra-thin membranes.
(d) Limit electrochemical gas compression to stay below potentials triggering catalyst or PTL degradation or pressures resulting in significant hydrogen embrittlement in PTL. Clearly, the cross-over safety limits should never be exceeded.

The added benefit of operating at lower overpotentials and temperatures is that a wider spectrum of stable support and coating materials become available that can further help drive down the cost of the components:

- Better dispersion of Ir catalyst on stable support materials (e.g. carbides or nitrides of transition metals) can improve catalyst utilization.
- PTL and BPP can be made from SS and instead of scarce and expensive metal coatings (e.g. Ir and Au) and cost effective Ti/Nb coatings could be used, for instance.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https:// doi.org/10.1016/j.elecom.2020.106704.

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