

Energy & Environmental Science

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

Paper

www.rsc.org/xxxxxx

Vitamin E Assisting Polymer Electrolyte Fuel Cells

Yingfang Yao^{a,b,c} Jianguo Liu^{a,b,*} Wenming Liu^{a,c} Ming Zhao^a Bingbing Wu^a Jun Gu^{a,b} and Zhigang Zou^{a,b,c,*}

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Breathing O₂ on the earth, vertebrates suffer from diseases originating from oxidative stress, which however can be relieved by various antioxidants. Similarly, proton exchange membrane fuel cells (PEMFCs) remain a major challenge of limited lifetime caused by chemical attacking of reactive oxygen species (ROS). Learning from vertebrates ourselves, we herein show that incorporation of a natural antioxidant acting as the free radical scavenger, α -tocopherol (α -TOH), the most abundant component of vitamin E, enables performance maintenance for PEMFCs that is impossible for fuel cells in the absence of α -TOH. It was notable that oxidized α -TOH can be in turn reduced by permeated H₂ during fuel cell operation, resulting in the regeneration. Such reversibility builds in a chemical circulation system, which ensures not only effective recycling of α -TOH, but also permits efficient protection of PEMs that allows long-term operation.

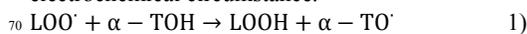
Introduction

Inhaled into lungs, respired in cells, oxygen [1] is indispensable that supports all vertebrates, including human beings, for the daily metabolic activities. Paradoxically, reactive oxygen species (ROS), by-products of oxygen use, such as oxygen ions, free radicals and peroxides, oxidatively damage and deteriorate organisms, including lipids, proteins, DNA, etc., causing disorders, diseases, cancers and aging. [2–4] Similarly oxygen also plays a vitally essential role in a series of energy conversion systems. For example, PEMFCs “inhale” oxygen; “digest” hydrogen; generate energy in electrical and heating forms; and finally “excrete” water as the waste. [5] However, oxidative stress exists in PEMFCs likewise. [6, 7] Nafion, one representative of the commercialized perfluorosulfonic acid PEMs, has been demonstrated chemically attacked by ROS, such as hydroxyl and peroxy radicals that stem from H₂O₂, leading to performance loss of fuel cells, and even catastrophic failure. [7–10] The chemical degradation of PEMs is one of the major problems that shorten the lifespans of PEMFCs. And finding out a proper method to level up the durability and reliability of PEMs has become a prerequisite and worthwhile goal that attracts worldwide research interest in the past decade. [11–24]

Antioxidants, especially non-enzymatic antioxidants that protect cellular systems from over-oxidized, such as ascorbate, tocopherol, glutathione, carotenoids, and polyphenols, [3, 25–28] might be a proper recipe for the dilemma of unexpected corrosion of PEMs, as they are functioning “*in vivo*” of PEMFCs. Within this family, vitamin E is water-insoluble and thermally stable

($\geq 503\text{K}$), [29, 30] acting as a peroxy radical scavenger, preventing chain breaking and lipid peroxidation. [25] In view of the varying temperature and humidity that PEMFCs need to sustain, vitamin E seems a great additive candidate for PEMs without weight and functional loss caused by dissolving into water or decomposing under heat.

Vitamin E refers to a group of eight compounds that include both tocopherols and tocotrienols, [3] among which α -TOH is the most naturally abundant, fully methylated, and biologically active. The major antioxidating function of α -TOH in mammalian tissues majorly includes two principal steps. First, α -TOH reacts with an oxidized lipid radical (LOO[•]) to yield a hydroperoxide molecule (LOOH) and the tocopheroxy radical (α -TO[•]) (reaction 1). Second, the α -TO[•] radical further reduces another LOO[•] radical (reaction 2), so that one α -TOH molecule is able to inhibit two peroxide radicals. [25] Cyclic voltammogramic research of α -TOH has also demonstrated that in protic solvent there can be two one-electron (ECE) processes at the potential of around +0.6 and +1.4 V v.s. Fc/Fc⁺ respectively, [31–34] indicating the recyclability of α -TOH with appropriate electron donors. [35] Owing to this, it can be rationally estimated that α -TOH can be potentially applied in PEMs, e.g. Nafion, as the radical scavenger to minimize Nafion decay under severe electrochemical circumstance.



Results and discussion

Even though α -TOH is a great peroxy radical scavenger, no clue

leads to the conclusion that it can hinder all ROS from being generated and corroding PEMs, especially hydroxyl radicals. It has been literally demonstrated that the reactivity of α -TOH to hydroxyl radicals is much limited compared with that to peroxy radicals. [3, 36] As a result, it is quite questionable that whether α -TOH can inhibit hydroxyl radicals attacking on Nafion macromolecules. For the purpose to identify the hindrance efficiency of α -TOH on hydroxyl radicals, chromogenic experiments were implemented with rhodamine B as the colorant in aqueous solution. Certain amount of H_2SO_4 was added to simulate the acidic environment of PEMs; and the oily α -TOH was dispersed in the solution as uniform emulsions (see Fig. S1). Aliquots of H_2O_2 were then added, and catalyzed with transition metal ions, e.g. Fe^{2+} , converted to hydroxyl radicals (Fenton mechanism). And the decrease in UV-vis light absorbance was evaluated as a function of the amount of H_2O_2 , owing to the linear relationship between the concentration and absorbance intensity of rhodamine B (see Fig. 1). It is notable that the decrease of colorant intensity was only recorded after the system achieved equilibrium, [37] as determined by monitoring the change in absorbance as function of time upon the addition of H_2O_2 . For each H_2O_2 addition, the system achieved equilibrium in less than 2 min. The experiment was repeated without catalyst ions Fe^{2+} , and it was shown that rhodamine B was only sensitive towards hydroxyl radicals, rather than H_2O_2 . (Fig. S2)

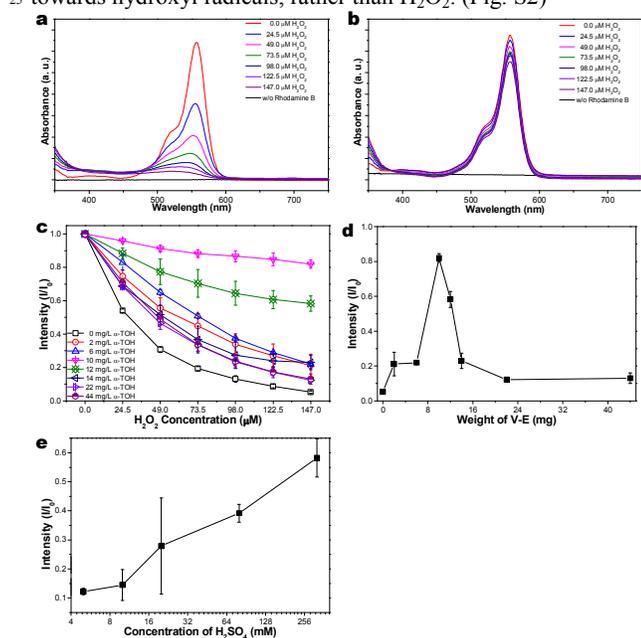


Fig. 1 Ex situ chromogenic experiments between rhodamine B and hydroxyl radicals, illustrating the α -TOH protection of Rhodamine B against Fenton agents. Absorbance response of Rhodamine B **a)** without α -TOH, and **b)** with $10 \text{ mg}\cdot\text{L}^{-1}$ α -TOH to aliquots of H_2O_2 . **c)** Absorbance intensity of Rhodamine B (wavelength = 550 nm) as the function of the concentration of H_2O_2 . Different amount of α -TOH was dispersed into the solution for comparison of antioxidant efficiency. **d)** Absorbance intensity of Rhodamine B with different amount of α -TOH was dispersed in the solution when $147 \mu\text{M}$ H_2O_2 was added. In **(a-d)**, 5mM H_2SO_4 was added to simulate the acidic environment of PEMs. **e)** The influence of the concentration of H_2SO_4 on the absorbance intensity of Rhodamine B for the solution containing $22 \text{ mg}\cdot\text{L}^{-1}$ α -TOH and $147 \mu\text{M}$ H_2O_2 .

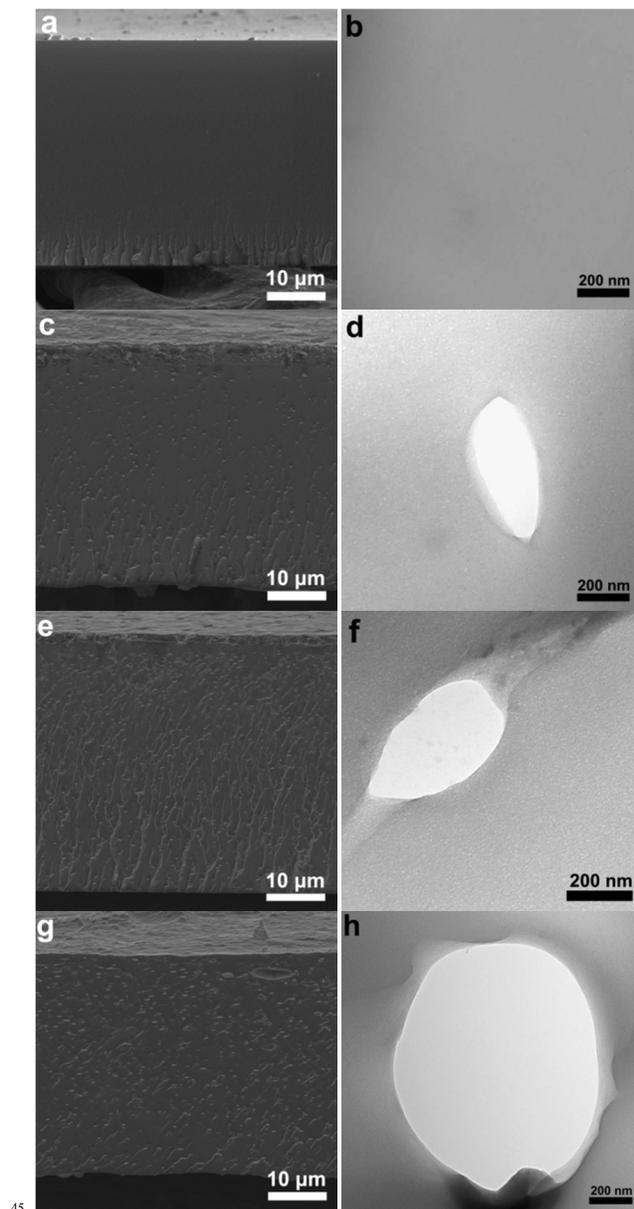


Fig. 2 Cross-sectional morphological characterization of PEMs. SEM images of cross-sectional views of **a)** recasted Nafion, **c)** Nafion/0.5% α -TOH, **e)** Nafion/1% α -TOH, and **g)** Nafion/3% α -TOH composite membrane. Magnified TEM images in which holes were remained due to oily α -TOH was removed were also shown for **b)** recasted Nafion, **d)** Nafion/0.5% α -TOH, **f)** Nafion/1% α -TOH, and **h)** Nafion/3% α -TOH composite membrane, respectively.

With aliquots of H_2O_2 continuously trickled into the solution, the fading response of rhodamine B was obviously inhibited after the addition of α -TOH (Fig. 1). As seen in Fig 1a and 1b, the absorbance intensity at the wavelength of 550 nm (peak) could be preserved at 82.0% with $10 \text{ mg}\cdot\text{L}^{-1}$ α -TOH, while it decreased to around 5.2% in absence of α -TOH with $147.0 \mu\text{M}$ H_2O_2 added in both solution, indicating the predominant reactivity of α -TOH with hydroxyl radicals compared with that of rhodamine B. However, it should be noted the nonlinear relationship between the added amount of α -TOH and the remnant absorbance intensity of rhodamine B with the same amount of H_2O_2 added.

As shown in Fig. 1d, with 147.0 μM H_2O_2 , the highest absorbance signal appears at the concentration of 10 $\text{mg}\cdot\text{L}^{-1}$ α -TOH, while either inadequate or excess, α -TOH could hardly hinder effectively oxidation of H_2O_2 on the colorant, leading to lower remained intensity. This may probably caused by better dispersion of α -TOH in more acidic solution, leading to higher interfacial areas, and thus higher reactivity. As a result, with fixed concentration of H_2SO_4 , only proper amount of α -TOH could achieve the highest interfacial areas to expose to the radicals; while higher concentration of H_2SO_4 should lead to better reactivity of α -TOH with certain amount, which was demonstrated in Fig. 1e. H_2SO_4 was then replaced with Nafion, and similar phenomena were observed, as seen in Fig. S3. The chromogenic experiments clearly demonstrated that α -TOH could efficiently trap ROS, and may protect Nafion from being oxidized.

α -TOH was then incorporated into Nafion to fabricate composite membranes for further investigations. Increasing percentage of α -TOH, from 0, 0.5, 1, to 3 wt% versus Nafion, were added to Nafion/DMSO solution to cast pristine/composite PEMs with thicknesses at around 40 μm (Fig. 2a, c, e, and g). SEM and TEM images of corresponding PEMs were illustrated in Fig. 2. Compared with the pristine Nafion (Fig. 2a, b), nanoparticulate droplets with the size of around 200 nm were uniformly dispersed in composite PEMs with 0.5, and 1% α -TOH (Fig. 2c-f), demonstrating the formation of α -TOH/Nafion composite membranes. However, polydispersity (Fig. 2g) and size enlargement (Fig. 2h) can be observed when the percentage increased to 3%. On account of the proton non-conductivity property of α -TOH, oversized oily droplets might block the routes for proton transport, leading to lower conductivity. As a result, it was supposed that the morphological differences may lead to a performance downfall especially for PEMs with 3% α -TOH. Furthermore, the successful fabrication of Nafion/ α -TOH composite membranes could also be confirmed with the FT-IR spectra, which was shown in Fig. 4.

Single cells that contained membrane electrode assemblies (MEAs) with different PEMs mentioned above were then constructed. It was noticed that though oily liquid, α -TOH could be stably in the membranes for as long as months. 24-hour open circuit voltage (OCV) holding tests were operated to investigate chemical degradation. The data in Fig. 3 proved the supposition that α -TOH additive had few effects on the fuel cell performance until 3% was added. Before OCV holding tests, the initial potential at 1000 $\text{mA}\cdot\text{cm}^{-2}$ for PEMs with 0, 0.5 and 1% α -TOH was 560, 530, 570 mV, respectively; while the potential dropped to 473 mV for that with 3% α -TOH. After OCV holding tests, it was occasionally noticed that with subsequent 8-hour discharging under high current density, i.e. $\geq 1000 \text{ mA}\cdot\text{cm}^{-2}$, performance was recovered for all PEMFCs containing α -TOH. For example, single cell with PEM containing 0.5% α -TOH partially recovered 15 mV from 496 to 511 mV at 1000 $\text{mA}\cdot\text{cm}^{-2}$, other than the further reduction of 8 mV for that with pristine Nafion membrane (see Fig. 3a). This observation not only demonstrated the protection efficiency of α -TOH on PEMs, but steered the investigation to the further stage.

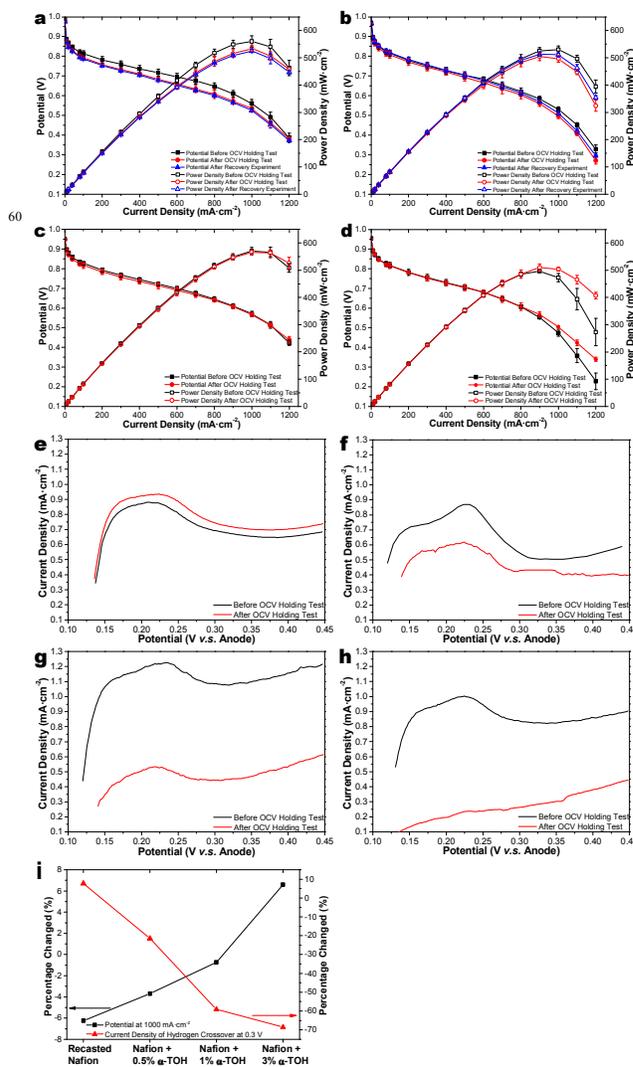
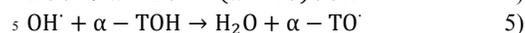
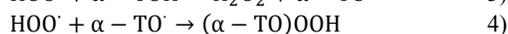
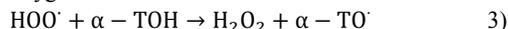


Fig. 3. Variation of fuel cell performance before and after OCV holding tests. Polarization curves and power output of PEM single fuel cells with a) recasted Nafion, b) Nafion/0.5% α -TOH, c) Nafion/1% α -TOH, and d) Nafion/3% α -TOH composite membrane. Comparison of performance between recasted Nafion and Nafion/0.5% α -TOH composite membrane after recovery procedure, i.e. 8-hour galvanostatic output at high current density, were shown in a) and b) respectively. Comparison of hydrogen crossover current density before and after OCV holding tests were illustrated with e) recasted Nafion, f) Nafion/0.5% α -TOH, g) Nafion/1% α -TOH, and h) Nafion/3% α -TOH composite membrane. i) Specifically, the variation of potential at current density of 1000 $\text{mA}\cdot\text{cm}^{-2}$ and hydrogen crossover current density at 0.3 V for PEMFCs with different concentrations of α -TOH before and after OCV holding tests was normalized from initial performance and was compared.

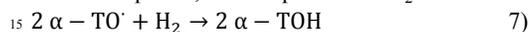
As the performance recovery has been extensively investigated, the major cause is generally the removal of catalyst contaminants, such as CO, [38] SO_2 , [39] H_2S , [40] etc., or temperature lifting. [41] And only a few reports mentioned the performance recovery as the result of electrolyte. [42 – 47] According to the abovementioned chromogenic experiments, it was believed that with the protection of incorporated α -TOH, reactive oxygen species (ROS) should preferentially react with the antioxidant. The reaction of α -TOH with ROS has been extensively

investigated [48], The major reactions between α -TOH and oxygen radicals in PEMFCs can be shown as follows:



In reaction 4 and 6, oxygen species of $(\alpha\text{-TO})\text{OOH}$ and $(\alpha\text{-TO})\text{OH}$ forms as tocophenoxonium cations, i.e. $\alpha\text{-TO}^+$ [31].

10 The products including $\alpha\text{-TO}^\cdot$ and $\alpha\text{-TO}^+$ are generally reversible. [3, 31] On account of the highly restricted hydrogen crossover rates after OCV holding tests for composite membranes (Fig. 3e – i), the oxidized $\alpha\text{-TOH}$ products should be reduced by more reductive species, such as permeated H_2 :



The abovementioned reactions are the major redox and intermediate reactions that probably happen in the composite membrane during PEMFC operating.

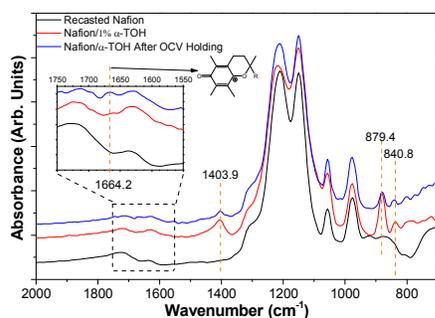


Fig. 4 FT-IR spectra of Nafion and Nafion/ α -TOH composite membranes. The peaks at 879.4, and 840.8 cm^{-1} should be assigned with the stretching vibration of epoxy group of α -TOH molecules; the peak of 1403.9 cm^{-1} should be associated with the bending vibration of phenolic hydroxyl group of α -TOH molecules; indicating the success fabrication of composite membrane of Nafion/ α -TOH. The small peak appeared at 1664.2 cm^{-1} for the composite membrane after OCV holding test should be due to the carbonyl stretching vibration, indicating the formation of reversible phenoxonium cations for oxidized species of α -TOH.

30 However, two major difficulties hindered the investigations from more precisely figuring out the detailed mechanism inside the membrane, including a bunch of side reactions during PEMFC operation (see Table S1), and the absence of a sophisticated characterization method to detect the chemical change inside PEMs. Although series of characterization techniques has been developed for the real-time monitoring the PEMFC operation, such as ambient pressure XPS [49], *in-situ* ATR-FTIR [50], electron paramagnetic resonance (ERP) [51], etc., because of the barrier of thick gas-diffusion layers and catalyst layers, it is still too difficult to monitor the chemical reactions occurring at the inner part of PEMFCs, i.e. electrolyte layer. In our investigation, although some reaction product is very stable, such as $\alpha\text{-TO}^+$, others can only exist in a very short lifespan. As a result, there is neither *in-situ* method to identify the products and/or by-products, nor enough time to transfer the samples.

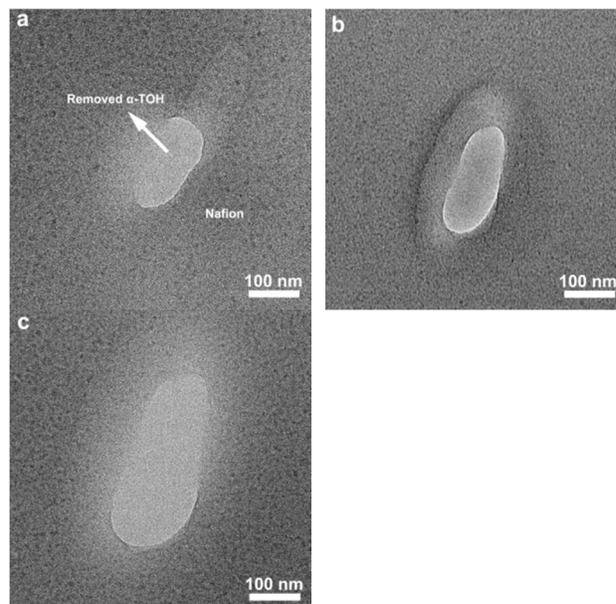


Fig. 5. Influence of variation of α -TOH on the ionic clusters of PEMs.

50 Highly magnified TEM of the Nafion/0.5% α -TOH composite membrane **a)** before OCV holding test; **b)** after OCV oxidation; and **c)** after subsequent H_2 regeneration; with the stain of Na^+ ions for clear observation of ionic clusters were shown. The dark spots in the Nafion region represent hydrophilic domains, i.e., ionic clusters.

55 For the purpose of supporting the suggested mechanism, two approaches were come up with to demonstrate the product and recyclability of α -TOH. As seen in Fig. 4, compared with the composite membrane before oxidation of OCV holding, a new band is detected at 1664.2 cm^{-1} for oxidized Nafion/ α -TOH composite membrane, which is assigned to a C=O stretch occurring at the wavenumber to band observed in the spectra of nonaromatic cyclic ketones [52], indicating the formation of $\alpha\text{-TO}^+$ cations. Furthermore, with the transformation from neutral α -TOH to $\alpha\text{-TO}^+$ cations, there should be a change on the interactions between α -TOH fillers and the Nafion matrix. $\alpha\text{-TO}^+$ was supposed to be attractive to the sulfonic anions, $-\text{SO}_3^-$. Fig. 5 shows that after oxidation of OCV holding test, a dark circle was observed around the α -TOH nano-droplets, illustrating that Na^+ stained ionic clusters in Nafion aggregates around oxidized $\alpha\text{-TO}^+$. However, such phenomenon cannot be observed in both composite membranes before OCV oxidation (Fig. 5a) and after 2 hr holding in H_2/N_2 atmosphere (Fig. 5c), indicating the regeneration of neutral α -TOH with the reduction of H_2 . The TEM images were another supportive evidence for $\alpha\text{-TO}^+$ production and regeneration of α -TOH. Conclusively, it is a rational supposition that α -TOH is oxidized by hydroxyl and peroxy radicals to form $\alpha\text{-TO}^+$. And the oxidized $\alpha\text{-TO}^+$ can then be reduced by permeating H_2 from the anode side, regenerating to reductive α -TOH. This chemical circulation ensures lower H_2 permeation through the electrolyte membrane, the hindrance of generation and transportation of ROS, [7] effective recycling of α -TOH as free radical scavenger, the decreasing rate of chemical degradation of Nafion matrices, and eventually the elongated lifespan of PEMs for fuel cell operation.

85 Finally, it can be observed that with the increasing amount of

added α -TOH, the fuel cell performances after 1 cycle OCV holding and recovery were increasingly improved. As seen in Fig. 3i, for pristine Nafion, potential loss was as high as 6.25%. This value decreased to 3.69% for Nafion/0.5% α -TOH, 0.73% for Nafion/1% α -TOH at 1000 mA \cdot cm $^{-2}$. And potential growth was even found for Nafion/3% α -TOH composite membranes, demonstrating the protecting efficiency of α -TOH on PEMs.

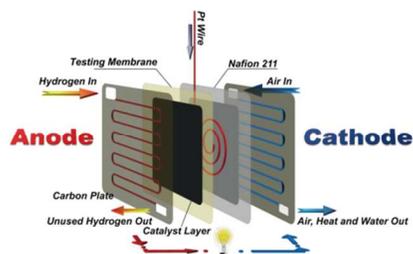


Fig. 6. Scheme of the setup for the detection of testing membranes. A scroll-like curved Pt wire was sandwiched in the recasted Nafion (anode side) and testing membranes (cathode side) as the detecting electrode for in-situ H_2O_2 monitoring during fuel cell operation.

In situ electrochemical detection could be further evidence for chemical protection and H_2 consumption of α -TOH. Herein triple-layer PEMs were used, with the testing membrane at the cathode side (air), pristine Nafion at the anode side (H_2), and a scroll-like Pt wire as the sandwiched detecting electrode. Owing to the ultrafast kinetics for free radical reactions, it was only possible to detect the permeated H_2O_2 , one of the major by-products, instead of hydroxyl and peroxy radicals. The thicknesses of the membranes at both sides were around 12 μm , as illustrated in the schematic diagram of Fig. 6. Recasted Nafion membrane was first assembled for comparison. The cyclic voltammogram (CV) for Nafion testing membrane can be seen in Fig. 7a. CV scans under various cathodic conditions were detected in both H_2/N_2 and H_2/air atmosphere with varying operating voltage. It could be seen a typical H_2 oxidation process at acidic environment in H_2/N_2 atmosphere. [53, 54] In H_2/air atmosphere, peaks at around 0.96 and 0.80 mV should be assigned to the oxidation and reduction of H_2O_2 , respectively. At low cathodic voltage, e.g. 613 mV, the current rise between 1.30 and 1.40 V should be assigned to H_2O . In order to eliminate the influence of H_2 oxidation, corresponding H_2/N_2 CV scan were subtracted from all H_2/air scans, nominated as “ $-\text{H}_2$ CV”, as illustrated in Fig. 7b, in which the H_2O_2 oxidation and reduction peaks could be clearly observed. Different from pristine Nafion, with 1% α -TOH added, the $-\text{H}_2$ CV scan showed no significant peaks except for minor negative current at potential below 0.80

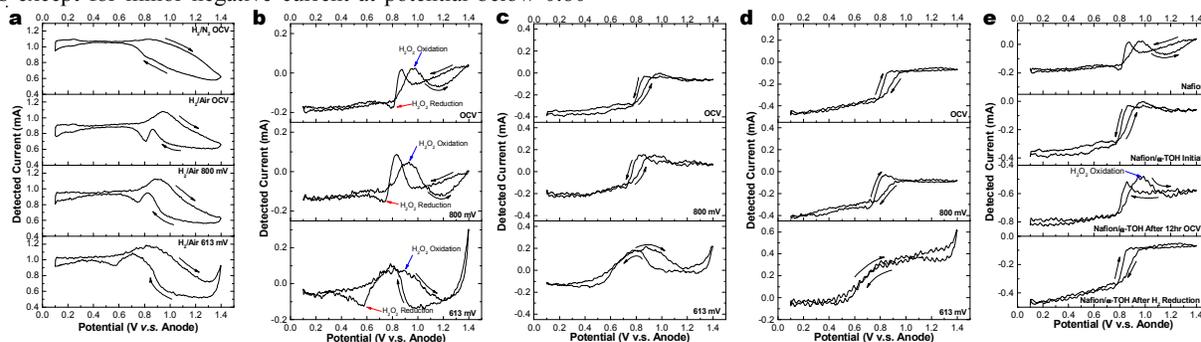


Fig. 7. In situ electrochemical detection of PEM. a) Cyclic voltammograms with sandwiched Pt wire as the working electrode with recasted Nafion as the testing membrane, at various cathodic conditions. “ $-\text{H}_2$ CV” diagrams were also shown with b) recasted Nafion, and c) Nafion/1% α -TOH composite membrane before 12-hour OCV holding test, and d) Nafion/1% α -TOH composite membrane after H_2 reduction. e) “ $-\text{H}_2$ CV” of Nafion/1% α -TOH composite membrane under cathodic OCV condition at different periods were compared. “ $-\text{H}_2$ CV” of recasted Nafion were also shown for comparison. An obvious peak at ~ 0.96 V was observed after 12hr OCV test, indicating the oxidation of α -TOH. However, the peak disappeared either before OCV test,

V, which resembled to that of oxygen reduction in acidic solution (Fig. S4c), thus could result from reduction of permeated oxygen from the cathode side or other impurities in the membrane, indicating that H_2O_2 generation and permeation were highly restricted (see Fig. 7c). After 12-hour OCV holding test, the peak of H_2O_2 oxidation emerged again at the potential of 0.96 V (Fig. 7e). The emergence of H_2O_2 suggested the exhaust of α -TOH because of oxidation, causing H_2O_2 reformation and permeation. However, this changing trend was reversible. The peaks of H_2O_2 oxidation vanished again after the Nafion/ α -TOH composited membranes being kept in H_2/N_2 atmosphere for 2 hours (see Fig. 7d, e), indicating the reformation of reductive α -TOH in the membrane. From the *in situ* electrochemical detection, it can be concluded that α -TOH was able to diminish ROS and to protect PEMs. Further, α -TOH could also be reduced under reductive environment, reforming from the oxidized species to the reductive conformation. As the evidence of the feasibility of *in situ* electrochemical detection, parallel *ex situ* electrochemical detection were also made, and the similar conclusions could be made, which can be seen in the supplementary information.

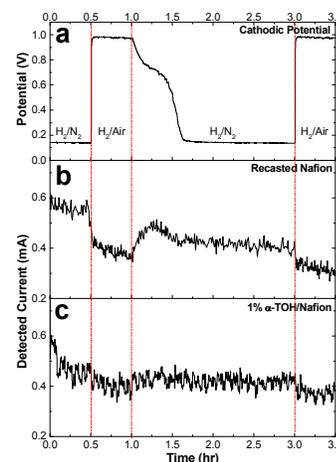


Fig. 8. Variation of current on the detecting electrode with the potential at 1.3 V with the switch of cathode gas conditions for PEMFCs. a) Variation of cathodic potential with the switch of cathode gas between N_2 and O_2 . Potentiostatic test for PEMFC with b) recasted Nafion and c) Nafion/1% α -TOH composite membrane.

or after H₂ reduction, suggesting the existence of reductive α -TOH.

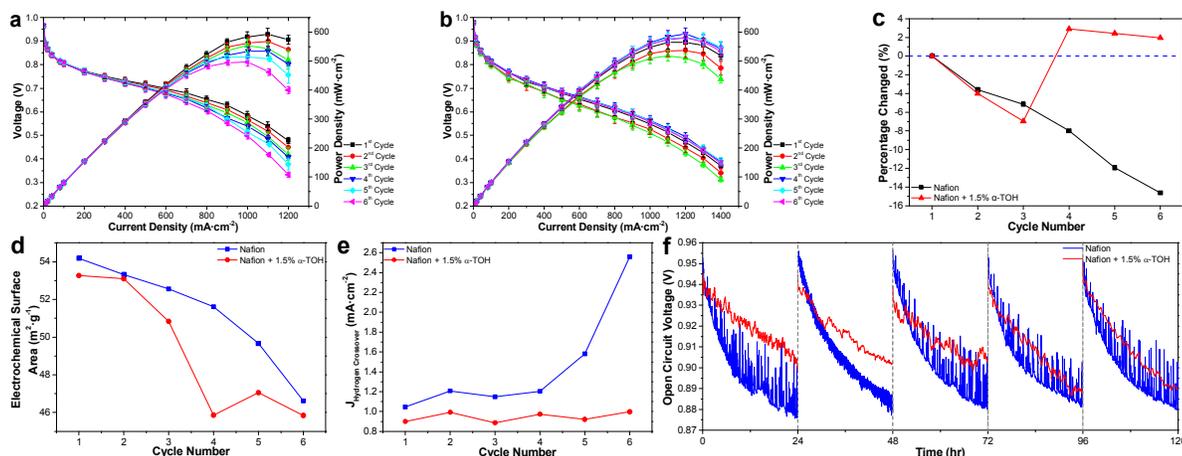


Fig. 9. 5-cycle OCV holding test for MEAs with pristine Nafion and composite Nafion/ α -TOH Membranes. Polarization curves and power output of PEM single cells with a) recasted Nafion, and b) Nafion/1.5% α -TOH. c) The variation of potential at current density of 1000 mA·cm⁻² after each OCV holding tests was normalized with Cycle 1 as the original denominator for each MEA. Comparison of d) electrochemical surface area, e) Hydrogen crossover current density (voltage = 0.3 V), and f) OCV drop for both membranes are shown.

H₂O₂ generation and permeation process with the switch of cathode gas conditions was also real-time monitored. The OCV at the cathode was recorded at Fig. 8a to monitor the gas change during fuel cell operation. It was observed both a sudden growth of OCV with the change of cathode gas from N₂ to air, and a gradual decline with a reverse gas change because of the remanent oxygen until the cathode was thoroughly purged with nitrogen. Considering that the major signal for the detecting electrode is H₂ oxidation, there should be a magnitude change when H₂O₂ participated in the electrochemical system. As a result the potentiostatic test was carried out at the sandwiched detecting electrode with the potential at 1.3 V, the potential level typically used for the detection of H₂O₂. [53, 54] As seen in Fig. 8, a notable decrease of detected current could be observed with Nafion testing membrane. This suppression probably originated from the generation of H₂O₂ at the cathode side in H₂/air atmosphere. The as-generated H₂O₂ permeated through the testing membrane to reach the detecting electrode. Oxidation of H₂O₂ on the detecting electrode became predominant that led to more Pt-O bonds formation, resulting in the decline of H₂ oxidation current, and thus, a current depression compared with that in H₂/N₂ atmosphere. In contrast, minor current change was observed with the Nafion/ α -TOH composite membrane, indicating the remarkable decrease of generated/permeated H₂O₂ that could be detected by the sandwiched electrode.

Finally, two types of MEA with different PEMs were assembled in single cells and operated with multiple OCV holding tests. The thickness of each membrane was around 35 μ m. As seen in Fig. 9a – c, while the voltage of recasted Nafion obviously decreased by 14.6%, better performance of Nafion/1.5% α -TOH composite membrane could be observed. The voltage at the current density of 1000 mA·cm⁻² increased by 2.0% after 5-cycle OCV holding tests compared with the initial voltage. (More cyclic performance can be found in Fig. S5) Meanwhile, the comparison of

electrochemical surface area of catalysts, hydrogen crossover current density, and OCV drop for these two membranes demonstrated the protection of α -TOH to the PEMs (Fig. 9d – f). The performance of the Nafion/ α -TOH composite membranes shows very high possibility of long-term fuel cell operation and power preservation. As a result, α -TOH can be treated as a great candidate as PEM additive for future industrialization and commercialization. It was notice the influence of the potential drop at activation-loss region of the polarization curve on the durability of MEAs, [55] and detailed discussion was shown in the *supplementary information*.

We recognize that in practical uses, fuel cells may suffer from series of circumstances that accelerate the chemical degradation of PEMs. However, the purpose of this paper is not to present a final, commercial, and practical solution, but rather to confirm the attempt of building up an inner chemical circulation system, and thereby keep the PEMs from being over-oxidized in a long-range operation, just as human bodies with a series of antioxidants. Resultantly the process of the ROS scavenging and the reason for the possibility of long-range PEMFC operation can be summarized as follows. Chemical degradation of PEMs was caused by the generation of ROS, which in the absence of α -TOH leads to severe performance loss in fuel cell operation. The α -TOH molecules, however, being uniformly dispersed in the electrolyte, were sacrificed to protect Nafion matrices from being attacked with ROS; then were reduced by permeated H₂ molecules and reversed to its reductive form. The overall effect can be shown as protected PEMs, recyclable α -TOH, and hindered H₂ crossover rate.

75 Conclusion

By incorporating a recyclable antioxidant molecule, here illustrated with α -TOH in the polymer electrolyte of PEMFCs, we demonstrated that it was possible for α -TOH to protect the

membranes from being attacked by ROS that can lead to a catastrophic performance loss. With a small percentage of α -TOH added (1%), almost 90% performance loss could be resisted that was impossible without the antioxidant in the same cell. The α -TOH was sacrificed first, forming its oxidized species, such as α -TO⁺, at high potential and then, oxidized the permeated H₂. In this process, these oxidized species were reduced back to α -TOH. By using an antioxidant, a far more effective protection of Nafion matrices is possible than can be achieved in its absence. The reversible formation of α -TOH was an essential process in the electrolyte membrane in such electrochemical cells, although questioning voices may come from the gradual α -TOH runoff, which is improbable in normal conditions, but may be caused by high squeezing pressures applied on the electrolyte membranes during fuel cell operation. Nonetheless it is probable that terminal groups of Nafion, such as the carboxyl groups, could be chemically bonded with α -TOH-like molecules to avoid the physical losses of antioxidants. Such chemical bonding would also eliminate the ROS attack on the terminal groups. The ability of a reversible antioxidant to prevent PEMs effectively from being oxidized by ROS, and to promote the chemical stability, and hence the long-range operation addresses one of the important challenges that face PEMFCs, and may also be available for other electrochemical systems, such as metal-air batteries.

Acknowledgement

This work was financially supported by 863 Program (2011AA11A271), National Basic Research Program of China (973 Program, 2013CB632404), Natural Science Foundation of China (21176111) and Natural Science Foundation of Jiangsu Province (BK2012217). Jianguo Liu also thanks to the support of Qing Lan Project of Jiangsu Province, China.

Notes and references

^a *Eco-materials and Renewable Energy Research Center, Department of Materials Science and Engineering, National Laboratory of Solid State Microstructures, Nanjing University, 22 Hankou Road, Nanjing 210093, China.*

^b *Kunshan Innovation Institute of Nanjing University, Nanjing 210093, China*

^c *Department of Physics, Nanjing University, 22 Hankou Road, Nanjing 210093, China*

*Corresponding author. Tel.: +86 25 83621219; fax: +86 25 83686632. Email: jianguoliu@nju.edu.cn

*Corresponding author. Tel.: +86 25 83686630; fax: +86 25 83686632.

⁴⁵ Email: zgzou@nju.edu.cn

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here. See DOI: 10.1039/b000000x/]

references

- [1] A. Stwertka, Guide to the Elements (Revised ed.). Oxford University Press. **1998**, pp. 48 – 49.
- [2] E. Niki, Free Radicals in the 1900's: from in Vitro to in Vivo. *Free Radical Res.* **2000**, *33*, 693 – 704.
- [3] E. Niki, N. Noguchi, Dynamics of Antioxidant Action of Vitamin E, *Acc. Chem. Res.* **2004**, *37*, 45 – 51.
- [4] B. N. Ames, M. K. Shigenaga, T. M. Hagen, Oxidants, antioxidants, and the degenerative diseases of aging, *PNAS*, **1993**, *90*, 7915 – 7922.

- [5] J. Larminie, J. Lowry, Electric Vehicle Technology Explained, Chichester, West Sussex, England : J. Wiley. 2003, pp. 81 – 85.
- [6] R. S. Sohal, R. Weindruch, Oxidative Stress, Caloric Restriction, and Aging, *Science*, **1996**, *273*, 59 – 63.
- [7] R. Borup, J. Meyers, B. Pivovar, Y. S. Kim, R. Mukundan, N. Garland, D. Myers, M. Wilson, F. Garzon, D. Wood, P. Zelenay, K. More, K. Stroh, T. Zawodzinski, J. Boncella, J. E. McGrath, M. Inaba, K. Miyatake, M. Hori, K. Ota, Z. Ogumi, S. Miyata, A. Nishikata, Z. Siroma, Y. Uchimoto, K. Yasuda, K. Kimijima, N. Iwashita, Scientific Aspects of Polymer Electrolyte Fuel Cell Durability and Degradation, *Chem. Rev.* **2007**, *107*, 3904 – 3951.
- [8] A. B. LaConti, M. Hamdan, R. C. McDonald In: W. Vielstich, A. Lamm, H. Gasteiger, editors. Handbook of fuel cells: fundamentals, technology, and applications, vol. 3. Chichester, England: Wiley; **2003**, pp. 647 – 662.
- [9] W. Schmittinger, A. Vahidi, A Review of the Main Parameters Influencing Long-term Performance and Durability of PEM Fuel Cells, *J. Power Sources*, **2008**, *180*, 1 – 14.
- [10] A. Colliera, H. Wang, X. Yuan, J. Zhang, D. P. Wilkinson, Degradation of Polymer Electrolyte Membranes, *Inter. J. Hydrogen Energy*, **2006**, *31*, 1838 – 1854.
- [11] T. Ous, C. Arcoumanis, Degradation aspects of water formation and transport in Proton Exchange Membrane Fuel Cell: A review, *J. Power Sources*, **2013**, *240*, 558 – 582.
- [12] A. Collier, H. Wang, X. Ziyuan, J. Zhang, D. P. Wilkinson, Degradation of polymer electrolyte membranes, *Inter. J. Hydrogen Energy*, **2006**, *31*, 1838 – 1854.
- [13] H. Tang, S. kang, S. Jiang, F. Wang, M. Pan, A degradation study of Nafion proton exchange membrane of PEM fuel cells, *J. Power Sources*, **2007**, *170*, 85 – 92.
- [14] N. Ramaswamy, N. Hakim, S. Mukerjee, Degradation mechanism study of perfluorinated proton exchange membrane under fuel cell operating conditions, *Electrochim. Acta*, **2008**, *53*, 3279 – 3295.
- [15] F. M. Collette, C. Lorentz, G. Gebel, F. Thominette, *J. Membr. Sci.* **2009**, *330*, 21 – 29.
- [16] T. Xie, C. A. Hayden, A kinetic model for the chemical degradation of perfluorinated sulfonic acid ionomers: Weak end groups versus side chain cleavage, *Polymer*, **2007**, *48*, 5497 – 5506.
- [17] Adriano C. Fernandes, Edson Antonio Ticianelli, A performance and degradation study of Nafion 212 membrane for proton exchange membrane fuel cells, *J. Power Sources*, **2009**, *193*, 547 – 554.
- [18] L. Ghassemzadeh, K.-D. Kreuer, J. Maier, K. Müller, Chemical Degradation of Nafion Membranes under Mimic Fuel Cell Conditions as Investigated by Solid-State NMR Spectroscopy, *J. Phys. Chem. C* **2010**, *114*, 14635 – 14645.
- [19] A. P. Young, J. Stumper, S. Knights, E. Gyenge, Ionomer Degradation in Polymer Electrolyte Membrane Fuel Cells, *J. Electrochem. Soc.* **2010**, *157*, B425 – B436.
- [20] D. Zhao, B.L. Yia, H. M. Zhanga, M. Liu, The effect of platinum in a Nafion membrane on the durability of the membrane under fuel cell conditions, *J. Power Sources*, **2010**, *195*, 4606 – 4612.
- [21] W. Yoon, X. Huang, Study of Polymer Electrolyte Membrane Degradation under OCV Hold Using Bilayer MEAs, *J. Electrochem. Soc.* **2010**, *4*, B599 – B606.
- [22] X. Fang, P. K. Shen, S. Song, V. Stergiopoulos, P. Tsiakaras, Degradation of perfluorinated sulfonic acid films: An in-situ infrared spectro-electrochemical study, *Polym. Degrad. Stabil.* **2009**, *94*, 1707 – 1713.
- [23] C. Bas, L. Flandin, A.-S. Danerol, E. Claude, E. Rossinot, N. D. Alberola, Changes in the Chemical Structure and Properties of a Perfluorosulfonated Acid Membrane Induced by Fuel-Cell Operation, *J. Appl. Polym. Sci.* **2010**, *117*, 2121 – 2132.
- [24] J. Xie, D. L. Wood III, D. M. Wayne, T. A. Zawodzinski, P. Atanassov, R. L. Borupa, Durability of PEFCs at High Humidity Conditions, *J. Electrochem. Soc.* **2005**, *152*, A104 – A113.
- [25] G. W. Burton, K. U. Ingong, Vitamin E: Application of the Principles of Physical Organic Chemistry to the Exploration of Its Structure and Function, *Acc. Chem. Res.* **1986**, *19*, 194 – 201.
- [26] H. Sies, Oxidative Stress: Oxidants and Antioxidants, *Exp. Physiol.* **1997**, *82*, 291 – 295.

- [27] D. P. Jones, Redefining Oxidative Stress, *Antioxidants Redox Signaling*, **2006**, *8*, 1865 – 1879.
- [28] K. B. Beckmen, B. N. Ames, The Free Radical Theory of Aging Matures, *Physiol. Rev.* **1998**, *78*, 547 – 581.
- [29] <http://www.beyondveg.com/tu-j-l/raw-cooked-2e.shtml>.
- [30] S. Arora, R. Bagoria, M. Kumar, Effect of alpha-tocopherol (vitamin E) on the thermal degradation behavior of edible oils, *J. Therm. Anal. Calorim.* **2010**, *102*, 375 – 381.
- [31] L. L. Williams, R. D. Webster, Electrochemically Controlled Chemically Reversible Transformation of α -Tocopherol (Vitamin E) into Its Phenoxonium Cation, *J. Am. Chem. Soc.* **2004**, *126*, 12441 – 12450.
- [32] S. B. Lee, C. Y. Lin, P. M. W. Gill, R. D. Webster, Transformation of α -Tocopherol (Vitamin E) and Related Chromanol Model Compounds into Their Phenoxonium Ions by Chemical Oxidation with the Nitrosonium Cation, *J. Org. Chem.* **2005**, *70*, 10466 – 10473.
- [33] R. D. Webster, Voltammetric studies on the α -tocopherol anion and α -tocopheroxyl (Vitamin E) radical in acetonitrile, *Electrochim. Commun.* **1999**, *1*, 581 – 584.
- [34] G. J. Wilson, C. Y. Lin, R. D. Webster, Significant Differences in the Electrochemical Behavior of the α -, β -, γ -, and δ -Tocopherols (Vitamin E), *J. Phys. Chem. B*, **2006**, *110*, 11540 – 11548.
- [35] K. Mukai, M. Nishimura, S. Kikuchi, Stopped-flow Investigation of the Reaction of Vitamin C with Tocopheroxyl Radical in Aqueous Triton X-100 Micellar Solutions. *J. Biol. Chem.* **1991**, *266*, 274 – 278.
- [36] X. Wang, P. J. Quinn, Vitamin E and its function in membranes, *Prog. Lipid Res.* **1999**, *38*, 309 – 336.
- [37] V. Prabhakaran, C. G. Arges, V. Ramani, Investigation of polymer electrolyte membrane chemical degradation and degradation mitigation using in situ fluorescence spectroscopy, *PNAS*, **2012**, *109*, 1029 – 1034.
- [38] G. Bender, M. Angelo, K. Bethune, R. Rocheleau, Quantitative analysis of the performance impact of low-level carbon monoxide exposure in proton exchange membrane fuel cells, *J. Power Sources*, **2013**, *228*, 159 – 169.
- [39] Y. Nagahara, S. Sugawara, K. Shinohara, The impact of air contaminants on PEMFC performance and durability, *J. Power Sources*, **2008**, *182*, 422 – 428.
- [40] W. Shi, B. Yia, M. Hou, Z. Shao, The effect of H₂S and CO mixtures on PEMFC performance, *Inter. J. Hydrogen Energy*, **2007**, *32*, 4412 – 4417.
- [41] S. Ge, C.-Y. Wang, Cyclic voltammetry study of ice formation in the PEFC catalyst layer during cold start, *J. Electrochem. Soc.* **2007**, *154*, B1399 – B1406.
- [42] E. Endoh, Development of Highly Durable PFSA Membrane and MEA for PEMFC Under High Temperature and Low Humidity Conditions, *ECS Trans.* **2008**, *16*, 1229 – 1240.
- [43] F. D. Coms, H. Liu, J. E. Owejan, Mitigation of Perfluorosulfonic Acid Membrane Chemical Degradation Using Cerium and Manganese Ions, *ECS Trans.* **2008**, *16*, 1735 – 1747.
- [44] J. Zhang, B. A. Litterer, F. D. Coms, R. Makharia, Recoverable Performance Loss Due to Membrane Chemical Degradation in PEM Fuel Cells, *J. Electrochem. Soc.* **2012**, *159*, F287 – F293.
- [45] Y. Buchmüller, A. Wokaun, L. Gubler, Polymer-bound antioxidants in grafted membranes for fuel cells, *J. Mater. Chem. A*, **2014**, *2*, 5870 – 5882.
- [46] A. Salimi, K. Abdi, G. Khayatian, Amperometric Detection of Dopamine in the Presence of Ascorbic Acid Using a Nafion Coated Glassy Carbon Electrode Modified with Catechin Hydrate as a Natural Antioxidant. *Microchim. Acta*, **2004**, *144*, 161 – 169.
- [47] L. Wang, K. Li, G. Zhu, J. Li, Preparation and properties of highly branched sulfonated poly(ether ether ketone)s doped with antioxidant 1010 as proton exchange membranes, *J. Membr. Sci.* **2011**, *379*, 440 – 448.
- [48] Afaf Kamal-Eldin, L.-A. Appelqvist, The Chemistry and Antioxidant Properties of Tocopherols and Tocotrienols, *Lipids*, **1996**, *37*, 671 – 701.
- [49] H. S. Casalongue, S. Kaya, V. n Viswanathan, D. J. Miller, D. Friebe, H. A. Hansen, J. K. Nørskov, A. Nilsson, H. Ogasawara, Direct observation of the oxygenated species during oxygen reduction on a platinum fuel cell cathode, *Nat. Commun.* **2013**, *4*, 2817.
- [50] H. Hanawa, K. Kunimatsu, M. Watanabe, H. Uchida, In Situ ATR-FTIR Analysis of the Structure of Nafion–Pt/C and Nafion–Pt₃Co/C Interfaces in Fuel Cell, *J. Phys. Chem. C*, **2012**, *116*, 21401–21406.
- [51] A. Panchenko, H. Dilger, E. Moller, T. Sixt, E. Roduner, In situ EPR investigation of polymer electrolyte membrane degradation in fuel cell applications. *J. Power Sources*, **2004**, *127*, 325–330.
- [52] S. Chen, H. M. Peng, R. D. Webster, Infrared and UV–vis spectra of phenoxonium cations produced during the oxidation of phenols with structures similar to vitamin E, *Electrochim. Acta*, **2010**, *55*, 8863 – 8869.
- [53] W. Liu, D. Zuckerbrod, In Situ Detection of Hydrogen Peroxide in PEM Fuel Cells, *J. Electrochem. Soc.* **2005**, *152*, A1165 – A1170.
- [54] A. V. Tripkovic, K. D. Popovic, B. N. Grgur, B. Blizanac, P. N. Ross, and N. M. Markovic, *Electrochim. Acta*, **2002**, *47*, 3707 – 3714.
- [55] Y. S. Kim, M. Einsla, J. E. McGrath, B. S. Pivovar, The membrane-electrode interface in PEFCs: II. Impact on fuel cell durability. *J. Electrochem. Soc.* **2010**, *157*, B1602 – B1607.

Table of Content

Vitamin E is an efficient antioxidant to elongate the lifetime of fuel cells and circulate itself for long-term use.

