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The Role of Solvated Electrons in Direct Methanol Fuel Cells

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Dedicated to the memory of Prof. Per Jacobsson and Prof. C. Austen Angell.

Direct methanol fuel cells, DMFCs, have for long been considered as a superior alternative to rechargeable batteries for various portable applications with respect to significantly higher theoretical power densities and faster recharging by simply filling up with new liquid fuel. In reality, however, DMFCs so far have much low power densities, suffer from high fuel losses, and require extremely expensive catalysts at high loadings. Here we show that an until now not considered

process at the DMFC electrodes may cause these severe losses in performance. The process is that electrons generated at nano-structured catalyst loaded electrodes become solvated into the surrounding electrolyte. Taking this new process and resulting reaction mechanism(s) fully into account, material and catalyst/electrode design should be reconsidered to realize the true potential of DMFCs.

1. Introduction

Ever since the possibility of injection of electrons from an electrode into a surrounding liquid was first verified, the role of free electrons in solution reactions has been an area of paramount scientific interest, for instance as one of the very foundations of radiation chemistry.^[1,2] A free electron is by definition the simplest and most powerful reducing agent^[3] and vividly reacts with molecules in the receiving environment, and hence the risks of ionizing radiation. Alternatively, the injected electron can be surrounded by solvent and become solvated (e^-_{solv}). This process was documented for the first time by Davy as early as in 1808,^[4] while properly identified by pulse radiolysis experiments as late as in 1962.^[5] In more detail, the injected electron instantaneously creates an imbalance in the solvent and its first solvation shell is formed within less than 600 fs.^[6]

Upon solvation part of the reactivity is lost, but the reductive power remains exceptional.^[3]

Fuel cells (FCs) are exceptional clean energy converters as they have, theoretically, high power densities and conversion efficiencies over 80%.^[7] The direct methanol fuel cell (DMFC) is in turn one of the most promising FC technologies, especially for portable/mobile applications as a liquid fuel is optimal for storage, transportation, and refuelling. In practice, however, both power densities, conversion efficiencies, and lifetimes are yet very modest,^[8,9] why the interest in DMFCs have decreased substantially. In a DMFC, an aqueous solution of methanol, CH_3OH , is catalytically converted to carbon dioxide (CO_2), protons (H^+), and electrons (e^-) at the anode. The electrons perform work in an outer circuit while the protons are transported across a polymeric membrane to be recombined with oxygen gas fed at the cathode to create water as a secondary reaction product.

The electrodes used in DMFCs, both anodes and cathodes, typically consist of expensive Pt and Pt–Ru catalyst particles embedded in a perfluorinated polyelectrolyte matrix, such as Nafion® (same as the membrane), which is swollen by the fuel and the reaction products. In order to reduce the cost and maximise the power output per footprint area, the catalyst particle sizes have been optimised and engineered at the nano-scale. The catalyst particles are usually ~4 nm in diameter and the loading is preferably $< 5 \text{ mg/cm}^2$.^[10]

We here argue that this optimisation has been done without a prior understanding of all consequences. Poorly conductive zones are highly disruptive to electron transport and when electrodes are composed of millions of nano-particles physically bound together only by an electrically non-conductive polyelectrolyte, complete discontinuities are likely to occur. Indeed, using a combined analysis employing X-ray tomography and transmission electron microscopy of the electrochemically active surface areas, up to 87%(!) of the catalyst particles were found to be *inactive* under normal FC operation, due to being part of poorly connected networks.^[11] When the electrons

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Supporting information for this article is available on the WWW under <https://doi.org/10.1002/celec.202300357>

Part of a Special Collection celebrating the 140th anniversary of the Swedish chemical society.

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cannot be conducted along connected electrode catalyst particles, they either have to pass through more resistive barriers by tunnelling or are forcibly injected into the surrounding polyelectrolyte matrix (Figure 1). The probability for the latter depends on many parameters, e.g. electrode work function, voltage, electrolyte composition, etc. At first order approximation, it should simply be forbidden in a low-voltage device such as a DMFC, but if a significant number of the generated electrons are injected, the consequences would be truly extraordinary. This process would be followed either by the creation of solvated electrons, as outlined above, or by direct reactions of the electrons with the methanol and water molecules in the electrolyte. Neither of these scenarios has ever been presented as a possibility for DMFCs before, but here we outline why we believe both to occur, the substantial impact they have on the overall DMFC performance, and some first relevant experimental indications supporting these hypotheses.

Herein, we start by describing the prerequisites for an unambiguous *in situ* identification of solvated electrons in a DMFC and thereafter outline the special, nano-physics based, conditions that allow for electron injection and solvation. Subsequently, we discuss the direct consequences and connect our observations with the until now prevailing picture of the DMFC performance limitations. Finally, a reformulation of the DMFC reactions is suggested.

Furthermore, while solvated electrons are suggested to truly limit DMFCs, other very important high-tech devices such as organic and polymer light-emitting devices (OLEDs and PLEDs) have operation principles very much *relying* on electron injection from nano-structured electrodes to a polyelectrolyte. Solvated electrons have also been suggested to take an active part in the creation of the solid electrolyte interphase (SEI) layer^[12] formed at the graphite anode surface of today's lithium-ion batteries (LIBs), a layer crucial for them to at all function, but they may on the other hand also contribute to continuous solvent degradation and thereby shortened device lifetime. An

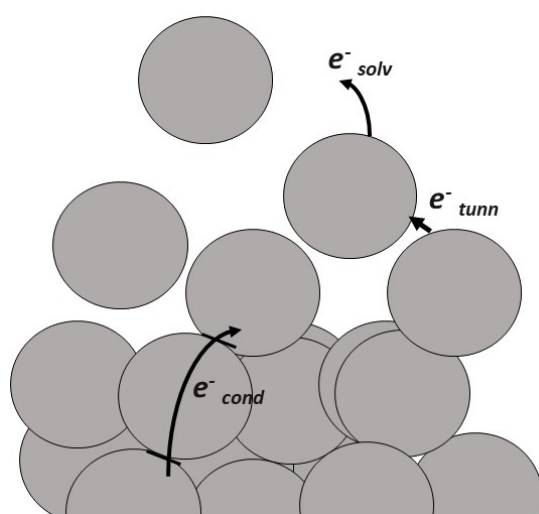


Figure 1. Schematic of the creation of solvated electrons. The electrons are conventionally conducted (e^-_{cond}) along the nano-sized catalyst particles and only if necessary by tunnelling (e^-_{tunn}) at very limited distances.

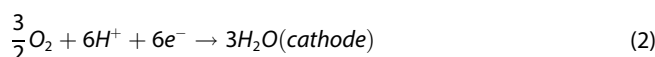
increased understanding of the possibilities and conditions necessary for electron injection and solvation is thus also useful for optimising the performance of several other electrochemistry-based technologies.

2. Results

Solvated electrons (e^-_{solv}) are usually readily identified by Vis-NIR spectroscopy; they absorb strongly at ~ 720 nm and ~ 630 nm in water^[13] and methanol,^[14] respectively, with a molar extinction coefficient of $16000 \pm 1600 \text{ M}^{-1} \text{ cm}^{-1}$ at 750 nm.^[13] Common spectral features are broad absorption peaks and a red-shift of the peak maxima positions with increasing temperature.^[15] In a DMFC, due to the high concentration of protons and thus hydronium ions, pair radicals $\text{H}_3\text{O}^+ \cdots e^-$ can be envisaged, which would absorb at ~ 920 nm.^[6] From the above at least three possibilities to directly detect solvated electrons by an *in situ* DMFC Vis-NIR spectroscopy set-up exists and to this also a few indirect features/reactions can be added.

The recording, analysis, and interpretation of the *in situ* DMFC Vis-NIR spectra are, however, all very complex, especially as the signals arising from the DMFC itself and the fuel must be excluded. Therefore both half and full electrochemical cells must be employed. Furthermore, while standard Vis-NIR samples typically are on the millimetre scale or thicker, the DMFC electrode catalyst layers are on the order of micrometres. However, due to their extreme light absorption, they must be even further reduced in thickness. Combined with the very short lifetime (ns-ps) of both the solvated electrons and the reaction intermediates,^[5,6] an extensive electron injection is required for any successful *in situ* detection of solvated electrons to at all be possible.

The standard basic half-cell reactions of a DMFC are:



Thus, the DMFC ideally only generates protons and electrons at the anode side (Eq. 1). However, as fuel crossover usually is extensive in a DMFC, the situation is again more complex with unreacted methanol most often found also on the cathode side. This is why there are overlapping signals in all our Vis-NIR spectra,^[8] and why several special set-ups must be used. First, a complete full "DMFC" supplied with only pure water as fuel is used, resulting in a reference spectrum (Figure 2, blue) with the only significant features being a strong peak at ~ 698 nm and a strong anti-peak at ~ 684 nm, the latter likely resulting from chemiluminescence, which might be caused by the presence of Pt and Pt–Ru nanoparticles in the cell during the measurement.^[16] The large broad peak with a maximum at 975 nm is attributed to the luminescence of the Pt and Pt–Ru nanoparticles (ca. 4 nm diameter). Using this spectrum, we construct subtraction spectra to analyse the measurements on different DMFCs fuelled with 5 M methanol. For a DMFC with a

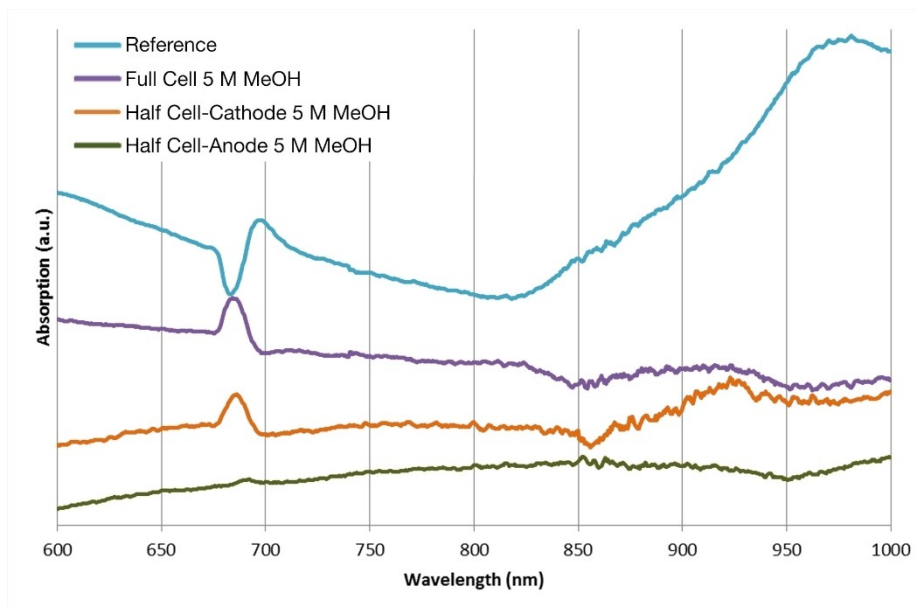


Figure 2. In situ Vis-NIR spectra of DMFC half and full cells. The reference spectrum is for a cell fuelled with pure water and the subtraction spectra are for cells fuelled with 5 M methanol solutions.

catalyst layer only on the anode side, the subtraction spectrum lacks significant features (Figure 2, green). In stark contrast, when there is a catalyst layer only on the cathode side the subtraction spectrum (Figure 2, orange) has a peak at ~680–700 nm and a new broad peak at ~925 nm. The weak anti-peak at 860 nm is an artifact due to the intrinsically imperfect subtraction of the spectrum from the reference spectrum. The latter is approximately where the pair radicals $\text{H}_3\text{O}^+\cdots\text{e}^-$ are expected to absorb.^[6] Indeed, also the spectrum of the full cell (Figure 2, purple) features both peaks, with the latter peak now being even broader. Taken together this indicates that solvated

electrons are formed primarily on the *cathode side*, which is logical given that this is where the injection of electrons would occur (Eq. 2).

With the working hypothesis being that the methanol itself is crucial for the creation of solvated electrons, the effect of different methanol concentrations was investigated (Figure 3). Indeed, the broad peak at ~920 nm is significantly enhanced as a function of the methanol concentration. A “fresh” 10 M methanol fuel, with only partial mixing of water and methanol, likely, but somewhat speculatively, due to slow disruption of local structures such as MeOH dimers, resulted in a slight

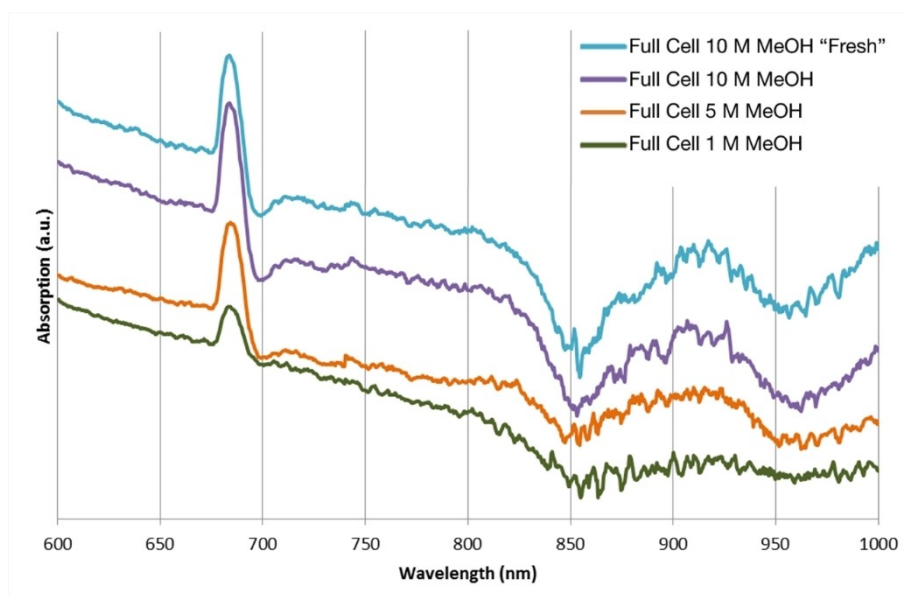


Figure 3. In situ Vis-NIR spectra of a DMFC fuelled with differently concentrated methanol solutions.

further enhancement in the peak sharpness and intensity. Moving to the spectral regions typically used for identification and quantification of solvated electrons, *i.e.* 600–670 nm (Figure 4A) and 700–750 nm (Figure 4B), marked in yellow, all features are much less pronounced. Still, it is clear that the weak peak at ~635–638 nm increases with the methanol concentration to finally be clearly visible for the 10 M fuel, and indicates electrons solvated by methanol,^[14] while the broad peak at ~710–720 nm, visible only for the higher methanol concentrations, indicates electrons solvated by water.^[13]

3. Discussion

Our observations allow for an, albeit very phenomenological, yet self-consistent picture, of the prerequisites needed to create solvated electrons in DMFCs and furthermore also to explain the particular nano-physics present – clearly needed. While this is far from straightforward and arguably remains somewhat speculative, we here outline three major lines of reasoning and chains of arguments: one rather general, one specific to FCs, and one (almost) exclusive to DMFCs.

The first line of reasoning is based on that for electron injection from an electrode to a surrounding electrolyte to occur the work function of the former is important. There is, for example, abundant data on the nano-physics of electron injection needed to produce the emitted light from PLEDs and OLEDs, and both devices are fundamentally based on and limited by the work function of the electrodes employed.^[17–19]

Nano-structuration of these electrodes, primarily by tailoring the curvature of the nano-particles constituting them, is used to lower the work function and thereby the potential of emission and thus the onset voltage.^[20] While there indeed is a large difference between PLEDs, at ~2.5 V^[17] and the DMFC voltage of ~0.7 V, electron injection from nano-structured electrodes has been verified (electrochemically) at voltages as low as 1.2 V.^[20] In addition, as nano-particle based electrodes are rather imperfect conductors,^[9] sites with high electric resistance are prone to exist, where local heating may occur and thus contribute to thermally assisted electron injection.^[21]

The second line of reasoning is based on more FC specific nano-physics and here we argue that the FC half-cell reactions may take place even under open-circuit voltage (OCV) conditions, *i.e.* with no electrons being conducted in the outer circuit. The reason for this is that the catalyst nano-particles, especially at the cathode side, can create local “nano-FCs”.^[22] The accumulated electrons “sense” the chemical potential, with the OCV as a proxy, and will eventually be released and move towards the lower potential, preferably along the catalyst nano-particles, but again risk passages through more resistive barriers that may lead to electron injection and solvation. While this is very much based on the assumption of the OCV to be an appropriate proxy of the electrochemical potential, it is supported experimentally by the continuous formation of hydrogen gas under OCV conditions in FCs.^[22]

The third and final line of reasoning, and the most pertinent, is based on that also in real full DMFCs hydrogen gas evolution is observed under OCV conditions. Additionally, any

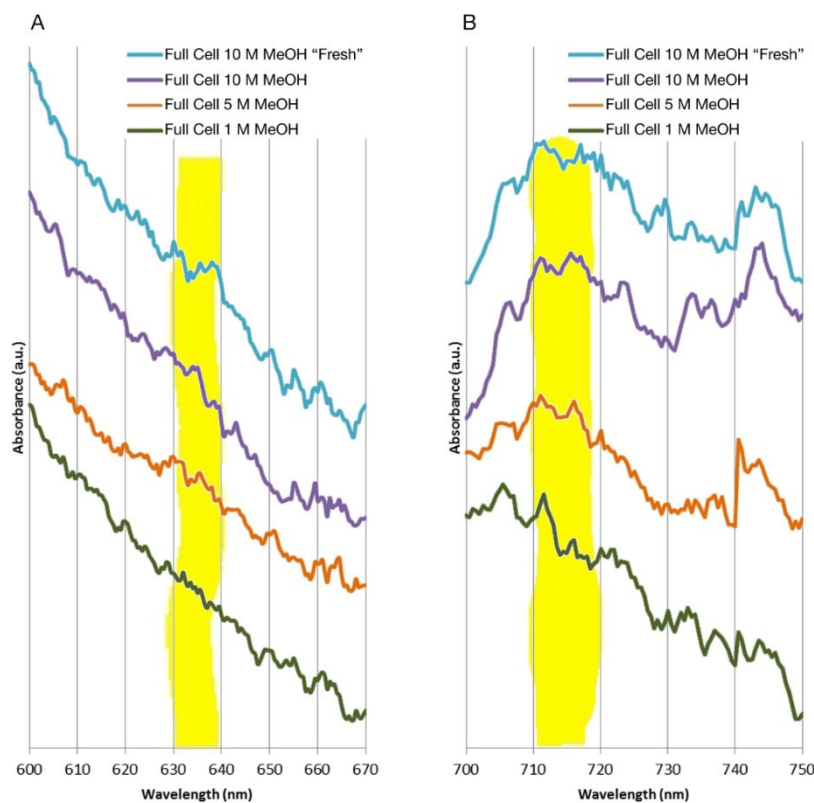
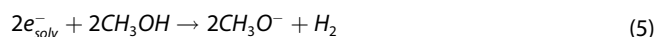


Figure 4. Detailed in situ Vis-NIR spectra: A) 600–670 nm and B) 700–750 nm.

load added and causing local heating is expected to further enhance the probability of electron injection. The most important difference to the above observations and arguments for FCs in general is of course the presence of methanol. Strikingly, one strategy found in the literature to improve the performance of PLEDs and OLEDs, and especially to lower the onset voltage, is the pre-treatment of the electrodes with methanol.^[17,18] A plausible reason is that the methanol partially solvates the catalyst nano-particles and thereby creates tiny local highly resistive regions. In addition, even the presence of sulfonic acid groups in Nafion® membranes has been argued to lower the work function of PLEDs.^[23]

4. Concluding Remarks

Overall, moving to nano-scale in FC design causes an unexpected extensive injection of electrons from the electrodes into the electrolyte, creating solvated electrons. While the Vis-NIR DMFC signals are always very weak from our *in situ* set-up, and the spectra rather noisy, the electron solvation must indeed be extensive to allow for the anyway clear identification with our very low collection depth. Due to the high reactivity of solvated electrons a major revision of the DMFC reaction scheme is therefore required, which can explain both the limited efficiency and the limited power output as well as the short lifetime. It is truly remarkable, and rather surprising to us, that solvated electrons have never before been at all considered to affect DMFCs, neither with respect to the main reactions nor for the various side-reactions possible. Here, based on the presence and high reactivity of solvated electrons in water and/or methanol and their known reactions with water, protons/hydronium ions, methanol, CO, and CO₂,^[13,24,25] respectively, the following reactions are suggested to be relevant for DMFCs:



In addition to these five reactions, solvated electrons can possibly also react with DMFC reaction intermediates, e.g. formaldehyde and formic acid,^[26] and with the electrolyte membrane. In fact, stability problems of halogenated, and especially in this context fluorinated, polyelectrolytes have been connected to reactions with solvated electrons.^[3,13,21] Hence both the traditional DMFC reactions and the reactions suggested above should be seriously considered in any studies aimed at a detailed understanding of DMFC performance and mechanisms. The reactions above would both deteriorate DMFCs by secondary reactions of the radicals created and reduce the number of electrons performing useful work. To

prevent solvated electrons from being created is not easy, but more compacted electrodes, possibly by improved production methods, such as calendaring (applying pressure), to create fewer disconnected pathways and poorly conductive zones is likely a must. At the same time this reduces the accessible electrode surface and thus reduce the theoretical maximum current density fundamentally, why a sweet-spot must be found, which also will be highly chemistry, and possibly also operation parameter, dependent.

Finally, acknowledging the role of solvated electrons at electrode-electrolyte interfaces more broadly could, and should, have a huge impact in many associated areas of science and technology. This goes for both OLEDs and PLEDs, which rely on electron injection to occur for their functionality, as well as LIBs, which more likely are limited by the same phenomenon. In general, whenever nano-structured electrodes are employed, a proper understanding of the conditions creating solvated electrons and the extent thereof is likely crucial to rationally improve the stability and efficiency for whatever the device.

Experimental

Nafion® 117 (DuPont) membranes were purified by submerging in 1 M H₂SO₄ (J.T. Baker Analysed) for 2 h at 75 °C followed by 3 wt% H₂O₂ (J.T. Baker Analysed) for 1 h at 60 °C. Between each step, the membranes were rinsed vigorously in de-ionized water (Millipore Direct-Q, > 18.2 MΩ) at least three times. The membranes were left to dry in a clean oven for 1 h at 60 °C.

Catalyst solutions were prepared by weighing 1.5 mg/cm² of Pt–Ru (50/50%, Alfa Aesar HiSPEC 6000) for the anode and 1.0 mg/cm² of Pt black (Alfa Aesar HiSPEC 1000) for the cathode, followed by adding 1.2 g/cm² of deionised water for each. The solutions were sonicated for 10 min using a stick sonicator (Sonics Vibra Cell VCX 134) made from a titanium alloy. While cooling the samples with cold water, 3.2 mg/cm² of Nafion® solution (10 wt%) was added by a pipette with disposable tips. The solutions were then further sonicated for 10 min.

Two production methods were used for the membrane electrode assemblies (MEAs) to confirm that no contamination was introduced. The MEAs were made either by a fine mist created from airbrushing the sample with pressurised air or an atomisation method where the catalyst slurry was sonicated to a fine mist. The airbrushed MEAs were made by placing a dry and purified Nafion® membrane on a hot glass plate (90 °C) and cover with a 2 mm thick polydimethylsiloxane plate (Atos Medical Silatos) with a rectangular opening in the middle. An IR heater was used from above to provide additional heat, providing a surface temperature of 80 °C as verified by a thermal imaging camera (FLIR i50). The catalyst ink was applied to the membrane by an airbrush (Badger AirBrush model 200). The atomised MEAs were set up in the same way and had the catalytic layer coated by sonication of the catalyst slurry through a hollow tube connected to the sonicator, thus forming a fine mist of catalyst slurry which was deposited on the surface of the membrane. The MEAs were then dried for 24 h at 60 °C and subsequently cleaned with 1 M HCl (J.T. Baker Analysed) at 75 °C for 1 h followed by thorough rinsing with de-ionized water. The final MEAs were stored in de-ionized water until use.

The MEAs were then tested in a custom polycarbonate casing consisting of two halves; a sealing effect was achieved by compressing the final MEA between the two halves. The gas

diffusion layers (GDLs) AvCarb P75 and P75T (Ballard Power Systems Inc.) were used for the anode and cathode, respectively. Graphite plates were used as current collectors; once machined to the correct shape the anode graphite plates were treated with 65% HNO₃ (J.T. Baker Analysed) for 4 h at 90 °C to make them hydrophilic, they were then cleaned by repeated boiling in methanol and water. The graphite current collectors were attached to the polycarbonate using THF (J.T. Baker Analysed) and allowed to dry in the oven at 60 °C for 48 h.

A Jasco V-670 UV-Vis-NIR spectrophotometer was used with an integrating sphere (Jasco ISN-723). The fuel cell (Figure 1S) was placed so that the spectrophotometer beam passed through the length of the membrane and then collected in the range of 600–1000 nm with a slow response and a scan speed of 40 nm/min, 5 nm UV-Vis and 20 nm NIR bandwidths, and baseline correction. A graphite slit was placed in front of the polycarbonate part of the casing to prevent interference from the polycarbonate peaks. The methanol solution (Merck EMSURE) was flowed through the anode side of the cell for 30 min before the measurements in order to fully hydrate the membrane and then stopped to avoid any occurrence of eddies during the measurements.

Acknowledgements

This paper is dedicated to the memory of Prof. Per Jacobsson, Chalmers, and C. Austen Angell, ASU, both heavily involved in research on the basic science of proton transfer, the creation and study of various proton conductors, and the practical application of different fuel cells. MP acknowledges the support from University of Helsinki, while MEA and PJ acknowledge the support from several of Chalmers Areas of Advance: Materials Science, Energy and Transport.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Fuel cell · degradation · efficiency · power density · solvated electrons

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Manuscript received: July 26, 2023

Revised manuscript received: September 29, 2023

Version of record online: October 23, 2023