

Proceedings of 7th Transport Research Arena TRA 2018, April 16-19, 2018, Vienna, Austria

Optimization of the Catalyst and Membrane Performance by addition of various Additives for the alkaline Direct Ethanol Fuel Cell

Viktor Hacker^a, Johanna Ranninger^a, Bernd Cermenek^{a*}
Birgit Feketeföldi^b, Christina Spirk^b, Jan Hesse^b
Volker Ribitsch^c

^a Institute of Chemical Engineering and Environmental Technology, Graz University of Technology, Inffeldgasse 25C; 8010 Graz, Austria.

^b JOANNEUM RESEARCH Forschungsgesellschaft mbH/Materials, Institute for Surface Technologies and Photonics, Franz-Pichler-Straße 30, 8160 Weiz, Austria.

^c University of Graz, Institute of Chemistry, Heinrichstraße 28, 8010 Graz, Austria.

Abstract

Alcohol fuel cells are promising energy converters especially for portable applications. Ethanol as fuel is an attractive candidate for fuel cells due to the high volumetric energy density and to the easy handling, transport and storing. The chemical energy of ethanol is converted directly in electricity without any treatment step. The operation of the direct ethanol fuel cell (DEFC) in alkaline media compared to acidic media includes the advantages of the use of non-precious metals e.g. nickel or manganese as catalysts, the improved water management and reduced ethanol-crossover using anion exchange membranes (AEMs) which conduct the hydrated anions in the opposite direction than the electro-osmotic drag and the kinetic enhancement of the ethanol oxidation reaction (EOR) and oxygen reduction reaction (ORR).

Keywords: Direct fuel cell; decentralized electricity generation; auxiliary power unit

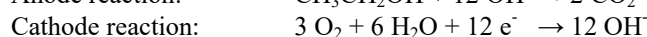
* Corresponding author. Bernd Cermenek, Viktor Hacker
E-mail address: bernd.cermenek@tugraz.at, viktor.hacker@tugraz.at

Nomenclature

AEM	Anion exchange membrane
CA	Chronoamperometry
CV	Cyclic voltammetry
DAFC	Direct alcohol fuel cell
DC	Degree of cross-linking
DEFC	Direct ethanol fuel cell
DQ	Degree of quaternization
EGDGE	Ethylene glycol diglycidyl ether
EOR	Ethanol oxidation reaction
EPTMAC	(2,3-Epoxypropyl) trimethylammonium chloride
GA	Glutaraldehyde
HTCC	N-[(2-Hydroxy-3-trimethylammonium)propyl] chitosan chloride
IEC	Ion exchange capacity
IPN	Interpenetrating polymer network
MEA	Membrane electrode assembly
MWCO	Molecular weight cut off
ORR	Oxygen reduction reaction
PEI	Polyethylene imine
PTFE	Polytetrafluorethylene
QPEI	Quaternized polyethylene imine
RDE	Rotating disk electrode

1. Introduction

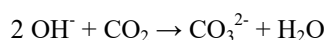
In the alkaline DEFC, ethanol is directly oxidized by hydroxide (OH⁻) ions at the anode and 12 e⁻ are released. Oxygen reacts at the cathode with the electrons and water to form the hydroxide ions, which are transported through the membrane to the anode. Alkaline solution along with ethanol fuel is provided at the anode to facilitate the oxidation of ethanol.



The complete oxidation of ethanol at the anode is not reached with state-of-the-art catalysts in the alkaline DEFC at ambient temperature. Instead of CO₂, the main product of the ethanol oxidation reaction (EOR) is acetic acid – (acetate). In the incomplete oxidation pathway, only four electrons instead of 12, for the complete oxidation, are released. This loss in electrons leads to a reduction of the theoretical efficiency (97%) to 11%^{1,2}. Therefore, anode catalysts with high activity, stability and byproduct tolerance have to be developed. The most promising catalysts are Pd-based catalysts which outperform Pt-based catalysts in alkaline medium³. The performance of Pd-based anode catalysts is improved by alloying Pd with co-catalysts which can also be non-noble metals like Ni, Bi, P or Zn⁴⁻⁸.

In the alkaline DEFC, the direction of the ion mobility through the membrane is in the opposite direction than the electro-osmotic drag leading to reduced ethanol-crossover⁹. However, ethanol-crossover through the membrane cannot be totally prevented which makes the development of ethanol tolerant cathode catalysts also an important research topic. In acidic medium, mainly Pt is used as catalyst for the ORR. Ag, Mn_xO_y and Ag/Mn_xO_y have been reported as Pt-free cathode catalyst materials with high activity, stability and higher ethanol tolerance in alkaline cells than Pt¹⁰.

Aside from the advantages of the alkaline DEFC, one challenge concerning alkaline fuel cells represents the carbonation of the electrolyte. The OH⁻ ions react with CO₂ in the air and the CO₂ formed during the ethanol oxidation to carbonate (CO₃²⁻) ions⁹.



The carbonate ions form solid precipitation which blocks the pores of the electrodes and increase the pH value. Hence, the activity of the oxidation and reduction reactions is reduced as well as the conductivity of the electrolyte ⁹.

With the development of polymer electrolyte membranes like Nafion, the development of direct alcohol fuel cells (DAFCs) was mainly focused on acidic DAFCs, however, in previous years, the synthesis of anion exchange membranes (AEM) lead to new research interests in alkaline DAFCs. When an AEM is applied instead of liquid alkaline electrolyte, the formation of carbonate can be drastically decreased ^{9,11}.

Within the scope of the Austrian Research Promotion Agency (FFG) project “e!Polycat”, Pt-free catalysts with high activities and stabilities toward alkaline EOR and ORR and high anion conductive and chemically, mechanically, thermally stable polysaccharide-based membranes (-> performance improvement by addition of various “additives” e.g. ad-metals for catalysts and cross-linkers for membranes) were developed for the alkaline DEFC.

A series of novel bi- and tri-metallic Pt-free anode catalysts were synthesized by means of the simultaneous reduction method. The addition of one or two metals to monometallic anode catalysts results to high EOR activities and stabilities due to bifunctional, electronic and synergistic effects in an alkaline electrolyte containing ethanol. Additionally, novel perovskite cathode catalysts for the alkaline DEFC have been developed. Those catalysts exhibit high activity toward the ORR, high stability and excellent ethanol tolerance ¹². Within the framework of the project, ethanol tolerant cathode catalysts based on manganese oxide and silver were also synthesized and characterized for the alkaline DEFC ¹³.

Furthermore, a series of novel AEMs based on chitosan were blended with water-soluble polyethylene imine. Chitosan can be modified due to its exchangeable functional groups¹⁴ and polyethylene imine (PEI) is an inexpensive polymer with a high density of reactive amino groups. In order to use the polymers as solid polyelectrolytes in alkaline fuel cells both polymers were quaternized. A common strategy of introducing ionic conductive groups into polymeric matrices is the quaternization with trimethylammonium (-N(CH₃)₃) groups onto the backbone or side chains of the polymers ^{15-19,26} or in case of polyethylene imine the N-alkylation with iodomethane or with the less toxic reagents iodoethane ²⁰. To our best knowledge there is very little data available on the usage of quaternized polyethylene imine (QPEI) for alkaline fuel cells. Due to the high mass of the amino groups of PEI a high degree of quaternization (DQ) was obtained, thus resulting in a high hydrophilic polymer matrix with a high degree of swelling and subsequently modest membrane stability. To prepare durable membranes with improved chemical, mechanical and thermal properties, a cross-linking method consisting of a combination of different network was developed. The characteristics of the composite membranes were evaluated for potential application in alkaline DEFCs.

2. Experimental

2.1. Preparation of HTCC

N-[(2-Hydroxy-3-trimethylammonium) propyl] chitosan chloride (HTCC) was synthesized according to Wu *et al.* and Feketeföldi *et al.* ^{21,26}.

2.2. Preparation of QPEI

Branched quaternized polyethylene imine (QPEI) was prepared by a method similar to those described elsewhere²⁰. Briefly, PEI (1.0 g, 23 mmol of monomer unit) was dissolved in 15 ml of absolute ethanol. N-alkylation was conducted as follows: iodoethane (19.4 g, 124.4 mmol) was added and the reaction was carried out under reflux conditions for 24 hours at 72 °C. An excess of potassium carbonate (K₂CO₃) was added to neutralize the released acid. The reaction was continued for 72 hours at the same conditions. Formed KI and unreacted K₂CO₃ were discarded by filtration. Ethanol was removed by evaporation and the product was lyophilized. To remove traces of inorganic salts, the product was dialyzed (MWCO 3,5 kDa) against water for three days and the product was lyophilized again.

2.3. Preparation of the cross-linked HTCC/QPEI membrane

HTCC was dissolved in 1wt.% acetic acid solution, yielding a 5wt.% solution, a prescribed amount of 10wt.% ethylene glycol diglycidyl ether (EGDGE) in ethanol was added (see Table 1) under stirring at 60 °C for one hour. QPEI was dissolved in deionized water in order to prepare a 5wt.% solution. HTCC (5 g) and QPEI (5 g)

were mixed. To this solution, 0.3 mL of 10wt.% glutaraldehyde (GA) was added under stirring for 0.5 h. The solution was filtered with a 5 µm PTFE membrane filter and coated onto the surface of a plexiglass petri dish and dried at 60 °C overnight. Afterwards, the membrane was dried at 130 °C for 2 min²⁶.

A series of HTCC/QPEI membranes was prepared. The membranes were cross-linked with varying amounts of EGDGE, while the amount of the second cross-linking reagent (GA) was maintained constant. These series are referred to as HTCC/QPEI-i (i = 1, 2, 3, 4 and 5)²⁶.

2.4. Anode catalyst synthesis

Different binary and ternary anode catalysts were prepared via the simultaneous reduction method²⁷. Therefore, various metal precursor salts are dissolved in aqueous media and mixed with carbon black Vulcan XC72R as support material. These metal precursor salts are reduced to respective metals on the support material by adding e.g. sodium borohydride (NaBH₄) or other reducing agents. As additives e.g.: Ni, Bi, P or Zn was used to improve the activities and stabilities of Pd based catalysts³⁰⁻³².

2.5. Methods

2.5.1. Degree of membrane cross-inking

The degree of membrane cross-linking for QPEI and HTCC with EGDGE was calculated according to Equation 1^{22, 26}.

$$DC(\%) = \frac{10\% \times V_{Agent}/M_{wAgent}}{5\% \times V_{Q-Polymer}/M_{wQ-Polymer}} \times 100\% \quad (1)$$

Where, DC (%) is the molar ratio of EGDGE to the composite membrane in repeat units, V_{Agent} is the volume [mL] of cross-linking agent (EGDGE, 10wt.%), $V_{Q-Polymer}$ is the volume [mL] of quaternized polymer solution (QPEI and HTCC, 5wt.%), $M_{w, Agent}$ is the molecular weight of EGDGE (174.19 g mol⁻¹). $M_{w, Q-Polymer}$ is corresponding to the averaged molecular weight of HTCC/QPEI monomers (361.0 g mol⁻¹)²⁶.

2.5.2. Alkaline water uptake

The alkaline water uptake (WU) of the membranes was performed by measuring the change in mass of the membranes before and after hydration²⁶. The membranes were immersed in 1 M KOH at room temperature for 24 h. The surplus aqueous alkaline solution was wiped with filter paper and weighted immediately. The alkaline water uptake was calculated using the following relation (see Equation 2)²⁶:

$$WU(\%) = \frac{m_w - m_d}{m_d} \times 100 \quad (2)$$

where m_w is the mass [g] of wet membrane and m_d is the mass [g] of dry membrane²⁶.

2.5.3. Ion exchange capacity

The ion exchange capacity (IEC) was determined by back titration²⁶. The membranes (0.2 g) were soaked in 1.0 M KOH for 24 h, washed with deionized water and equilibrated with 40 mL of 0.01 M HCl standard solution for 24 h, followed by potentiometric titration with 0.01 M NaOH standard solution. 40 mL of 0.01 M HCl standard solution was used as blank sample. The IEC value was calculated by the following Equation 3²⁶:

$$IEC = \frac{(V_{blank} - V_{membrane}) \cdot C_{HCl}}{m_d} \times 1000 \quad (3)$$

where V_{blank} and $V_{membrane}$ were the consumed volumes [mL] of the NaOH solution for the blank sample and the HTCC/QPEI membrane sample, respectively, C_{HCl} was the concentration [M] of HCl solution, and m_w is the mass [g] of dry membrane sample²⁶.

2.5.4. Product and membrane characterizations

The content of surface charge was determined by streaming potential method using Mütek PCD system. The chemical stability in alkaline medium was evaluated by immersing the membranes in 1.0 M KOH solution at 60 °C for different periods of time²⁶. The compactness and appearance of leaks of the membranes were visually observed. The structure of the unmodified PEI and quaternized QPEI was characterized by Fourier transform infrared spectroscopy (FT-IR)²⁶. The infrared spectrometer (Bruker Tensor 27) was used to obtain spectra in the range from 4000 to 600 cm⁻¹ with a wavenumber resolution of 4 cm⁻¹²⁶. Thermal gravimetric analysis (TGA) was conducted using a TGA/DSC system (NETZSCH STA 449, Germany)²⁶. Samples were heated from 25 to 600 °C at a heating rate of 10 °C min⁻¹ using a flow of 20 mL min⁻¹ nitrogen as inert gas²⁶.

2.6. Anode catalyst investigation

Different binary and ternary Pd-based anode catalysts were tested in a rotating disk electrode (RDE) experiment via cyclic voltammetry (CV) and chronoamperometry (CA) to get an impression of their activities and stabilities. The RDE experiments were carried out in aqueous solution containing 1 M KOH and 1 M ethanol at 30 °C with a scan rate of 10 mV s⁻¹. The CA was performed at 0.83 V for one hour. The elemental composition, structure and the morphology of the catalysts were investigated by different physical methods such as ICP-OES, XRD, XPS and TEM-EDX³⁰⁻³².

3. Results and Discussion

3.1. Synthesis of HTCC and QPEI

Anion exchange membranes with chitosan and PEI as polymer matrix and polyelectrolytes were prepared. Chitosan was quaternized with (2,3-Epoxypropyl) trimethylammonium chloride resulting in a high degree of quaternization of 80% averagely. PEI has a high mass of amine groups on its polymer chain and can provide a high ion exchange capacity after modification by N-alkylation (see Fig. 1). The resulting degree of quaternization for QPEI was 82.4%. The ¹H-NMR spectra of QPEI and HTCC are not shown.

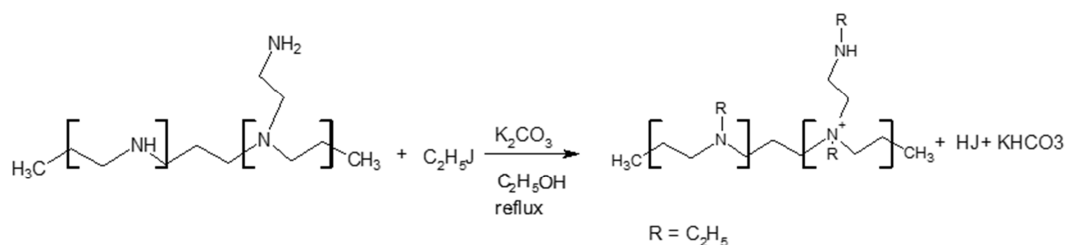


Fig. 1 Schematic representation of preparing QPEI

It was found, that quaternized chitosan with a degree of quaternization (DQ) of 80.2% had an average amount of surface charge of 3830 C/g. Compared to the HTCC-product, the quaternized PEI exhibited an average amount of surface charge of 575 C/g. The previous result was obtained from a dialyzed QPEI-product with a DQ of 82.4% and an ion conductivity of 740 μS cm⁻¹.

3.1.1 Fourier transform infrared spectroscopy

The FT-IR spectra of PEI and QPEI are shown in Fig. 2. The two peaks at 1020 and 1250 cm⁻¹ in the spectra of the materials are characteristic for C-N bonds. The signal at 1650 cm⁻¹ for unmodified PEI is assigned to the N-H bending of primary amines (R-NH₂)²³. QPEI consists of secondary (R₂-NH) and tertiary (R₃-N) amines, although the expected peak at 1650 cm⁻¹ could not be observed. Absorption bands between 3250 and 3500 cm⁻¹ were recorded, corresponding to the N-H bending of primary and secondary amines. The unmodified PEI offered two peaks at 3265 and 3355 cm⁻¹, attributed to the N-H bending of primary amines. A broad band around 3430 cm⁻¹ was attributed to the secondary amines of the modified QPEI. It is noted that the absorption peaks of the primary amines could also not be observed for the QPEI-product.

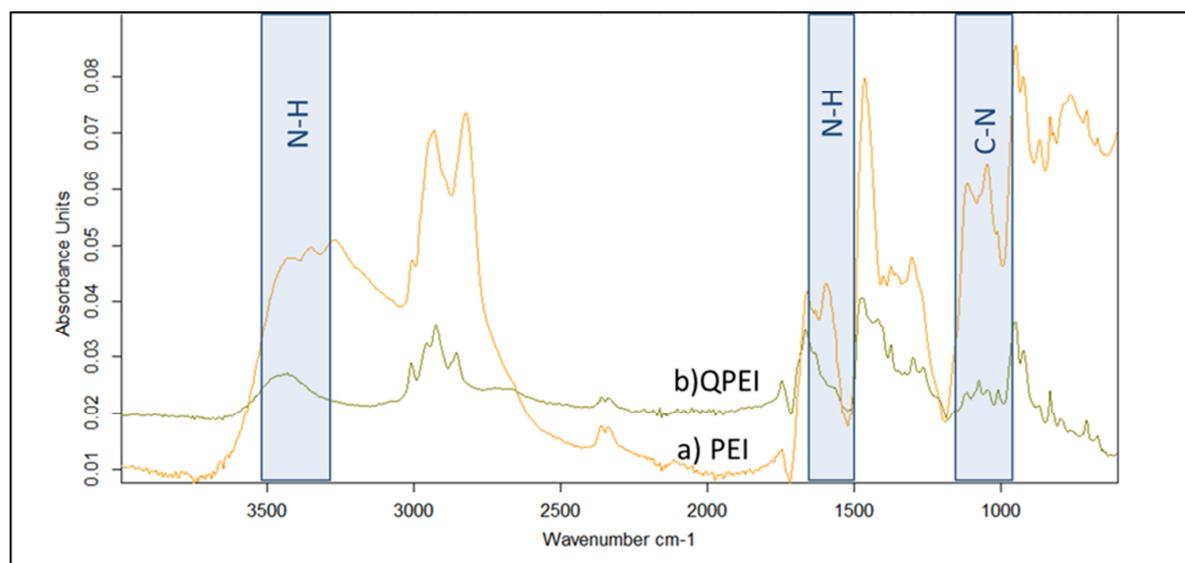


Fig. 2 FT-IR spectra of PEI and QPEI

3.2. Membrane Preparation

3.2.1. Cross-linking HTCC/QPEI membranes

To increase chemical, mechanical and thermal stability, the composite materials were cross-linked in order to form three-dimensional polymer networks. The effect of the degree of cross-linking on the membrane structure and the chemical/physical properties were investigated²⁶. In this work, we used GA and EGDGE to cross-link the polymer membranes. The amount of the first cross-linking agent (GA) was constant, whereas the amount of the second cross-linker (EGDGE) was varied²⁶.

Table 1. Cross-linking conditions for HTCC/QPEI composite membrane with EGDGE²⁶.

Membrane ^{a,b,c}	Molar ratio of EGDGE to membrane [mmol mmol ⁻¹]	Degree of cross-linking QPEI [%]
HTCC/QPEI-1	1.1/2.2	69,1
HTCC/QPEI-2	1.2/2.2	78,9
HTCC/QPEI-3	1.3/2.2	88,8
HTCC/QPEI-4	1.4/2.2	98,6
HTCC/QPEI-5	1.7/2.2	118,4

a All membranes were prepared using a same kind of HTCC and QPEI, the degree of quaternization (DQ) was 80,2% and 82,4%, respectively, determined by elemental analysis.

b The molar ratio of GA to composite membrane was 0.3/2.2 mmol mmol⁻¹, with a degree of crosslinking (DC) of 13.7%.

c The thickness of membranes was 85 nm, +/- 4 nm dry state.

GA and EGDGE are common cross-linking agents for PEI and chitosan^{24,26}. The network formation takes place between the amino groups of the blend materials (HTCC and QPEI) and the aldehyde groups of GA. For gaining the highest possible mechanical and chemical stability, a second cross-linking agent - EGDGE - was used in this work²⁶. Due to the presence of two reactive epoxy groups, EGDGE facilitates the cross-linking reaction with two amino groups of two different quaternized chitosan molecules and quaternized PEI molecules during drying process^{25,26}. The blend materials form an interpenetrating polymer network (IPN), wherein both polymers are cross-linked independently in the presence of the other and do not interfere with one another (see Fig. 3).

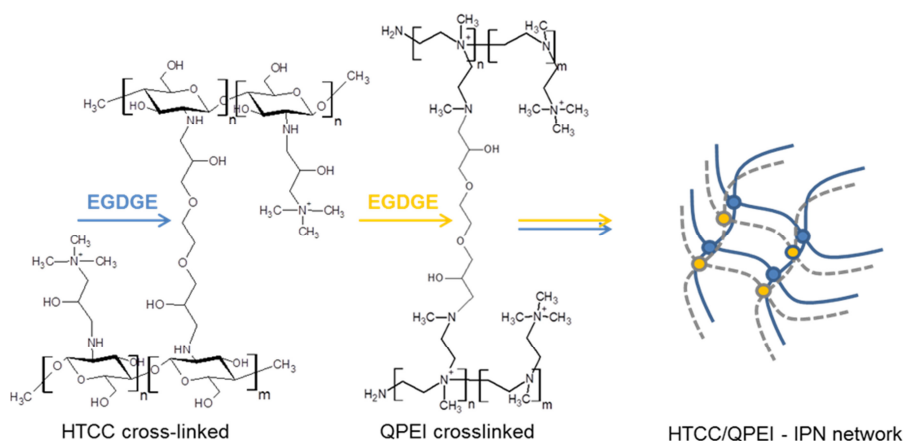


Fig. 3 HTCC/QPEI – IPN network

The cross-linking conditions for these membranes are summarized in Table 1. In the present study, all cross-linked membranes were prepared using HTCCs and QPEIs with a DQ higher than 80%. The stability of the membranes toward alkaline media was observed visually from physical appearance of fragmented membranes after immersion in 1.0 M KOH solution for a certain period of time²⁶. By increasing the amount of cross-linker, the membranes became more stable with an optimum range of 0.3/2.2 mmol mmol⁻¹ for GA and 1.4/2.2 mmol mmol⁻¹ for EGDGE²⁶. At a degree of cross-linking of 88.8%, the alkaline stability of the membrane sustained for 360 h in 1.0 M KOH solution at 60 °C.

3.3. Water uptake and ion exchange capacity

The presence of water in the solid electrolyte affects the chemical and mechanical stability of the membranes²⁶. The degree of water uptake is related to the amount of polymer cross-linking agents and the hydrophilic properties due to the quaternary ammonium groups. In the present study, the amount of the ammonium groups of the HTCC/QPEI membranes was approximately the same (DQ of HTCC and QPEI higher than 80%). The parameter that primarily influenced the swelling of the membranes was the degree of cross-linking. The water uptake of the composite membranes cross-linked with GA and EGDGE is given in Fig. 4.

The results indicate that with an increased DC, the water uptake of the membranes gradually decreased from around 168% to 120%. The differences in water uptake can be assigned to the interactions in the polymer matrix of the cross-linkers²⁶. With increased amount of cross-linking reagents, the IPN-networks became more dense. The heating procedure during the membrane preparation (60-130 °C) resulted only in a higher mechanical and chemical stability, the swelling properties of the membranes (60 °C) remained the same²⁶.

The composite membranes exhibit the same behavior in terms of water uptake and ion exchange capacity²⁶. A higher water uptake in membranes forms transferring channels and creates a higher accessibility for ammonium ions, whereas a high amount of cross-linking reagents reduces the ion transport²⁶. It was found that, at a constant DQ, an increase of the amount of cross-linkers leads to a gradually decreased IEC of the HTCC/QPEI membranes from 1.6 meq g⁻¹ to 0.9 meq g⁻¹. The IEC of anion exchange membranes describes the amount of exchangeable ammonium groups in the membrane²⁶.

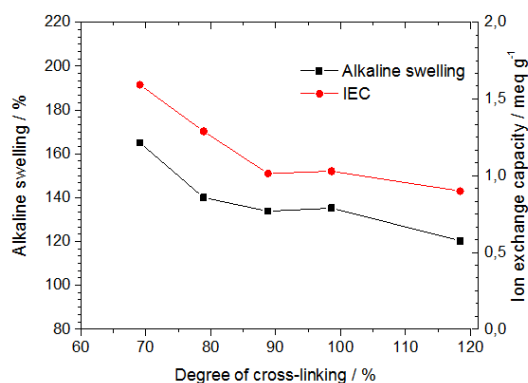


Fig. 4 Water uptake and ion exchange capacity of the cross-linked HTCC/QPEI membranes vs. degree of cross-linking

3.4. Thermogravimetric analysis (TGA)

The thermal degradation behavior of HTCC/QPEI composite membranes cross-linked by EGDGE is shown in comparison to HTCC/QPVA membranes in Fig. 5. The preparation and properties of the HTCC/QPVA membranes are described in a previous paper²⁶. The mass decrease at around 100 °C is due to the bonded water evaporation of all membranes. The HTCC/QPVA and the HTCC/QPEI composite membranes cross-linked with EGDGE were stable up to 260 °C and 190 °C, respectively. The thermal stability of the membranes was mainly determined by QPVA and QPEI. Pure chitosan is thermally not stable enough and starts to degrade continuously at around 120 °C. Two stages of thermal degradation were found for the cross-linked membranes. The weight loss of the two composite membranes that occurs within a range of 180-280 °C is due to the degradation of quaternary ammonium groups. At the degradation stage in the range of 260-480 °C, the mass degradation is attributed to the break of the C-C backbone of the main polymer chains of HTCC, QPVA and QPEI²⁶.

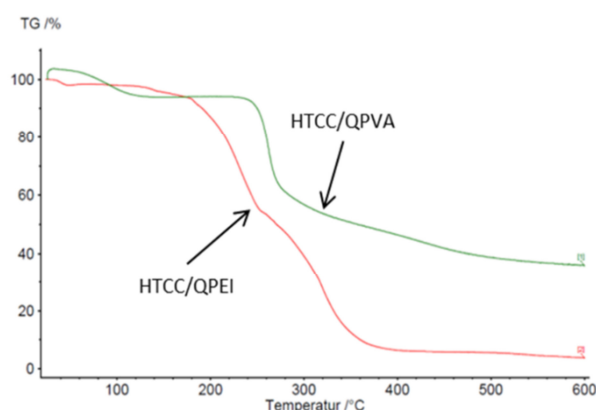


Fig. 5 TGA curve of HTCC/QPVA – and HTCC/QPEI composite membranes²⁶

3.5. Anode Catalyst Testing

Carbon supported binary and ternary Pd based anode catalysts were successfully synthesized by the instant reduction method ($\text{Pd}_{80}\text{Ni}_{20}/\text{C}$)²⁷ and by the “aqueous solution phase synthesis method” ($\text{Pd}_{80}\text{Ni}_{10}\text{P}_{10}/\text{C}$)²⁸. The activities and stabilities of the catalysts were investigated by CV/CA using a RDE. Fig. 6 shows that the EOR performances (activity and stability) of both Pd based catalysts are higher than the Pt/C catalyst (benchmark). The poisoning of CO similar species on Pd based catalysts is drastically reduced thus results in an improvement in terms of activity and stability toward the alkaline EOR^{5,7,28}.

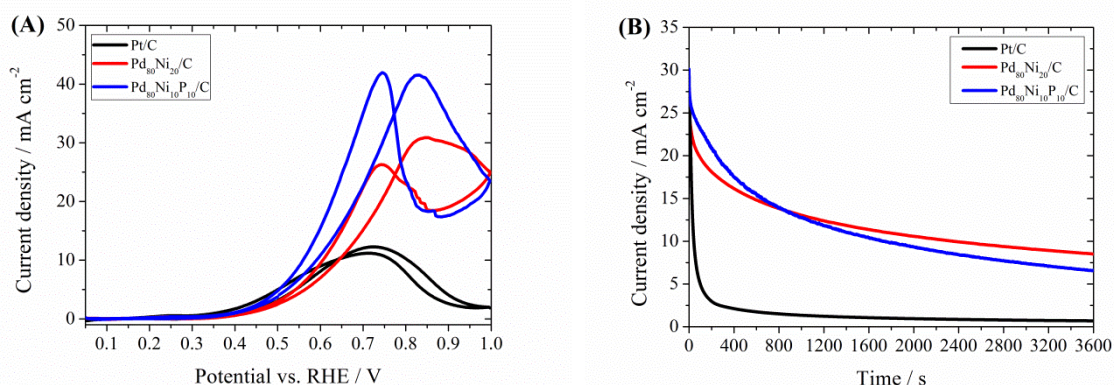


Fig. 6 (A) EOR activity of Pt/C, $\text{Pd}_{80}\text{Ni}_{20}/\text{C}$ and $\text{Pd}_{80}\text{Ni}_{10}\text{P}_{10}/\text{C}$ in an aqueous solution containing 1 M ethanol and 1 M KOH recorded with a scan rate of 10 mV s^{-1} at 30 °C; (B) EOR stability of Pt/C, $\text{Pd}_{80}\text{Ni}_{20}/\text{C}$ and $\text{Pd}_{80}\text{Ni}_{10}\text{P}_{10}/\text{C}$ in an aqueous solution containing 1 M ethanol and 1 M KOH recorded at 0.83 V for one hour at 30 °C

But the tolerances of the synthesized Pd based catalysts toward the intermediates of ethanol oxidation are not good enough by half for use in a long term operation. The byproduct tolerance is evaluated by the ratio of the current density of the forward scan and the backward scan according to Lee et al.²⁹. Therefore, Pd catalysts with

further “additives” were investigated for the alkaline EOR. Within the scope of the project, a ternary Pd based catalyst system with high EOR performance (high byproduct tolerance, low onset-potential for the alkaline ethanol oxidation reaction, high produced peak current density) was developed for the alkaline DEFC^{30,31}. The EOR performance of the ternary Pd based catalyst system outperformed the results of the in-house carbon supported Pd and binary Pd based catalysts, respectively. With the optimized catalysts, anodes are fabricated via drop-coating on a carbon cloth which were further processed to a membrane electrode assembly (MEA) and characterized in an in-house designed direct single cell at various operating conditions (see Fig. 7)^{31,32}.

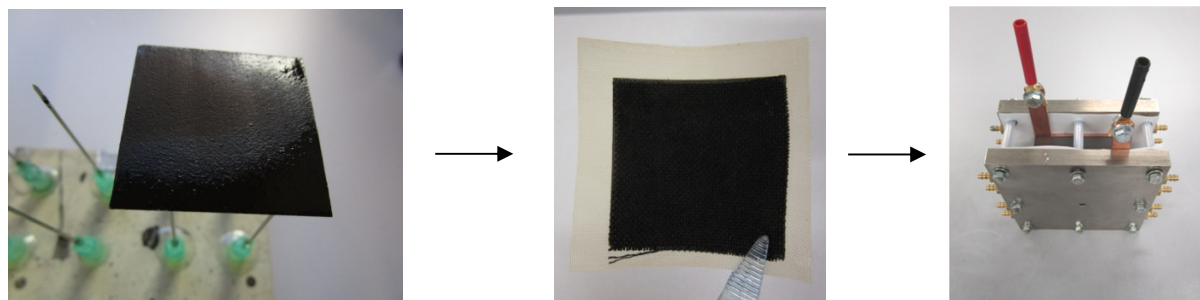


Fig. 7 Drop-coating process for anode preparation; Membrane electrode assembly (MEA); In-house direct single cell (left to right)^{31,32}

4. Conclusion

A series of novel quaternized chitosan/PEI membranes were prepared. The chitosan and QPEI molecules were cross-linked with the cross-linking agents GA and EGDGE. During the polymerization procedure the quaternized polymers formed an IPN-network, wherein HTCC and QPEI were not connected with each other. The composite membranes showed ionic properties for anions and concurrently mechanical and chemical stability in alkaline environment. The IPN-network was stable up to 190 °C. This study demonstrates that the resulting membranes are suitable for direct ethanol fuel cells. Future investigations will focus on the screening of improvement of ionic conductivity and reduction of chemical degradation of the quaternized matrix.

A novel ternary anode catalyst with high EOR performance has been prepared by alloying of Pd with other metals. The results have been confirmed via CV and CA measurements using RDE and also in single cell tests using an in-house designed cell. The characterization results of the novel ternary Pd-based anode catalyst and the novel quaternized chitosan/PEI AEMs for the alkaline DEFC will be presented and discussed in detail.

Acknowledgements

Financial support by the Austrian Climate Energy Fund, Austrian Federal Ministry of Transport, Innovation and Technology (BMVIT), The Austrian Research Promotion Agency (FFG) through the program “Energy Mission Austria” and the IEA research cooperation is gratefully acknowledged.

5. References

- (1) Liang, Z. X.; Zhao, T. S.; Xu, J. B.; Zhu, L. D. Mechanism study of the ethanol oxidation reaction on palladium in alkaline media. *Electrochim. Acta* **2009**, *54* (8), 2203–2208.
- (2) An, L.; Zhao, T. S.; Li, Y. S. Carbon-neutral sustainable energy technology: Direct ethanol fuel cells. *Renew. Sustain. Energy Rev.* **2015**, *50*, 1462–1468.
- (3) Xu, C.; Cheng, L.; Shen, P.; Liu, Y. Methanol and ethanol electrooxidation on Pt and Pd supported on carbon microspheres in alkaline media. *Electrochem. commun.* **2007**, *9* (5), 997–1001.
- (4) Shen, P. K.; Xu, C. Alcohol oxidation on nanocrystalline oxide Pd/C promoted electrocatalysts. *Electrochem. commun.* **2006**, *8* (1), 184–188.
- (5) Shen, S. Y.; Zhao, T. S.; Xu, J. B.; Li, Y. S. Synthesis of PdNi catalysts for the oxidation of ethanol in alkaline direct ethanol fuel cells. *J. Power Sources* **2010**, *195*, 1001–1006.
- (6) Neto, A. O.; Tusi, M. M.; De Oliveira Polanco, N. S.; Da Silva, S. G.; Coelho Dos Santos, M.; Spinacé, E. V. PdBi/C electrocatalysts for ethanol electro-oxidation in alkaline medium. *Int. J. Hydrogen Energy* **2011**, *36* (17), 10522–10526.
- (7) Jiang, R.; Tran, D. T.; McClure, J. P.; Chu, D. A Class of (Pd – Ni – P) Electrocatalysts for the Ethanol Oxidation Reaction in Alkaline Media. *ACS Catalysis* **2014**, *4*, 2577–2586.

- (8) Bianchini, C.; Bambagioni, V.; Filippi, J.; Marchionni, A.; Vizza, F.; Bert, P.; Tampucci, A. Selective oxidation of ethanol to acetic acid in highly efficient polymer electrolyte membrane-direct ethanol fuel cells. *Electrochem. commun.* **2009**, *11* (5), 1077–1080.
- (9) Yu, E. H.; Krewer, U.; Scott, K. Principles and materials aspects of direct alkaline alcohol fuel cells. *Energies* **2010**, *3* (8), 1499–1528.
- (10) Tang, Q.; Jiang, L.; Qi, J.; Jiang, Q.; Wang, S.; Sun, G. One step synthesis of carbon-supported Ag/MnyOx composites for oxygen reduction reaction in alkaline media. *Appl. Catal. B Environ.* **2011**, *104* (3–4), 337–345.
- (11) Kamarudin, M. Z. F.; Kamarudin, S. K.; Masdar, M. S.; Daud, W. R. W. Review: Direct ethanol fuel cells. *Int. J. Hydrogen Energy* **2013**, *38* (22), 9438–9453.
- (12) Grimmer, I.; Zorn, P.; Weinberger, S.; Grimmer, C.; Pichler, B.; Cermenek, B.; Gebetsroither, F.; Schenk, A.; Mautner, F.-A.; Bitschnau, B.; Hacker, V. Ethanol tolerant precious metal free cathode catalyst for alkaline direct ethanol fuel cells. *Electrochim. Acta* **2017**, *228*, 325–331.
- (13) Chaiburi, C.; Cermenek, B.; Pichler, B. E.; Grimmer, C.; Schenk, A.; Hacker, V. Ethanol - Tolerant Pt-free Cathode Catalysts for the Alkaline Direct Ethanol Fuel Cell. *Journal of New Materials for Electrochemical Systems* **2017**, *19* (4), 199–207.
- (14) Merle, G.; Wessling, M.; Nijmeijer, K. Anion exchange membranes for alkaline fuel cells: A review. *J. Memb. Sci.* **2011**, *377* (1–2), 1–35.
- (15) Wan, Y.; Peppley, B.; Creber, K. A. M.; Bui, V. T.; Halliop, E. Preliminary evaluation of an alkaline chitosan-based membrane fuel cell. *J. Power Sources* **2006**, *162* (1), 105–113.
- (16) Wan, Y.; Creber, K. A. M.; Peppley, B.; Bui, V. T. Chitosan-based electrolyte composite membranes. II. Mechanical properties and ionic conductivity. *J. Memb. Sci.* **2006**, *284* (1–2), 331–338.
- (17) Wan, Y.; Creber, K. A. M.; Peppley, B.; Tam Bui, V. Chitosan-based solid electrolyte composite membranes. I. Preparation and characterization. *J. Memb. Sci.* **2006**, *280* (1–2), 666–674.
- (18) Xiong, Y.; Liu, Q. L.; Zhang, Q. G.; Zhu, A. M. Synthesis and characterization of cross-linked quaternized poly(vinyl alcohol)/chitosan composite anion exchange membranes for fuel cells. *J. Power Sources* **2008**, *183* (2), 447–453.
- (19) Xiong, Y.; Fang, J.; Zeng, Q. H.; Liu, Q. L. Preparation and characterization of cross-linked quaternized poly(vinyl alcohol) membranes for anion exchange membrane fuel cells. *J. Memb. Sci.* **2008**, *311* (1–2), 319–325.
- (20) Domb, A. J.; Yudovin-Farber, I.; Golenser, J.; Beyth, N.; Weiss, E. I. Quaternary ammonium polyethyleneimine: Antibacterial activity. *J. Nanomater.* **2010**, *2010*, Article ID 826343.
- (21) Wu, J.; Su, Z. G.; Ma, G. H. A thermo- and pH-sensitive hydrogel composed of quaternized chitosan/glycerophosphate. *Int. J. Pharm.* **2006**, *315* (1–2), 1–11.
- (22) Tian, G.; Liu, L.; Meng, Q.; Cao, B. Preparation and characterization of cross-linked quaternised polyvinyl alcohol membrane/activated carbon composite electrode for membrane capacitive deionization. *Desalination* **2014**, *354*, 107–115.
- (23) Peng, Z. X.; Wang, L.; Du, L.; Guo, S. R.; Wang, X. Q.; Tang, T. T. Adjustment of the antibacterial activity and biocompatibility of hydroxypropyltrimethyl ammonium chloride chitosan by varying the degree of substitution of quaternary ammonium. *Carbohydr. Polym.* **2010**, *81* (2), 275–283.
- (24) Aeshala, L. M.; Uppaluri, R.; Verma, A. Electrochemical conversion of CO₂ to fuels: tuning of the reaction zone using suitable functional groups in a solid polymer electrolyte. *Phys. Chem. Chem. Phys.* **2014**, *16* (33), 17588–17594.
- (25) Merle, G.; Hosseiny, S. S.; Wessling, M.; Nijmeijer, K. New cross-linked PVA based polymer electrolyte membranes for alkaline fuel cells. *J. Memb. Sci.* **2012**, *409–410*, 191–199.
- (26) Feketeöldi, B.; Cermenek, B.; Spirk, C.; Schenk, A.; Grimmer, C.; Bodner, M.; Koller, M.; Ribitsch, V.; Hacker, V. Chitosan-Based Anion Exchange Membranes for Direct Ethanol Fuel Cells. *J. Membr. Sci. Technol.* **2016**, *6* (1), 145.
- (27) Grimmer, C.; Zacharias, R.; Grandi, M.; Cermenek, B.; Schenk, A.; Weinberger, S.; Mautner, F. A.; Bitschnau, B.; Hacker, V. Carbon Supported Ruthenium as Anode Catalyst for Alkaline Direct Borohydride Fuel Cells. *J. Phys. Chem. C.* **2015**, *119*, 23839–23844.
- (28) Wang, Y.; Shi, F.-F.; Yang, Y.-Y.; Cai, W.-B. Carbon supported Pd-Ni-P nanoalloy as an efficient catalyst for ethanol electro-oxidation in alkaline media. *J. Power Sources* **2013**, *243*, 369–373.
- (29) Lee, Y. W.; Han, S. B.; Park, K. W. Electrochemical properties of Pd nanostructures in alkaline solution. *Electrochem. commun.* **2009**, *11* (10), 1968–1971.
- (30) Ranninger, J. Development and Characterization of Pd-based Catalysts for the alkaline Direct Ethanol Fuel Cell. *Masterarbeit* **2017**, Graz University of Technology, Graz.
- (31) Cermenek, B.; Hacker, V.; Feketeöldi, B.; & Ribitsch, V. e!Polycat - Pt-freie Katalysatorsysteme und ethanolbeständige Polysaccharid-Membranen für die alkalische DEFC. *Final report* **2017**, FFG Austrian Research Promotion Agency, Climate and energy funds, Vienna. <https://www.energieforschung.at/assets/project/final-report/ePolycat-publizierbarer-Endbericht.pdf>
- (32) Hacker, V.; Cermenek, B. IEA AFC Annex 35: Brennstoffzellen für portable Anwendungen: Arbeitsperiode 2014-2017. *Nachhaltig Wirtschaften* vol. Berichte aus Energie- und Umweltforschung **28/2017** edn, Bundesministerium für Verkehr, Innovation und Technologie, Vienna. https://nachhaltigwirtschaften.at/resources/iea_pdf/endbericht_201728_afc-annex-35-848118.pdf