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Influence from sea water constituents on the efficiency of water electrolysis by PEM-cells

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Abstract

Among the sea-water specific impurities tested, magnesium has the most profound effect on PEM-cell degradation. Significant amounts of the cation was retrieved in the NAFION®-membrane structure after testing. Degradation was seen from a magnesium concentration as low as 3 10^{-7} mol/l, and increasing with concentration it led to a 86% increase of the area specific resistance at a concentration of 3 10^{-5} mol/l; equivalent to a conductivity of ~5 µS/cm. Other species (Cl^-, Na^+, SO_4^{2-}) seems to affect, though slowly, the performance negatively. If PEM will be used for electrolysis it seems therefore necessary to purify the feed water to ~1 µS/cm or even further while particularly focusing on the concentrations of polyvalent cations. e.g. magnesium.

Introduction

A Offshore energy harvesting has attracted interest [1] as an alternative to land-based energy harvesting, and since water electrolysis with proton conducting polymer cells (PEM-EC) recently has been employed in also larger scales [2] the current work has undertaken to study possible influences from sea-water constituents on the performance and durability of PEM-EC, which lend itself better than eg. alkaline electrolysis (AE) to the sometimes rapidly fluctuating power production rates offshore, cf. Figure 1.
Screening of selected constituents (Cl^-, Na^+, Mg^{2+}, Ca^{2+} SO_4^{2-}) has been done at significantly higher activities than equivalent to the usually prescribed purity level for PEM-EC of <1 µS/cm, in order to investigate if sea water purification may be targeted to only fewer constituents, leaving the majority at higher levels. It is known that chloride from sea water may impede the electrolysis process through competition with oxygen [3] and that insoluble precipitates tend to build up at the electrode in Alkaline electrolysis, when sea water is used directly [4], but very little information has been retrieved on possible influence from constituents used in lower concentrations for neither Alkaline- or PEM-electrolysis.

Experimental

Firstly a set of screening experiments and secondly experiments more targeted on the influence of magnesium and chloride were run at 70˚C and at -1 A/cm² with PEM-EC cells from NAFION® membranes with platinum and iridium oxide based electrodes. Prior to the exposure to sea water constituents, all cells were run with pure water for a week to stabilise performance. The electrolysis processes were characterized by both DC- and AC-techniques, and particularly the latter (EIS) enabled a more detailed assessment of the influence on electrode- and membrane processes from the sea water constituents. Cells and electrodes were subjected to microscopy and element analysis (SEM/EDX) after the experiments.

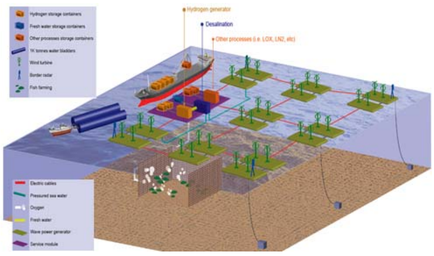

Figure 1: Early schematic outline for the offshore energy conversion platform in H2Ocean. Presently, the central platform has been divided and each operation, desalination, electrolysis, gas storage etc. is located separately on floating plants (FPSOs) permanently connected by sea-bed piping.

Substance, mg/l	Seawater	1 stage RO	2nd stage RO
Calcium	0.70	0.64	0
Magnesium	2.50	1.97	1.0
Sodium	63.60	58.75	0.38
Potassium	4.00	3.69	0.04
Chloride	106.00	97.06	0.62
Sulphate	5.00	4.40	0.01
Bi-carbonate	1.00	0.87	0
Carbonate	0.00	0	0
Boron	0.80	0.80	0.44
Free CO_2	1.22	1.26	1.35
Total as meq/l	3.11	2.84	0.02
EC µS/cm	359	318	4.49
pH value	6.2	6.06	4.20

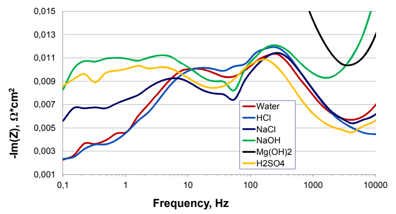

Figure 2: NAF117 with electrodes at 70˚C and @ 1 A/cm² after exposure to impurities of 3 10^{-5} mol/l

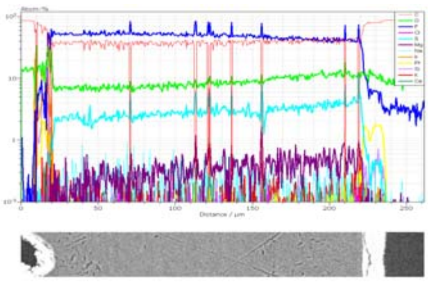

Figure 4: EDS line scan on cross section of a NAF115 membrane exposed to 2 * 10^{-4} mol/l $Mg(OH)_2$

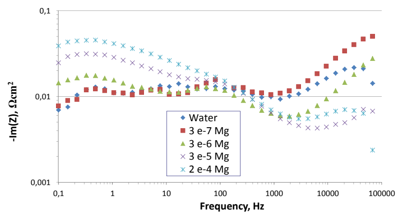

Figure 3: NAF115 with electrodes at 70˚C after exposure to various concentrations of $Mg(OH)_2$

Results and Discussion

Impurities fed to the PEM-cell at levels (3*10^{-5} mol/l) comparable to the levels coming out of the desalination system of the H2Ocean platform, cf. table, does not seem – except for magnesium – to significantly reduce the performance of the cells in a short time span (<500h).
But since all impurities, except chloride, do show a significantly increased contribution to the diffusional resistance, as seen by EIS, cf. Figure 2, it is likely to assume that they may affect the cell performance negatively over longer time spans.
Sodium, both in the form of NaCl and NaOH, shows larger contribution to the impedance in the low-frequency range than seen for chloride. When NaCl is usen in higher concentrations, a quite strong response in the low-frequency dominates the polarization resistance and sodium in generally is more detrimental to cell performance than chloride.

Magnesium has the strongest negative impact on the cell performance and is already at the lowest level of testing (3*10^{-7} mol/l) contributing to an increased resistance; an effect that increases proportionally with the concentration, cf. Figure 3, and results in a 86% increase of the area specific resistance of the cell at a concentration of 3*10^{-5} mol/l. Magnesium is seen accumulating in the membrane and is retrieved there after testing, as shown in the Figure 3, which is in accordance with the strong negative impact on cell performance. Calcium shows a comparable influence on cell performance.
Although a threshold for Magnesium impact on electrolysis performance may lie close to concentrations of 3*10^{-7} mol/l, it has not yet been verified in detail and more work lies ahead for clarifying the mechanisms and threshold levels of polyvalent catrions.

Conclusion and outlook

It seems reasonable to conclude that divalent cations will show a strong negative influence on the PEM cell performance already at very low concentrations (3*10^{-7} mol/l). Desalination of feed water for offshore PEM-EC will therefore have to put more focus on removal of polyvalent cations than on attaining a generally low conductivity.

Acknowledgements:

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