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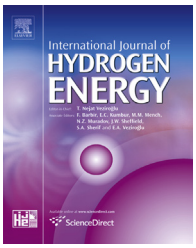

Modelling of the mechanical durability of constrained Nafion membrane under humidity cycling

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ABSTRACT

Several degradation processes limit the lifetime of polymer electrolyte membranes in fuel cells. One of these processes is humidity changes during the operation of the cell, which causes swelling and shrinking of the polymer electrolyte membrane. Changes in membrane size lead to periodic mechanical stresses, which damage the polymer. This damage leads to the formation of cracks in the membrane and, thus, results in early failure of the fuel cell.

This study presents a theoretical model that predicts the membrane lifetime depending on the thickness of the membrane and operating conditions of the periodic humidity cycle such as: amplitude of the humidity variation in the cycle, cycle duration, and temperature. The model is based on the assumption that mechanical destruction of the polymer electrolyte membrane, constrained in the fuel cell, occurs when the deformation energy applied to the membrane reaches a maximum value. The mechanical stress and deformation energy are estimated using the modified Eyring equation [Burlatsky et al., 2012]. The proposed model takes into account the influence of the temperature and water concentration on the membrane mechanical properties. The water concentration in the membrane is simulated by considering the water sorption/desorption kinetics and water sorption isotherm of the membrane.

The model was used to predict the lifetime of the non-reinforced membrane Nafion. The calculation results show that membrane mechanical durability correlates positively with increasing membrane thickness and temperature. The increase in the amplitude of the humidity cycle decreases membrane mechanical durability. At very short humidity cycles ($\leq$50–100 s), the membrane lifetime declines with increasing period of the humidity cycle. At higher humidity cycle period (>50–100 s), the increase of the cycle duration leads to continuous growth of the membrane lifetime.

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Nomenclature

Latin symbols

A	area, m^2
C_1	integration constant
C_2	integration constant, $1/s$
E	Young's modulus, Pa
F	force, N
f	frequency, Hz
k_B	Boltzmann's constant, J/K
L	membrane thickness, μm
N	mechanical membrane lifetime, *cycles*
N_h	mechanical membrane lifetime, h
q_T	amount of heat energy in a polymer entanglement, J/m^3
RH	relative humidity, %
s	distance in direction of F, m
T	temperature, °C
t	time, s
V	volume, m^3
V_{rel}	relative volume of an entanglement, m^3
w	specific energy, J/m^3
$\overline{w}_{def,max}$	mean maximal deformation energy, J/m^3

Greek symbols

α	dimensional change coefficient
ε	elongation
ε_x	elongation of the PEM in direction x
$\overline{\lambda}$	average water concentration in the membrane
λ_{mem}	water concentration inside membrane
λ_{sur}	water concentration on the membrane surface
λ_0	starting water concentration in the PEM
σ	tension, Pa
σ_x	tension parallel to the membrane surface, Pa
τ_{period}	cycle period, s
ϕ_{relax}	polymer relaxation time, s

Superscripts and Subscripts

abs	absorption
def	deformation
des	desorption
exp	value from experimental data
max	related to a maximal value
mem	membrane
min	related to a minimal value
sim	value obtained by simulation
sur	surface of the membrane
x	direction parallel to the surface of the PEM

Abbreviations

CFD	computational fluid dynamics
MEA	membrane electrode assembly
NMR	nuclear magnetic resonance
PEM	polymer electrolyte membrane
PEMFC	polymer electrolyte membrane fuel cell

Introduction

The mechanical stability of proton exchange membranes is one of key factors limiting the life expectancy of low temperature fuel cells [1–3]. During the last two decades, numerous experimental and theoretical studies have been performed in order to investigate the mechanical properties of proton exchange membranes in PEMFC and to identify influential factors [1,4–34].

The experimental investigations [11–15] showed that the Young's modulus of Nafion membranes decreases as the membrane hydration level and temperature increase. The papers [20,23] report the results of studies on the influence of the strain rate of Nafion, performed at various humidity levels and temperatures. The true stress in the membrane declines as a degree of polyelectrolyte swelling and temperature increases. Similar results have been observed for the yield stress.

The works [31–34] discuss the experimental results on Nafion membrane relaxations obtained using the dielectric spectroscopy and dynamic mechanical analysis at various temperature and relative humidity. The following relaxations were detected in the sulfo-cationic perfluorinated polymer electrolytes: α–relaxation (at f~10^0–10^1 Hz) is related to the mobility of the ionomer main and side chains via thermally activated destabilization of the electrostatic interactions; β-relaxation (at f~10^4–10^5 Hz) is associated with the motion of side chains; while γ–relaxation is attributed to local motions of the fluorocarbon –CF2- backbone segments. Nafion shows stiffening for temperatures and relative humidities above 90 °C and 60 %, which is related to α-relaxation [32].

In order to describe the stress behavior of Nafion under different conditions, such as various levels of strain or types of hydro thermal cycling, several models have been presented in the past [1,18–26].

Solasi et al. [16] proposed a nonlinear, time-dependent, constitutive model to predict the hydro-thermo mechanical behavior of Nafion membrane. The two-layer viscoplasticity model, which consisted of elastoplastic and elastic-viscous networks, takes into account the rate-dependent and rate-independent behavior of the polyelectrolyte. The model calculations of the mechanical stress in the membrane at different strain rates were found to agree satisfactorily with the relation test results.

Bograchev et al. [9] developed a linear elastic–plastic 2D finite elements model and applied this model to analyze the mechanical stress distribution in MEA taking into account the clamping condition in the fuel cell. The study showed that a maximum and strongly heterogeneous mechanical stress was observed under the junction seal joint/graphite plate in the membrane.

Al-Baghdadi [18] studied the hydro-thermal stress distribution in PEM fuel cells under regular operating conditions by using a CFD simulation. The obtained results demonstrated