

A Study of the Durability and Performance of a Proton Exchange Membrane Electrode Assembly used in the separation of Hydrogen from Helium

Michael Angelo, Keith Bethune, Richard Rocheleau

Hawaii Natural Energy Institute, University of Hawaii at Manoa, Honolulu, HI 96822, USA

Proton exchange membrane fuel cells (PEMFCs) have been successfully demonstrated as a technology for purifying helium (He) by electrochemically separating hydrogen (H₂) from a mixed gas stream where H₂ was considered a contaminant. Used in this capacity, PEMFCs are more energetically efficient, clean, and potentially cost effective than other separation methods such as cryogenic distillation. One specific application for this technology is to purify He gas that was used to purge cryogenic H₂ storage tanks and gaseous boil-off in fuel lines for rocket engines that utilize liquid H₂ as the fuel. Separation of He and H₂ using PEMFCs is beneficial to organizations such as the National Aeronautic and Space Administration (NASA) that require liquid H₂ fueled engines.

Previous work demonstrated that a PEMFC operated as an electrolytic cell at the limiting current could attain outlet streams with less than 50 parts per million (ppm) H₂ by controlling the flow rate of gases in the feed (1). The fuel cell operating conditions that resulted in the greatest He purity were also identified (2). However, the effects of continuous operation for an extended duration on the fraction of H₂ removed by the PEMFC (i.e. the He purity or equivalently the membrane electrode assembly (MEA) performance) and durability were not investigated. This is an important consideration because most commercially available MEAs were designed to be operated as a galvanic cell with water production on the cathode. In electrolytic H₂/He separation, H₂ is oxidized on the anode and reduced on the cathode. Thus, the effect of long-term operation without water production was unknown.

To study MEA performance and durability over time, a PEMFC was operated as an electrolytic cell at its limiting current with an inlet stream consisting of 10 % H₂ in nitrogen (N₂) (dry-gas basis) for 1100 load hours. Commercially available MEAs with platinum catalysts and carbon supports (Pt/C) were used. N₂ was employed as a surrogate gas for He during long-term operation due to the cost considerations of continuous testing with He. The H₂ and N₂ were supplied to the anode stream and the cathode inlet was capped. The anode outlet consisted of purified N₂ and the cathode outlet was primarily H₂.

To quantify MEA performance over time, the inert gas was periodically switched from N₂ to He during the long duration experiments to mirror actual operating conditions and the fraction of H₂ in the anode outlet stream was measured using gas chromatography.

The results of these experiments were given in Fig. 1 and showed that the fraction of H₂ in the outlet increased with number of hours that the cell was under load.

Additional experiments were conducted to evaluate how the fraction of H₂ removed by the fuel cell was affected by the type of inert gas in the feed. For these experiments, the outlet fraction of H₂ was measured with either N₂ or

He as the inert gas for several different inlet fractions of H₂ up to 50 %. These tests were not performed for extended durations, but showed that the fraction of H₂ in the outlet was greater when N₂ was the inert due to greater gas phase resistance to H₂ diffusion to the Pt/C catalyst.

To investigate MEA durability over time, diagnostic measurements were performed periodically to evaluate changes in MEA properties. Diagnostics included: (i) cyclic voltammetry to quantify the electrochemically active area (ECA) of the anode and the cathode, (ii) linear sweep voltammetry to measure H₂ crossover to investigate membrane thinning and quantify the membrane resistance to electrical shorting to assess possible pinhole formation, and (iii) H₂ pump experiments to calculate the proton conductivity of the MEA in order to observe changes in its hydration state.

The results of the MEA durability experiments showed no indications of membrane thinning, pinhole formation, or dehydration. Extended operation did, however, decrease the ECA of the catalyst on both the anode and the cathode. The decrease in He purity was attributed to losses in the ECA since less catalyst sites were available for the reaction of H₂. The mechanism for the loss in ECA was not definitively known.

Future work will consider operating strategies to mitigate ECA loss and identify the specific mechanism responsible for the decrease.

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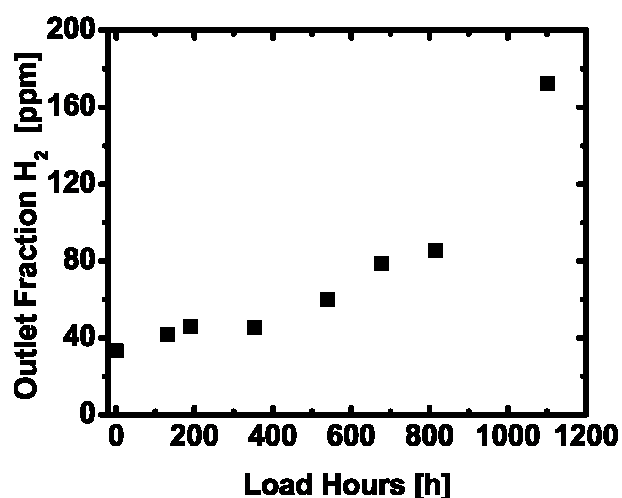


Fig. 1. Fraction of H₂ in outlet vs. load hours.