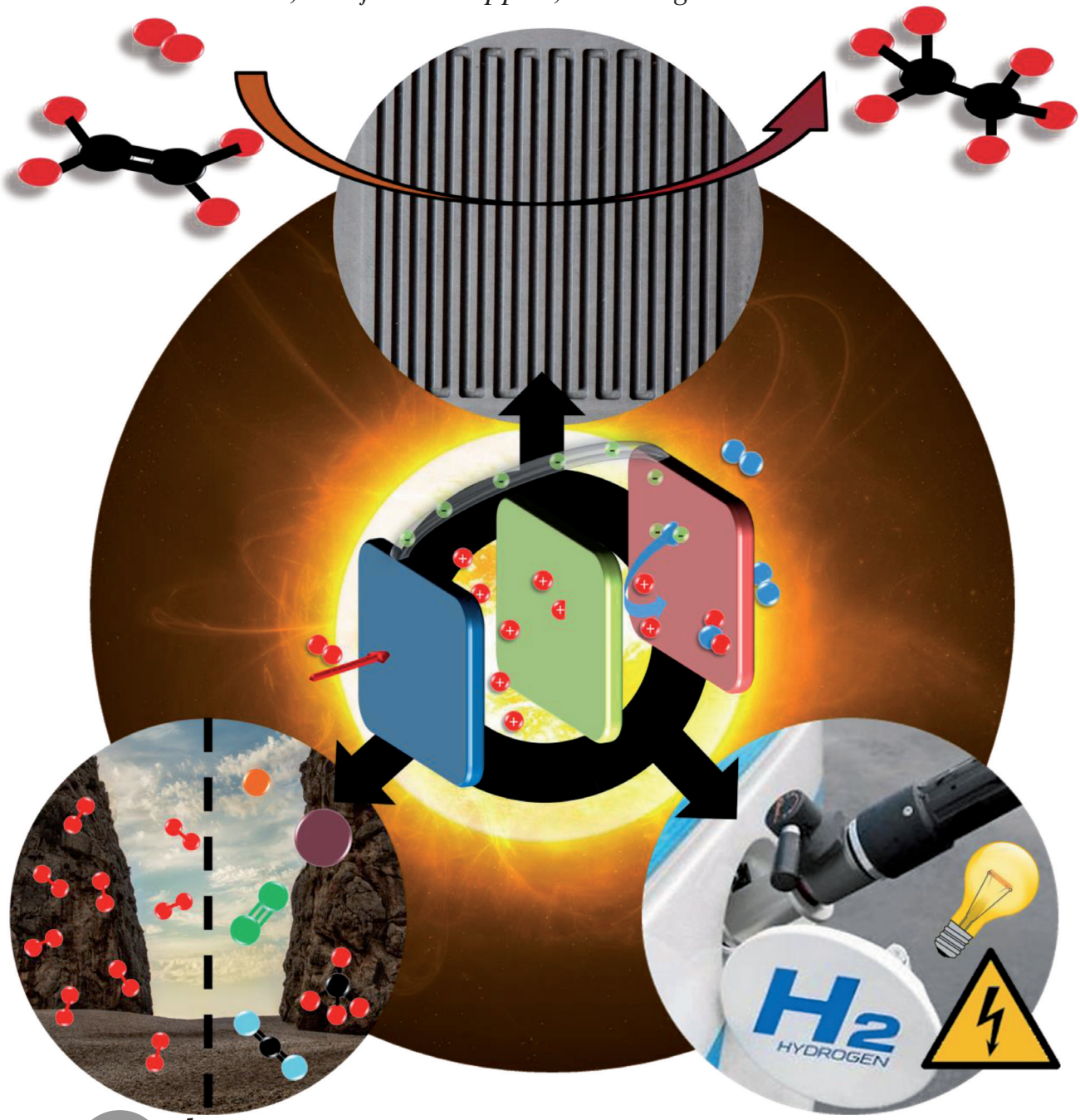
Hydrogen Separation | Hot Paper

International Edition: DOI: 10.1002/anie.201500751
German Edition: DOI: 10.1002/ange.201500751

Inverted Fuel Cell: Room-Temperature Hydrogen Separation from an Exhaust Gas by Using a Commercial Short-Circuited PEM Fuel Cell without Applying any Electrical Voltage**

*Sebastian Friebe, Benjamin Geppert, and Jürgen Caro**



Abstract: *A short-circuited PEM fuel cell with a Nafion membrane has been evaluated in the room-temperature separation of hydrogen from exhaust gas streams. The separated hydrogen can be recovered or consumed in an in situ olefin hydrogenation when the fuel cell is operated as catalytic membrane reactor. Without applying an outer electrical voltage, there is a continuous hydrogen flux from the higher to the lower hydrogen partial pressure side through the Nafion membrane. On the feed side of the Nafion membrane, hydrogen is catalytically split into protons and electrons by the Pt/C electrocatalyst. The protons diffuse through the Nafion membrane, the electrons follow the short-circuit between the two brass current collectors. On the cathode side, protons and electrons recombine, and hydrogen is released.*

Hydrogen is a high-demand product that is mainly produced by steam reforming and used for ammonia and methanol synthesis. Hydrogen is also used in oil reforming for the production of high-grade petrol and to remove sulfur compounds. Hydrogen is becoming increasingly attractive as an energy carrier because it can be combusted with oxygen (from air) to water. A proton-exchange membrane fuel cell (PEM FC) with a Nafion proton-exchange membrane (PEM) is usually applied to transform the chemical energy liberated during the electrochemical hydrogen combustion into electrical energy. The heart of the PEM FC is the proton-conducting Nafion membrane. Hydrogen is split on the anode side at the Pt/C electrocatalyst of the PEM FC into protons and electrons. The protons diffuse through the Nafion membrane, and the electrons follow the outer circuit and perform "work". On the cathode side of the PEM FC, water is formed from the protons, electrons, and oxygen from the air (Supporting Information, Figure S1). For the function of the PEM FC it is crucial that the Nafion membrane conducts only protons and no electrons because this would result in an "inner short-circuit". In our concept of a reverse PEM FC for hydrogen separation, we have deliberately caused this short-circuit by connecting the two brass current collectors which are attached to the Pt/C electrocatalyst layers on both sides of the Nafion membrane by a cable (Figure 1 a).

Herein we study a new principle to separate hydrogen from an exhaust gas that contains a few vol% hydrogen through a Nafion membrane using a commercial PEM FC with an external short-circuit. Our concept is similar in a way to oxygen or hydrogen high-temperature permeation through mixed conducting ceramics. Mixed conductivity means that these ceramic membranes show at their working temperature

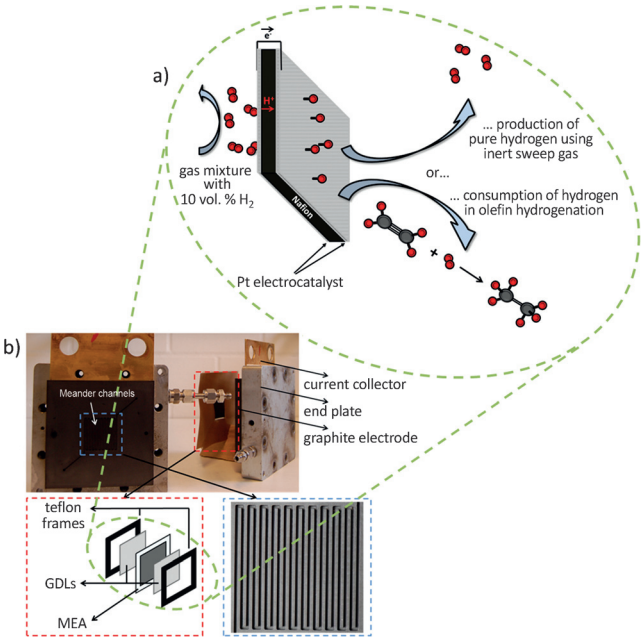


Figure 1. Principle of a reverse fuel cell for hydrogen recovery and olefin hydrogenation. a) Voltage-free hydrogen production and olefin hydrogenation in a fuel cell with an external short-cut. b) Setup of the fuel cell.

of about 800 °C sufficient oxygen-ion/electron[1–3] or proton/electron[4–6] conductivity in the case of oxygen and hydrogen transport, respectively. There are some attempts to increase the oxygen or hydrogen transport by an external short-circuit between the feed and the sweep side. For instance, Zhang et al. investigated the permeation of the above mentioned gases through short-circuited ceramics at high temperatures. However, the short-circuit was realized with silver paste and the fluxes of oxygen and hydrogen could be slightly improved at temperatures between 800 and 900 °C.[7–11]

Our concept for the hydrogen separation from exhaust gases works with a Nafion membrane in a commercial PEM FC at room temperature. As Nafion only conducts protons, the nascent electrons are conducted to the other side of the Nafion membrane via a cable between the two brass current collectors. The driving force for hydrogen transport is the concentration gradient of hydrogen between the two sides of the Nafion membrane. The steady-state concentration gradient is formed by supplying new hydrogen-containing gas to the feed side and using a sweep gas such as nitrogen to remove the permeated hydrogen from the cathode side. We could also reduce the hydrogen partial pressure on the anode side by consuming the hydrogen in a chemical reaction such as the ethylene hydrogenation to ethane. Additionally we analyzed the hydrogen permeance as a function of an adjustable resistor between the two brass current collectors, thus controlling the hydrogen flux by the electron flow as limiting parameter. Furthermore we calculated the proton conductivity across the membrane with the help of the Nernst–Einstein equation.

First of all we investigated the hydrogen separation from binary gas mixtures hydrogen/methane with different hydro-

[*] S. Friebe, B. Geppert, Prof. Dr. J. Caro
Institute of Physical Chemistry and Electrochemistry
Leibniz University Hannover
Callinstrasse 22, 30167 Hannover (Germany)
E-mail: caro@pci.uni-hannover.de

[**] We thank A. Bayer and E. Lerbs from SolviCore GmbH & Co. KG in Hanau for supplying the Nafion membranes and Dr. G. Hübner from Volkswagen Technologiezentrum Isenbüttel for supplying the fuel cell. PEM = proton exchange membrane.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201500751.

gen concentrations between 0 and 100 vol% (Figure 2). Figure 2a shows the hydrogen permeance for two operation modes: When nitrogen is used as a sweep gas to reduce the hydrogen partial pressure on the permeate side of the membrane, a remarkable hydrogen flux can be observed even for a gas mixture containing 5 vol%. This hydrogen flux comes to saturation with increasing hydrogen concentration in the feed. In a second experiment, air has been used as reactive sweep gas. In this experiment, the permeated hydrogen is burnt at the Pt/C electrocatalyst with the oxygen from air. Since in this operation mode the hydrogen partial pressure is reduced drastically on the permeate side by hydrogen combustion, the concentration gradient as driving force for hydrogen transport increases, and correspondingly the hydrogen permeance is doubled in comparison with the inert sweep gas nitrogen. We also studied the separability of hydrogen from other gases, namely N_2, CO_2, helium, and argon. For this we analyzed the permeances of the hydrogen in equimolar gas mixtures with the above-mentioned gases and checked if hydrogen is the only signal in the gas chromatograph. Figure 2b shows the results for the different gas mixtures.

Since the proton conductivity depends strongly on the moisture of the Nafion, small variations of the moisture can lead to even larger variations in the proton conductivity. Additionally, varying compression of the Nafion membrane can lead to changes in performance.[12] Nevertheless there were no other signals except the hydrogen signal in the gas chromatograph, meaning that the separation of hydrogen from other gases is also possible with a short-circuited fuel cell.

The idea behind these experiments was to identify the rate-limiting step of our hydrogen separation. Along with the measurements above, we analyzed the hydrogen permeance as a function of an adjustable resistor. Therefore, we placed a resistor in the "short-circuit way" and changed its resistance between 0 and 100 kΩ. Figure 3a indicates that the proton conductivity is rate limiting for the hydrogen permeance. If the resistance of the adjustable resistor is zero, the hydrogen permeance is identical to the measurements without resistor. With increasing resistance, the hydrogen permeance decreases. Already a resistance of 100 Ω decreases the permeance to 10% of its starting value, meaning that the electron transport becomes more and more the limiting parameter. With even higher resistances than 1 kΩ the permeance is approximately zero. This measurement clarifies that not only the proton conductivity through the Nafion is important to understand the mechanism of this process but also the flow of electrons.

Figure 3b shows the proton conductivity of the Nafion membrane as a function of the hydrogen concentration in the binary mixture hydrogen/methane. Therefore, we used different ratios between hydrogen and methane and calculated the proton conductivity by using the Nernst–Einstein Equation (1).

The PEM FCs work with Nafion membranes.[13] Nafion as a sulfonated tetrafluoroethylene polymer (Supporting Information, Figure S3) is known as a cation conductor and as an anion barrier. The highly selective proton exchange across the membrane proceeds over the sulfonic acid groups. The proton conductivity σ_{H^+} depends strongly on the moisture of the polymer membrane. Investigations on the influence of the moisture showed that more wet membranes lead to higher proton conductivity, but it should be annotated that an excessive moisture can also inhibit the protons to cross the membrane.[14–16] The conductivity of the dense polymer can be concluded with the help of the Nernst–Einstein equation (1):

$$\sigma_{H^+} = \frac{J_{H_2}\, z_{H^+}\, e\, L}{\Delta\phi} \qquad (1)$$

where J_{H_2} is the hydrogen flux, z_{H^+} the proton charge, e the elementary charge, L the membrane thickness, and $\Delta\phi$ the potential gradient.

Figure 3b clarifies that the proton conductivity is nearly constant over the whole range of hydrogen concentration in the mixed gas which recommends Nafion as a separating membrane also for low hydrogen concentrations. This means that if hydrogen is available in the gas mixture, the proton transport through the Nafion membrane is almost the same for any hydrogen concentration. This result is in good agreement with Figure 2a, which shows the fast saturation

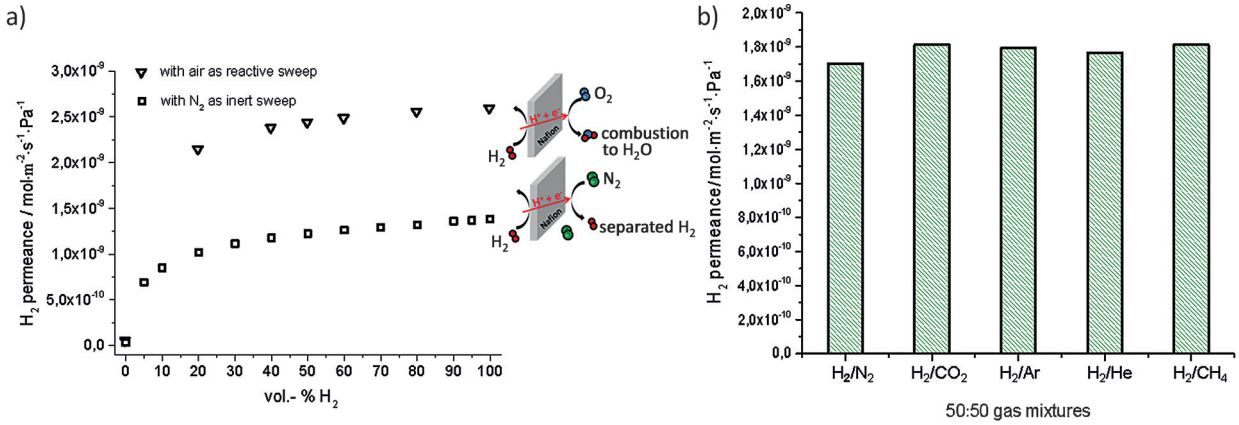


Figure 2. Hydrogen purification from a simulated waste gas. a) Hydrogen permeance as a function of the hydrogen concentration in a binary gas mixture with methane at room temperature. b) Hydrogen separation from different simulated waste gases at room temperature. Nitrogen was used as sweep gas except for the binary mixture of H_2/N_2, where argon was the sweep gas.

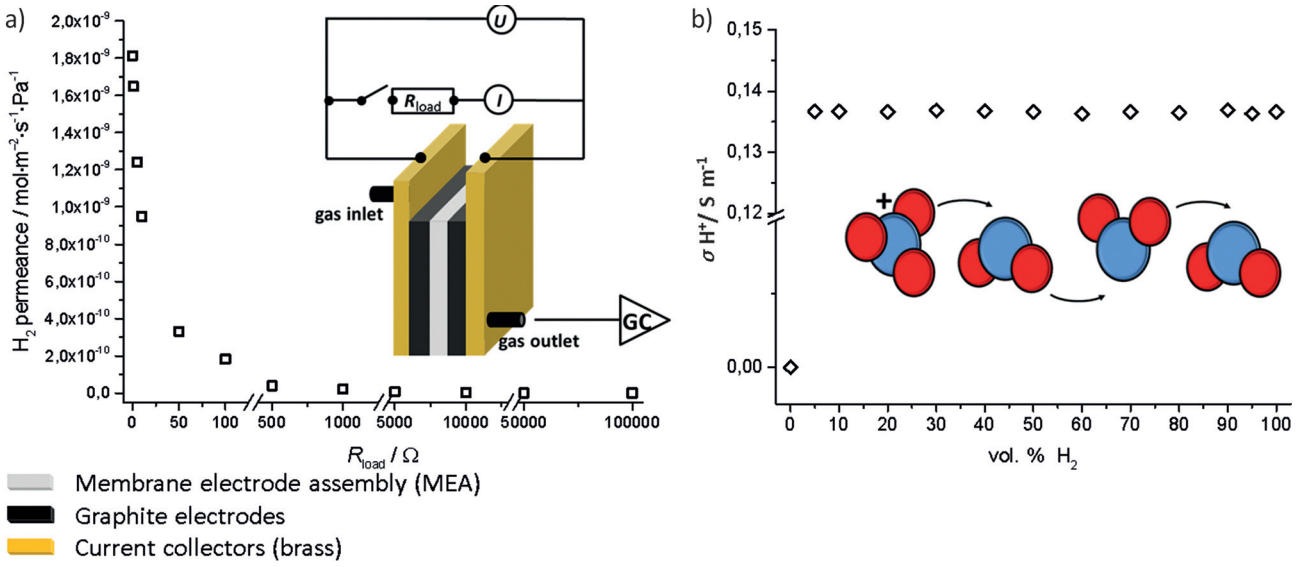


Figure 3. Influence of electron transport and hydrogen concentration in the feed. a) Influence of a limiting electron flux caused about by an adjustable resistor on the hydrogen permeance in a binary, equimolar mixture with methane (N_2 as inert sweep). Inset: the setup for the limiting electron flux. b) Proton conductivity as a function of the hydrogen concentration in a binary mixture with methane (N_2 as inert sweep). Inset: the common Grotthus proton-transport mechanism through the Nafion membrane.[17,18]

of the hydrogen permeance with increasing hydrogen concentration in the gas mixture.

Along with the hydrogen separation and purification processes, we tested our short-circuited PEM FC as catalytic membrane reactor for in situ ethylene hydrogenation at room temperature. In this case, ethylene on permeate side of the Nafion membrane (Figure 1 a) can be considered as a reactive sweep gas that consumes the permeated hydrogen, thus reducing its partial pressure. Fortunately, we can use for this hydrogenation the same Pt/C electrocatalyst as for the hydrogen liberation on the permeate side of the Nafion membrane by recombining the protons and electrons to atomic and molecular hydrogen. From the gas chromatogram in Figure 4 it follows that remarkable amounts of ethane have been formed by the in situ hydrogenation of ethylene. Moreover, from the absence of any hydrogen signal it can be concluded that all permeated hydrogen has been consumed in the catalytic ethylene hydrogenation. As expected, only the hydrated short-circuited Nafion membrane transports hydrogen, since only wet Nafion is an excellent proton conductor. These results are in good agreement with the dependence of the proton conductivity on the moisture.[13–15]

In conclusion, we have shown the room-temperature separation of hydrogen from other gases by means of a short-circuited commercial proton exchange fuel cell with a Nafion membrane without applying an electrical voltage. If there is a gradient in the hydrogen partial pressure over the proton-transporting Nafion membrane, hydrogen can be separated from exhaust gases that contain a few vol% hydrogen. We separated hydrogen from different gases such as methane, carbon dioxide, nitrogen, argon, and helium. By using a vacuum pump or a condensable sweep gas on the permeate side, hydrogen can be recovered. The hydrogen partial pressure on the permeate side of the Nafion membrane can also be reduced by a hydrogen-consuming reaction. As

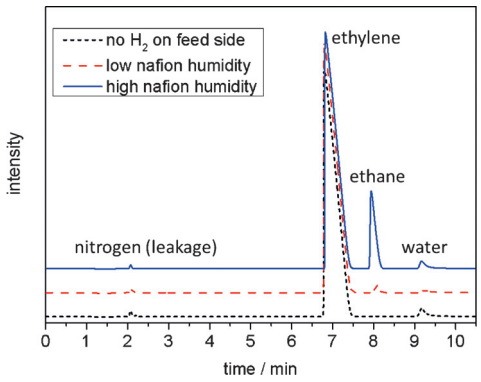


Figure 4. Gas chromatogram of the product gas for the olefin hydrogenation for Nafion membranes of different humidity.

a proof of principle, we showed the in situ hydrogenation of ethylene to ethane at room temperature operating our proton exchange fuel cell as catalytic membrane reactor. The hydrogen flux can be switched by a resistor that controls the electron flux in the short-circuit. The short-circuited fuel cell with proton exchange membrane is a good example of the combination of separation (hydrogen recovery), energy production (electric current), and catalysis (olefin hydrogenation).

Experimental Section

The experimental investigations focused on the hydrogen-separation performance and in situ olefin hydrogenation with the help of a Nafion-based PEM FC with an external short-circuit. We used a commercial Greenerity H600 STD MEA, gas-diffusion layers (GDLs; Supporting Information, Figure S2) and also Teflon frames from the company SolviCore GmbH & Co. KG to evaluate our

principle. The active area on the MEA membranes was 10 cm^2 with a platin coating of 0.85 $mg\,cm^{-2}$. The thickness of the platin coating was around 8–15 μm. The fuel cell, the flow field of which consisted of 20 equally spaced meander like channels with a total distance of around 0.6 m between the gas inlet and the exit, was supplied by Volkswagen AG, Technology Center Isenbüttel (Figure 1b).

Before the measurements, the MEA was moistened with distilled water to enhance the proton conductivity, whereas the used gas mixtures were purged through a water reservoir to maintain the moisture. For gas analysis we used a gas chromatograph (Agilent Technologies 7890 B). For controlling the hydrogen flux via the electron flux in the short-circuit, a resistive cascade (CML R1-1000) was used.

Keywords: electrocatalysis · fuel cells · hydrogen · membrane · separation

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 7790–7794
Angew. Chem. **2015**, *127*, 7788–7904

[1] J. M. Serra, V. B. Vert, O. Büchler, W. A. Meulenberg, H. P. Buchkremer, *Chem. Mater.* **2008**, *20*, 3867–3875.
[2] X. Chen, L. Huang, Y. Wei, H. Wang, *J. Membr. Sci.* **2011**, *368*, 159–164.
[3] J. Sunarso, S. Baumann, J. M. Serra, W. A. Meulenberg, S. Liu, Y. S. Lin, J. C. Diniz da Costa, *J. Membr. Sci.* **2008**, *320*, 13–41.
[4] X. Qi, Y. S. Li, *Solid State Ionics* **2000**, *130*, 149–156.
[5] S. Ricote, A. Manerbino, N. P. Sullivan, *J. Mater. Sci.* **2014**, *49*, 4332–4340.
[6] J. W. Phair, S. P. S. Badwal, *Ionics* **2014**, *12*, 103–115.
[7] K. Zhang, J. Sunarso, G. H. Pham, S. Wang, S. Liu, *Ceram. Int.* **2014**, *40*, 791–797.
[8] K. Zhang, B. Meng, X. Tan, L. Liu, S. Wang, S. Liu, *J. Am. Ceram. Soc.* **2014**, *97*, 120–126.
[9] K. Zhang, Y. Zou, C. Su, Z. Shao, L. Liu, S. Wang, S. Liu, *J. Membr. Sci.* **2013**, *427*, 168–175.
[10] K. Zhang, L. Liu, J. Sunarso, H. Yu, V. Pareek, S. Liu, *Energy Fuels* **2014**, *28*, 349–355.
[11] K. Zhang, Z. Shao, C. Li, S. Liu, *Energy Environ. Sci.* **2014**, *5*, 5257–5264.
[12] W.-k. Lee, C.-H. Ho, J. W. Van Zee, M. Murthy, *J. Power Sources* **1999**, *84*, 45–51.
[13] V. Mehta, J. S. Cooper, *J. Power Sources* **2003**, *114*, 32–53.
[14] C. Yang, S. Srinivasan, A. B. Bocarsly, S. Tulyani, J. B. Benziger, *J. Membr. Sci.* **2004**, *237*, 145–161.
[15] Y.-S. Ye, J. Rick, B.-J. Hwang, *Polymers* **2004**, *4*, 913–963.
[16] U. Pasaogullari, C. Y. Wang, *J. Electrochem. Soc.* **2004**, *151*, A399–A406.
[17] N. Miyake, J. S. Wainright, R. F. Savinell, *J. Electrochem. Soc.* **2001**, *148*, A898–A904.
[18] G. A. Ludueña, T. D. Kühne, D. Sebastiani, *Chem. Mater.* **2011**, *23*, 1424–1429.

Received: January 27, 2015
Published online: May 26, 2015

