



## Nafion–Titanate Nanotube Composite Membranes for PEMFC Operating at High Temperature

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Nafion–titanate nanotube composites were investigated as electrolytes for proton exchange membrane fuel cells (PEMFCs) operating at high temperature  $T$ . With the addition of 5–15 wt % of nanotubes to the ionomer, PEMFC performance can be significantly sustained for  $T$  up to 130°C. The polarization curves of PEMFCs using the composite electrolytes reflect a competing effect between an increase in water uptake due to the extremely large surface area of the nanotubes and a decrease in proton conductivity of the composites.

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Proton exchange membranes fuel cells (PEMFCs) are being considered as an efficient technology for electrical energy generation.<sup>1</sup> Such environmentally friendly technology is envisioned as a future power source for applications ranging from low-power portable electronic devices to kilowatt vehicle traction systems.<sup>1</sup> Despite the steady advances of this technology, key issues regarding PEMFC constituent properties (electrolyte and electrodes) still restrict its widespread application. For more than 20 years, the dominant PEMFC electrolyte has been the Nafion perfluorinated membrane.<sup>1</sup> This material, however, limits the cell operation temperature  $T$  to ~80°C due to its intrinsic proton transport mechanism, which is assisted by the presence of water molecules.<sup>2,3</sup> Operation at higher temperatures would significantly boost PEMFC performance, enhancing important parameters, such as electrode reaction kinetics, and CO tolerance, and allowing an easier thermal management of the system.<sup>4</sup>

Considerable research efforts have been devoted to the fabrication of Nafion-inorganic composite membranes in attempts to overcome such temperature limitation.<sup>2,5</sup> The main motivation for the dispersion of an inorganic phase (usually a ceramic oxide or an acid salt) in the polymeric matrix is to provide a hygroscopic surface for water retention, allowing PEMFC operation up to ~130°C. Several ceramic oxides, such as TiO<sub>2</sub>, SiO<sub>2</sub>, and ZrO<sub>2</sub>, have been tested in composite membranes.<sup>6–8</sup> The results indicate that oxide composition, particle size distribution, relative volumetric fraction, and physical–chemical properties of the oxide surfaces are important factors affecting PEMFC performance at high temperature (~130°C) and/or low relative humidity (RH).<sup>6,9,10</sup> In general, it is observed that PEMFCs using Nafion-based composite electrolytes operating with hydrogen exhibit a more pronounced enhancement of performance with decreasing RH (<100%) rather than with increasing temperature ( $T > 100^\circ\text{C}$ ).<sup>8,11</sup> Whereas, the performance of a direct alcohol fuel cell (DAFC) is clearly enhanced at high temperatures by using such composite electrolytes. In this case, the lower diffusion of methanol across the composite membrane due to presence of the inorganic phase is believed to be significant.<sup>9,10</sup> Nevertheless, the exact role played by the inorganic phase is still a matter of discussion, and different studies disagree whether the interaction between the inorganic phase and the sulfonic chains of the polymer or the specific surface area of the filler is the most relevant feature for the improvement of the performance of the PEMFC.<sup>6–8</sup> Moreover, the addition of an inorganic proton conductor, such as zirconium phosphates, in the ionomer matrix is also being investigated for high-temperature PEMFC operation.<sup>5,12</sup> In this case, both the

hygroscopic surface of the filler and the contribution for proton transport are believed to be responsible for increasing the operation temperature of the fuel cell with reasonable performance.<sup>5</sup> In this scenario, a composite membrane comprised of Nafion and an inorganic phase displaying both high surface area and proton-conducting properties can be considered as a promising PEMFC electrolyte.

The discovery of a simple and efficient alkaline hydrothermal method for production of titania nanotubes by Kasuga et al.<sup>13</sup> have spurred a number of studies regarding both the production and application of these nanostructures. It has been observed that subtle variations in the alkaline hydrothermal treatment and subsequent washing–neutralization processes result in materials having different morphologies (nanotubes, nanowires, and nanofibers) and/or different compositions (TiO<sub>2</sub>, H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>, Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>, etc.).<sup>14</sup> Several applications have been proposed for these fibrous structures, including dye-sensitized solar cells, lithium-intercalation, hydrogen storage, photocatalysis, etc.<sup>14</sup> In particular, H and Na titanate nanotubes have shown interesting electrochemical properties, including a fairly large protonic conductivity.<sup>15,16</sup> Based on this characteristic, it has been proposed that H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> nanotubes could be utilized as electrolytes in PEMFCs.<sup>16</sup>

Although the utilization of TiO<sub>2</sub> nanoparticles as fillers in composite electrolyte membranes has been already considerably studied, the utilization of TiO<sub>2</sub>-derived nanotubes to PEMFC technology, to the extent of our knowledge, has been restricted to catalysts support in the electrodes.<sup>17</sup>

### Experimental

**Preparation and characterization of titanate nanotubes.**—Titanate nanotubes (TNTs) were produced by a variation of the alkaline hydrothermal method.<sup>13</sup> Instead of treatment in autoclave, the nanotubes were produced by refluxing an aqueous solution of NaOH (10 mol L<sup>-1</sup>) and TiO<sub>2</sub> powder (Sigma Aldrich, 99% anatase) for 24 h in a Pyrex container. The resulting paste was thoroughly washed and neutralized with HCl solution (1 mol L<sup>-1</sup>), and dried. The TNTs were analyzed by transmission electron microscopy (TEM), X-ray diffraction (XRD), and energy dispersive X-ray spectroscopy (EDS).

**Preparation of Nafion–TNT membranes.**—Nafion–titanate nanotube composite membranes having 0–15 wt % of titanate nanotubes were prepared by casting. Initially, a commercial Nafion 5% solution (DuPont) was evaporated at ~80°C and redissolved in dimethylsulfoxide [(DMSO), Aldrich, PA] under magnetic stirring. The resulting solution was kept under stirring for 24 h at room temperature. The desired weight fraction of the nanotubes was dispersed in DMSO by ultrasonic bath for 1 h. The TNT dispersion was then added to the Nafion solution, and the resulting solution was further

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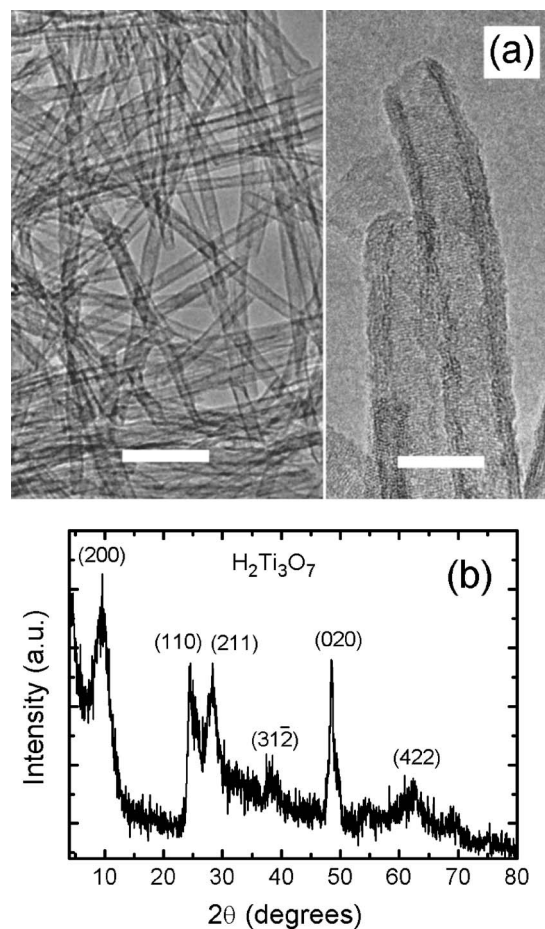
homogenized in ultrasound for 30 min followed by magnetic stirring for 24 h. The membranes were cast by pouring the Nafion–TNT solution in an aluminum mold. The mold was inserted into a resistive furnace, and the evaporation was carried out by heat treatments at increasing temperature from 80 to 160°C with 2 h of dwell time at each temperature.<sup>18</sup> Pure Nafion membranes were cast following the same thermal profile. The resulting membranes were cleaned and activated by heating in H<sub>2</sub>O at 80°C/1 h, followed by consecutive treatments at 80°C/1 h in 7 M HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, and H<sub>2</sub>SO<sub>4</sub>, with intercalated treatments with H<sub>2</sub>O and a final step of successive washings with H<sub>2</sub>O until pH 7 was reached.

**Characterization of Nafion–TNT membranes.**— The water uptake (WT) of the cast membranes, defined as WT (in percent) =  $(m_S - m_D)/m_D$ , was evaluated by weighing both the dry membrane ( $m_D$ ), after thermal treatment at 110°C/3 h, and the water saturated membrane ( $m_S$ ) after boiling in water for 1 h. The equivalent weight (EW) was determined by an exchange of acidic protons with Na<sup>+</sup> ions in solution.<sup>12</sup> The acidic membrane is placed in a NaCl solution (2 mol L<sup>-1</sup>) and allowed to exchange for 30 min. Then, the sodic membrane is titrated to the phenolphthalein end point with NaOH (0.025 M) to determine the quantity of exchanged H<sup>+</sup> ions. The EW was calculated by using the dry weight of the membrane and the quantity of exchanged protons. The obtained values of the EW are close to 1000 for all cast membranes, in good agreement with reported data for Nafion.<sup>3,12</sup> The apparent density of the samples was evaluated by the Archimedes' method. The obtained values are close to the reported ones for Nafion (~1.96 g/cm<sup>3</sup>), and increasing the nanotube content slightly increases the apparent density, in good agreement with the rule of mixtures. The electrical conductivity of the membranes was measured by impedance spectroscopy (IS) by using a frequency analyzer (Solartron 1260) and a homemade Teflon sample holder with Pt terminal leads and a K-type thermocouple. Two-probe electrochemical IS measurements were performed in the 25–80°C temperature range with RH ~98% in the 100 Hz to 1 MHz frequency range with applied amplitude of 200 mV.

**Preparation and characterization of PEMFC.**— To investigate the dependence of the nanotubes concentration on the PEMFC performance, membrane electrode assemblies (MEA) were fabricated. Single-cell gas electrodes were formed by independent diffusion and catalytic layers. The diffusion layer was prepared by deposition of a mixture of carbon black (Vulcan XC-72R, Cabot) and Teflon emulsion (PTFE–TE-306A, DuPont) on both sides of carbon cloth substrate (E-TEK). A catalytic layer was deposited by painting a mixture of Nafion solution and the electrocatalysts Pt/C, 20% (E-TEK) over the diffusion layers, with Pt load of 0.4 mg/cm<sup>2</sup>. MEAs, with 5 cm<sup>2</sup> area, were fabricated by hot pressing both electrodes to the fabricated membranes at 125°C and 1000 kgf cm<sup>-2</sup> for 2 min.

The polarization curves (*I*-*V*) were taken at different measuring temperatures by progressively heating the system from 80°C up to 130°C. For each measuring temperature, after temperature stabilization the system was conditioned by draining electrical current at a fixed voltage of ~0.7 V for 2 h before data collection in order to reach steady state. For measurements at 80°C, the reactant gases, O<sub>2</sub> and H<sub>2</sub>, were water saturated by passing them through humidifiers at 85°C and 95°C, respectively. For higher temperatures (100–130°C), the humidifiers were set at the same temperature of the cell. All experiments were performed under an absolute pressure of 3 bar to assure 100% of relative humidity.

For selected TNT concentrations, two batches of membranes were produced for checking the reproducibility of the *I*-*V* results. Both batches were observed to exhibit practically the same results within the experimental accuracy. In addition, the stability of the composite electrolytes was checked by cycling the single cells from 80°C up to 130°C and measuring the resulting *I*-*V* curves at high temperature. It was found that the samples are stable within the time



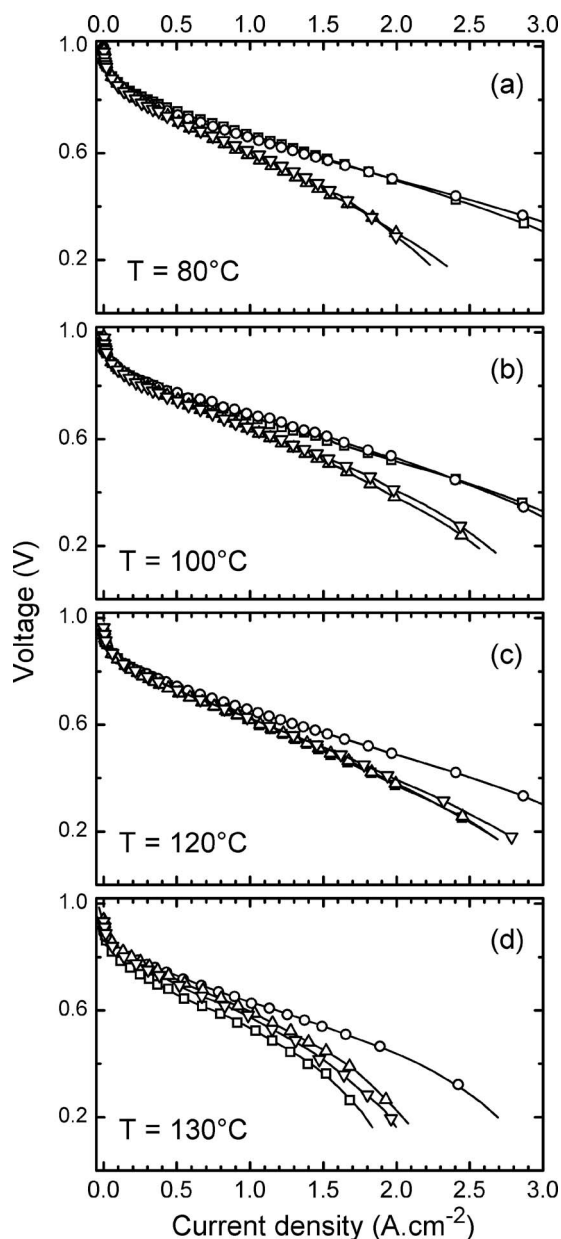
**Figure 1.** (a) Transmission electron microscopy images of the titanate nanotubes. Scale bars represent 50 nm and 10 nm in the left and right images, respectively. (b) X-ray-diffraction pattern of the titanate nanotubes. The identified reflections correspond to the H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> structure.

period of measurements, which accumulates ~50 h of operation at high temperature.

## Results

Figure 1a displays TEM images of the titanate nanotubes. The nanotubes present relatively narrow size dispersion, having 7–10 nm o.d., 3–5 nm i.d., and 200–400 nm length. In fact, the morphology of the obtained nanotubes is very similar to the ones obtained by the conventional hydrothermal methods.<sup>13,14</sup> Figure 1b depicts the XRD pattern of the TNT. Several peaks can be identified that correspond to the hydrogen titanate (H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>) structure. EDS analysis detected minor amounts of Na, Si, and Cl impurities in the as prepared materials (not shown).

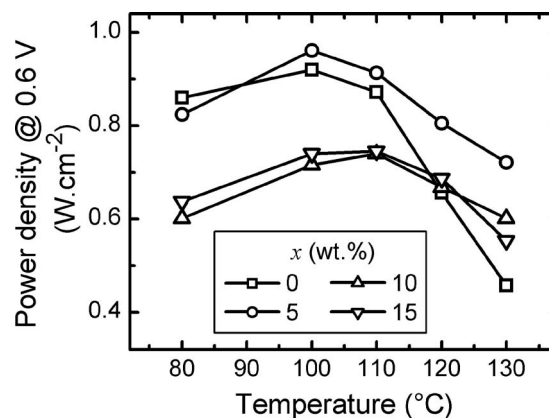
Nafion–titanate composite membranes with TNT concentration (*x*) ranging from 0 to 15 wt % were incorporated in MEA assemblies with standard Pt/C electrodes. The polarization curves of the resulting PEMFC measured between 80 and 130°C are displayed in Fig. 2. In order to provide a better comparison of the overall *I*-*V* results, the temperature dependence of the power density at 0.6 V for the studied cells is depicted in Fig. 3. The *I*-*V* curves for the cast Nafion membranes (*x* = 0%) are comparable to the ones of commercial Nafion membranes having similar thickness (~100 μm) obtained at similar operation conditions.<sup>19,20</sup> The performance of the Nafion cell is sustained up to ~110°C, and rapidly decreases with further increasing in temperature, as a result of water loss. As a general trend, the composite membranes cells display a performance enhancement when *T* is increased up to ~110°C, and a



**Figure 2.** *I-V* curves of membrane electrode assemblies using composite Nafion–titanate nanotubes electrolytes having different TNT concentration ( $x$ ) measured at (a) 80, (b) 100, (c) 120, and (d) 130°C. The symbols correspond to  $x = 0$  wt % ( $\square$ ), 5 wt % ( $\circ$ ), 10 wt % ( $\triangle$ ), and 15 wt % ( $\nabla$ ).

much less significant degradation for higher temperatures in comparison to the pure Nafion cell, as shown in Fig. 2 and 3. The effect of TNT addition to the polymeric electrolyte depends on the TNT concentration. PEMFC having  $x = 5$  wt % electrolytes slightly exceeds the performance of cast Nafion PEMFC for  $80^\circ\text{C} < T \leq 110^\circ\text{C}$ . Further increase in temperature results in a much lower degradation than the pure Nafion PEMFC. As a result, the  $x = 5$  wt % PEMFC exhibits similar performances when operating at  $80^\circ\text{C}$  and  $120^\circ\text{C}$ . Moreover, at  $130^\circ\text{C}$ , a 60% higher power density at 0.6 V is obtained when compared to the one of pure Nafion membrane.

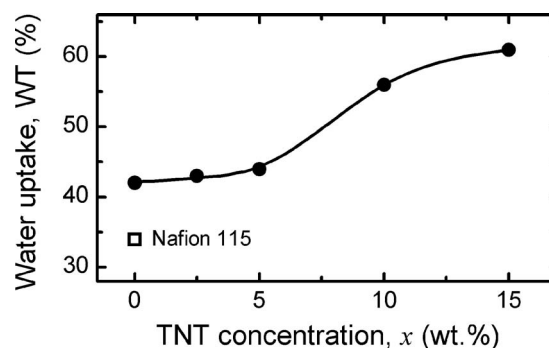
Cells having membranes with  $x = 10$  and 15 wt % were found to exhibit comparable properties and similar temperature dependence of the polarization curves, as displayed in Fig. 2 and 3. Their *I-V* curves exhibit large ohmic drops, which are possibly associated with a reduction in overall proton conductivity of the composite mem-



**Figure 3.** Temperature dependence of the power density at 0.6 V for membrane electrode assemblies using composite Nafion–titanate nanotubes electrolytes with different TNT concentration ( $x$ ).

branes. However, an appreciable enhancement of the power density is evident within the 100–110°C temperature range, whereas further increasing the temperature to 130°C results in slight performance degradation. Nevertheless, an important point is that the fuel cells with  $x \geq 10$  wt % operating at  $130^\circ\text{C}$  exhibit *I-V* curves similar to the ones measured at  $80^\circ\text{C}$ , and  $\sim 30\%$  higher power density as compared to the pure Nafion PEMFC at the same temperature.

It is well known that proton conductivity in Nafion depends, to a large extent, on the amount of water adsorbed.<sup>1,3</sup> Thus, in order to better identify the transport mechanisms in the PEMFC, the values of water uptake (WT) of the composite membranes at room temperature were evaluated. Figure 4 displays the dependence of WT on the TNT content in the composite. The measured value for commercial Nafion 115 is also included as a reference, and such value (WT  $\sim 34\%$ ) is in good agreement with previous results.<sup>19,20</sup> Figure 4 reveals that the casting procedure results in pure Nafion membranes with water retention capacity similar to the commercial polymer.<sup>19,20</sup> The addition of TNT up to 5 wt % results in slight increases in WT, whereas with further TNT incorporation ( $x > 5$  wt %), a remarkable increase in WT is observed. As a result, the absolute value for water uptake of the composite membranes becomes significantly large ( $\sim 60\%$  for the  $x = 15$  wt % membrane) and, most important, its relative increase with respect to the pristine polymer is also large ( $\sim 45\%$ ). Such a strong increase can be associated to the high specific surface area of the titanate nanotubes. Although in this work the specific surface area of the produced nanotubes has not been determined, different reports have shown that these values typically range from  $200 \text{ m}^2 \text{ g}^{-1}$  to  $400 \text{ m}^2 \text{ g}^{-1}$ .<sup>13,21</sup> These values are much larger than the correspond-



**Figure 4.** Dependence of water uptake on TNT concentration within Nafion–TNT composite membranes.



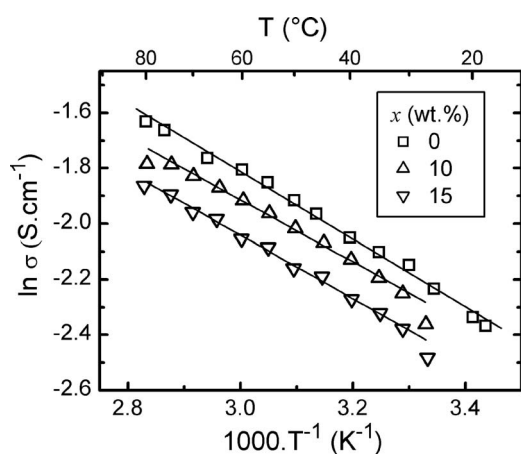


Figure 5. Arrhenius plot of the cast Nafion- $x$  titanate nanotube composites.

ing ones for commercial ( $50 \text{ m}^2 \text{ g}^{-1}$  for Degussa P25) or sol-gel prepared  $\text{TiO}_2$  nanoparticles ( $\sim 150 \text{ m}^2 \text{ g}^{-1}$ ), which are usually used in similar Nafion- $\text{TiO}_2$  composites.<sup>21</sup>

To gain further information on the electrical transport properties of the composites, the temperature dependence of their electrical conductivity [ $\sigma(T)$ ] was measured by electrochemical impedance spectroscopy (EIS). The Arrhenius plot of the samples with  $x = 0$ , 10, and 15 wt % of TNT are shown in the Fig. 5. The addition of TNT nanotubes resulted in a decrease in  $\sigma(T = 30^\circ\text{C})$  from 0.12 to  $0.09 \text{ S cm}^{-1}$  for  $x = 0$  wt % and 15 wt %, respectively. The ionic conductivity of the membranes shows a thermally activated Arrhenius-type behavior within the temperature range investigated. The calculated activation energy values were practically independent of TNT content and equal 0.1 eV. This value is the same as the reported for pure Nafion membranes.<sup>3</sup> These results evidence that the addition of the nanotubes does not appreciably alter proton transport mechanisms, but results in a decrease in the overall proton conductivity, as expected from the addition of a less conducting phase in the Nafion matrix. In fact, the proton conductivity of the TNT was found to be almost 2 orders of magnitude lower than the one of Nafion at  $80^\circ\text{C}$ , while having similar activation energy.<sup>16</sup> Results similar to those the presented here were reported for composites of Nafion and other inorganic proton conductors, such as zirconium phosphate,<sup>22</sup> wherein a more pronounced dependence of  $\sigma$  with RH than with temperature was observed in composite samples exhibiting higher WT and lower  $\sigma$  than the pure ionomer.

Usually, the addition of a dispersed inorganic second phase to Nafion is associated to a lower degradation in the performance of  $\text{H}_2/\text{O}_2$  PEMFC at high temperatures and/or low relative humidity.<sup>7,8,11,12</sup> In the present study, this behavior is also observed and PEMFC having Nafion-TNT membranes deliver power densities at  $120\text{--}130^\circ\text{C}$  that can be up to 60% larger than those corresponding to the unmodified Nafion membrane (Fig. 2 and 3). Such performance surpasses the results obtained in previous studies on equivalent systems.<sup>7,8,19</sup> In similar experimental conditions the reported performance enhancement at high temperature of Nafion/ $\text{TiO}_2$  membranes with respect to Nafion achieved a maximum of  $\sim 20\%$ .<sup>7,8</sup> The sustenance of the performance at  $T \geq 120^\circ\text{C}$  can be attributed to the much larger water retention capacity of the composite membranes that originates from the large specific surface area of the TNT, as demonstrated in Fig. 4. In addition, PEMFCs having Nafion-titanate composite membranes present a remarkable behavior. The power density augments with increasing temperature for temperatures within the  $80\text{--}110^\circ\text{C}$  range. This behavior is possibly related to the enhancement of thermally activated processes along with increased water retention; however, further studies are needed for its clarification. As a result, such PEMFCs have power densities at  $130^\circ\text{C}$  that are similar to the ones at  $80^\circ\text{C}$  (Fig. 3). This beneficial

effect could pave the way for significant enhancements in PEMFC efficiencies at higher temperature. Large ohmic drops are observed for membranes with high TNT content, which results in an appreciable decrease of PEMFC performance as compared to pure Nafion membranes at  $80^\circ\text{C}$ . However, this overall decrease in power density can be compensated by, e.g., a reduction in the membrane thickness. Finally, it is worth mentioning that, at operating conditions of high relative humidity and high temperature, a possible contribution to the protonic transport by the titanate nanotubes may be significant.<sup>16</sup> Nonetheless, such a contribution to the electrical transport seems to be less relevant to the overall cell performance than the improved water retention due to the high surface area of the titanate nanotubes.

## Conclusion

Proton exchange membrane fuel cell operating at high temperature using composite electrolytes comprised of Nafion and titanate nanotubes was demonstrated. The addition of titanate nanotubes to Nafion resulted in a significant enhancement of proton exchange membrane fuel cells operating up to  $130^\circ\text{C}$  in pure hydrogen. The presented results suggest that the high specific surface area of nanotubes improves the transport properties of the Nafion composite electrolytes at high temperature.

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