

Titanate Nanotubes as Inorganic Filler of Nafion Membranes for PEM Fuel Cells Operating at High Temperatures

B. R. Matos^a, E. I. Santiago^a, F. C. Fonseca^a, M. Linardi^a, V. Lavayen^b, R. G. Lacerda^b,
L.O. Ladeira^b, and A. S. Ferlauto^b

^a Instituto de Pesquisas Energéticas e Nucleares, São Paulo, SP, Brazil

^b Universidade Federal de Minas Gerais, Belo Horizonte, MG, Brazil

Nafion-titanate nanotubes composites were investigated as electrolytes for proton exchange membrane fuel cells (PEMFC) operating at high temperatures (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. This behavior reflects 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.

Introduction

Proton exchange membranes fuel cells (PEMFC) are being considered as an efficient technology for electrical energy generation.¹ Such environmentally friendly technology is envisioned as future power source for applications ranging from low-power portable electronic devices to kilowatt vehicle traction systems.¹ Despite the steady advances of this technology, key issues regarding its constituent properties (electrolyte and electrodes) still restrict a widespread application of PEMFC. For more than 20 years, the dominant PEMFC electrolyte has been the Nafion perfluorinated membrane.¹ This material, however, limits the operation temperature to ~80 °C due to its properties of charge transport, which needs water to promote protonic conductivity.^{2,3} 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 and water management of the system.⁴

Considerable research efforts have been devoted to the fabrication of Nafion-inorganic composite membranes in attempts to overcome such temperature limitation.^{2,5} 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 at higher temperature (~130 °C). Several composite membranes comprised of mixtures of Nafion and dispersed nanoparticles of ceramic oxides such as TiO₂, SiO₂, and ZrO₂ have been tested.⁶⁻⁸ 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).^{6,9,10} In general, it is observed that PEMFC 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 °C).^{8,11} Whereas, the performance of direct alcohol fuel cell (DAFC) is clearly enhanced at high temperatures by using such composite electrolytes. However, in this case the lower diffusion of methanol across the composite membrane due to presence of the inorganic phase is

believed to be relevant.^{9,10} Nevertheless, the exact role played by the inorganic second phase is still a matter of discussion, and different studies disagree whether the interaction between the inorganic phase and the sulfonic acid side 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.⁶⁻⁸ 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.^{5,12} 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.⁵ 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. Indeed, such features can be achieved by adding titania nanotubes to the polymeric matrix.

The discovery of a simple and efficient alkaline hydrothermal method for production of titania nanotubes by Kasuga et al.¹³ 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_2 , $\text{H}_2\text{Ti}_3\text{O}_7$, $\text{Na}_2\text{Ti}_3\text{O}_7$, etc).¹⁴ Several applications have been proposed for these fibrous structures including dye-sensitized solar cells, lithium-intercalation, hydrogen storage, photo-catalysis, etc.¹⁴ In particular, H and Na trititanates nanotubes have shown interesting electrochemical properties including a fairly large protonic conductivity.^{15,16} Based on this characteristic, it has been proposed that $\text{H}_2\text{Ti}_3\text{O}_7$ nanotubes could be utilized as electrolytes in PEMFC.¹⁶

Although the utilization of TiO_2 nanoparticles as fillers in composite electrolyte PEMFC membranes have been already considerably studied, the utilization of TiO_2 -derived nanotubes to PEMFC technology, to the extent of our knowledge, have been restricted to catalysts support in the electrodes.¹⁷ In this letter, a noticeable performance enhancement of a PEMFC operating at high temperatures (≥ 100 °C) was achieved by using a dispersion of trititanate nanotubes in the Nafion matrix. The obtained results suggest that the effect of the addition of nanotubes contribution is two fold. They provide a large surface area for water retention within the electrolyte membrane and, in a lesser extent, they alter its protonic conductivity.

Experimental

Trititanate nanotubes (TNT) were produced by a variation of the hydrothermal method. Instead of the treatment in auto-clave, the nanotubes were produced by refluxing an aqueous solution of NaOH (10 molL^{-1}) and TiO_2 powder (Sigma Aldrich, 99% anatase) for 24 hours in a Pyrex container. The resulting paste was thoroughly washed and neutralized with HCl solution (1 molL^{-1}), and dried. X-ray diffraction analysis (not shown) evidenced that the nanotubes have the hydrogen trititanate ($\text{H}_2\text{Ti}_3\text{O}_7$) structure, and energy dispersive X-ray spectroscopy analysis detected minor amounts of Na, Si, and Cl impurities in the as prepared materials.

Nafion-trititanate (N-TNT) composite membranes were obtained by casting¹⁸ from a mixture of Nafion and TNT solutions, both in dimethylsulfoxide. The Nafion solution was prepared by first evaporating a commercial Nafion 5% alcoholic solution (DuPont) and re-dissolving the resulting powder in dimethylsulfoxide. Membranes with TNT concentration (x) ranging from 0 to 15 wt.% were investigated. Membrane electrode

assemblies (MEA) were fabricated by hot pressing the cast composite membranes and Pt/C electrodes (Pt concentration: 20 wt.%; Pt load: 0.4 mg/cm²). Polarization curves (I-V) were taken between 80-130 °C by using water-saturated O₂ and H₂. The experiments were carried out under a fixed pressure (3 bar) to ensure 100% of relative humidity (RH) and a constant partial pressure of the reagents in the whole temperature range studied.

It is well known that proton conductivity in Nafion depends to a large extent on the amount of water adsorbed.^{1,3} Thus, in order to better identify the transport mechanisms in the PEMFC, the values of water uptake (WT) of the cast composite membranes were evaluated. WT is defined as $WT(\%) = (m_S - m_D) / m_D$; where m_S and m_D are the water-saturated and dry weights of the membranes, respectively, measured at room temperature.

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). Two-probe EIS measurements were performed from 25 °C to 80 °C at RH ~98 %.

Results and Discussion

Figure 1 displays transmission electron microscopy (TEM) images of the nanotubes. They present relatively narrow size dispersion, having 7-10 nm external diameter, 3-5 nm inner diameter, 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.^{13,14}

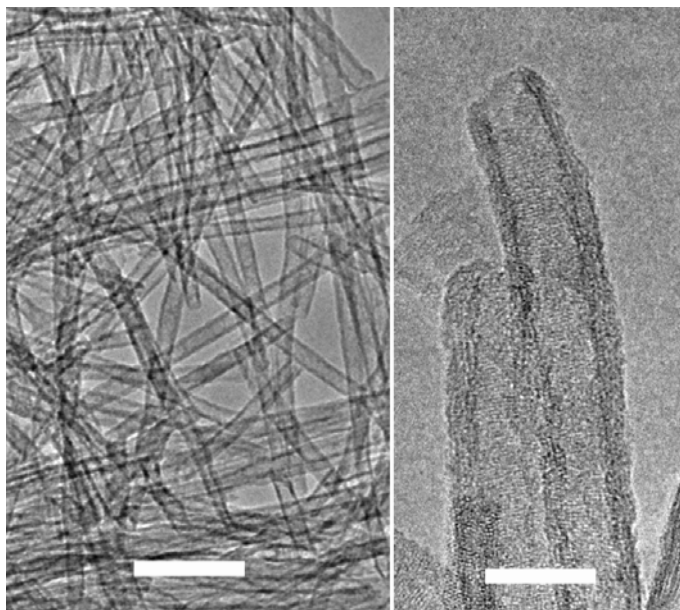


Figure 1. Transmission electron microscopy image of the trititanate nanotubes. Scale bars represent 50 nm and 10 nm in the left and right images, respectively.

The polarization curves measured between 80 °C and 130 °C are displayed in Figure 2. In addition, 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 Figure 3. The I-V curves for the cast Nafion membranes ($x = 0\%$) are comparable to the ones of commercial Nafion membranes having similar thickness obtained at similar operation conditions.^{19,20} The Nafion performance 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 display a performance enhancement when the temperature is increased up to $T \sim 110\text{ }^{\circ}\text{C}$, and a much less significant degradation for higher temperatures in comparison to bare Nafion, as shown in Figs. 2 and 3.

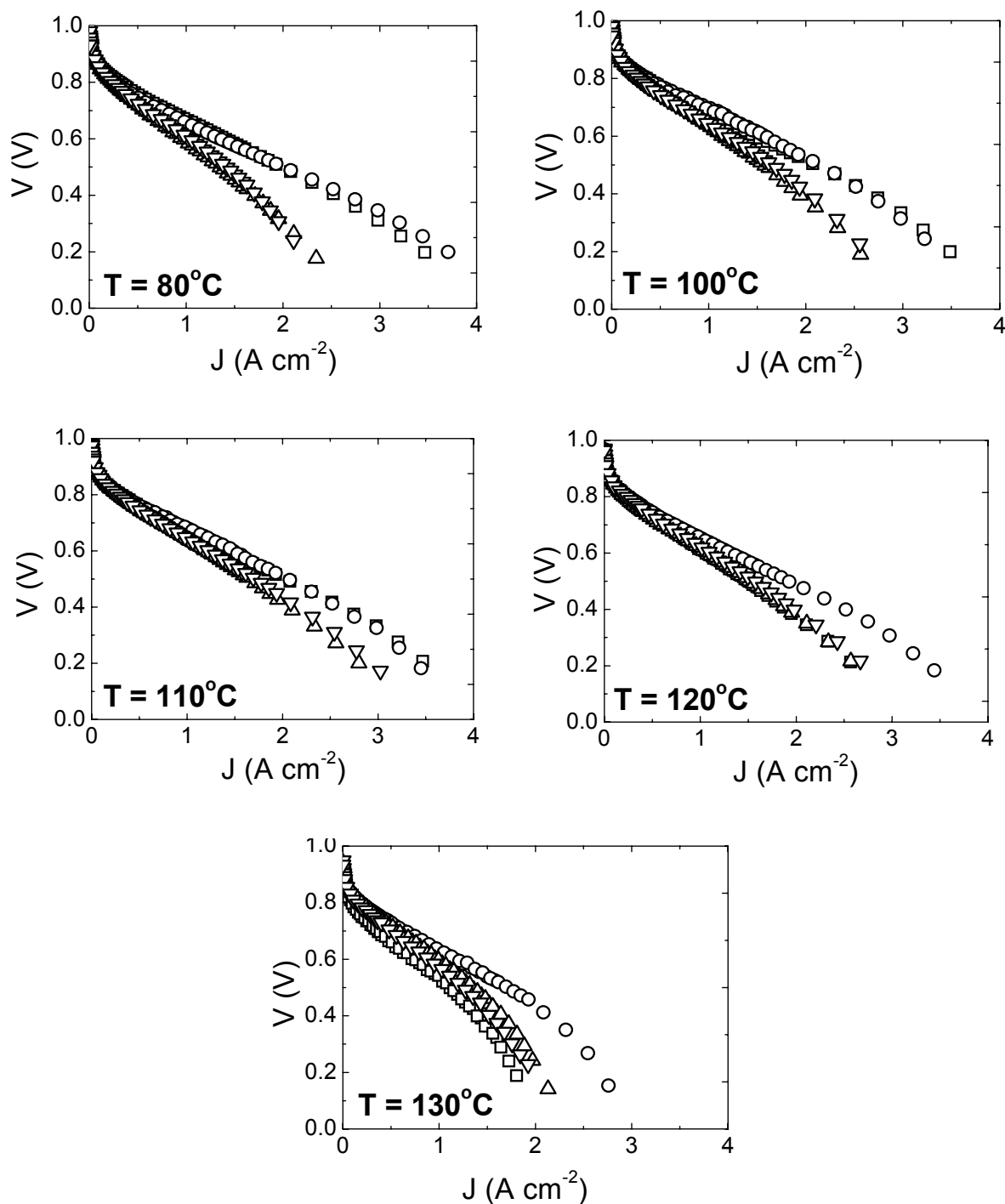


Figure 2. I-V curves of the membrane electrode assembly using the composite electrolyte Nafion - $x\text{ H}_2\text{Ti}_3\text{O}_7$ nanotubes with $x = 0$ (□), 5 (○), 10 (△), and 15 (▽) wt.%, measured at $80\text{ }^{\circ}\text{C}$ (a), $100\text{ }^{\circ}\text{C}$ (b), $120\text{ }^{\circ}\text{C}$ (c), and $130\text{ }^{\circ}\text{C}$ (d).

The effect of the addition of the TNT to the polymeric electrolyte depends on the TNT concentration. PEMFC having $x = 5$ wt.% electrolytes slightly exceeds the performance of cast Nafion PEMFC for $80 < T \leq 110$ °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 °C and 120 °C. Moreover, at 130 °C, a 60 % higher power density at 0.6 V is obtained when compared to the one of pure Nafion membrane.

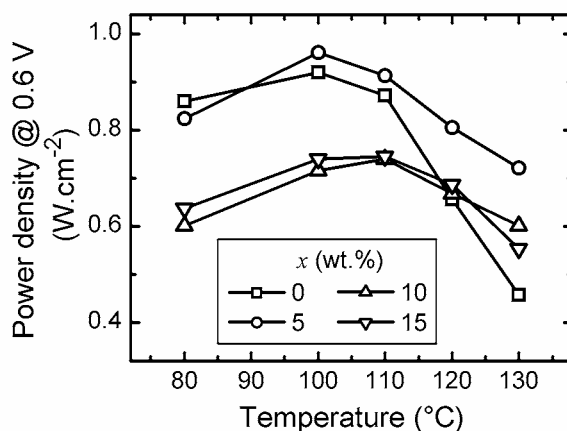


Figure 3. Temperature dependence of the power density at 0.6 V for the Nation-trititanate composite electrolytes with $x = 0$ (□), 5 (○), 10 (△), and 15 (▽) wt.%.

Membranes with $x = 10$ and 15 wt.% were found to exhibit comparable properties and similar temperature dependence of the polarization curves, as displayed in Figs. 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 membranes. 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 °C exhibit I-V curves similar to the ones measured at 80 °C, and ~30 % higher power density as compared to the pure Nafion PEMFC at the same temperature.

Figure 4 displays the dependence of WT on the TNT content of the membranes. The measured WT value for commercial Nafion 115 is also included as a reference, and such value is in good agreement with previous results.^{19,20} Fig. 4 reveals that the casting procedure results in pure Nafion membranes with water retention capacity similar to the commercial polymer.^{19,20} 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 (~60% for the $x = 15$ wt.% membrane) and, most important, its relative increase with respect to the pristine polymer is also large (~45%). Such strong increase can be associated to the high specific surface area of the trititanate 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 to 400 m²g⁻¹.^{13,21} These values are much larger than the corresponding ones for commercial

($50 \text{ m}^2\text{g}^{-1}$ for Degussa P25) or sol-gel prepared TiO_2 nanoparticles ($\sim 150 \text{ m}^2\text{g}^{-1}$), which are usually used in similar Nafion- TiO_2 composites.²¹

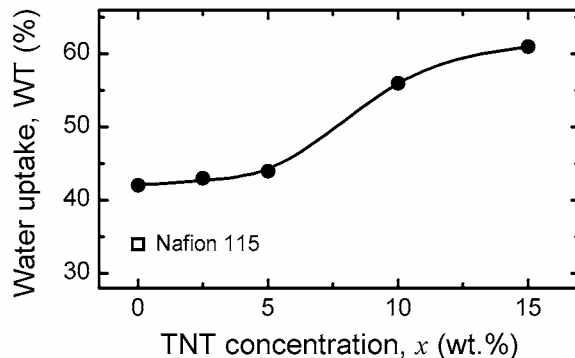


Figure 4. Water uptake measured at room temperature dependence on the trititanate nanotube concentration.

The Arrhenius plot of the samples with $x = 0, 10,$ and $15 \text{ wt.}\%$ of TNT are shown in the Figure 5. The addition of TNT nanotubes resulted in a decrease in $\sigma(T = 30 \text{ }^\circ\text{C})$ from 0.12 to 0.09 Scm^{-1} for $x = 0$ and $15 \text{ wt.}\%$, respectively. The ionic conductivity in 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 .³ 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 fact, the proton conductivity of the TNT was found to be almost two orders of magnitude lower than the one of Nafion at $80 \text{ }^\circ\text{C}$, while having similar activation energy.¹⁶ Results similar to the presented here were reported for composites of Nafion and other inorganic proton conductors, such as zirconium phosphate,²² wherein a more pronounced dependence of σ with RH than with temperature was observed in composite samples exhibiting higher WT and lower σ than the pure ionomer.

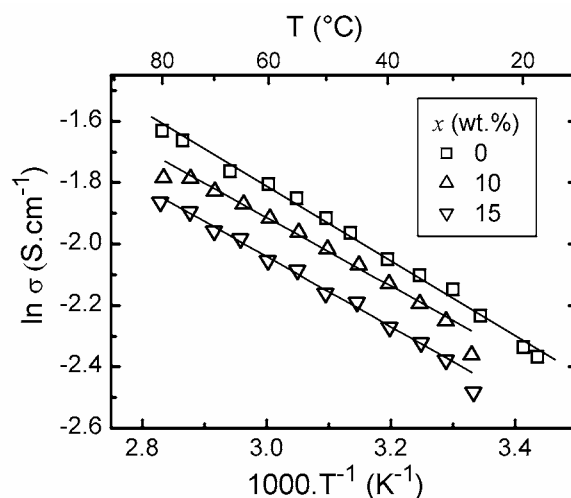


Figure 5. Arrhenius plot of the cast Nafion - x trititanate nanotube composites with $x = 0$ (\square), 10 (\triangle), and 15 (∇) wt.%.

Usually, the addition of a dispersed inorganic second phase to Nafion is associated to a lower degradation in the performance of H₂/O₂ PEMFC at high temperatures and/or low relative humidity.^{7,8,11,12} In the present study, this behavior is also observed, and PEMFC having Nafion-TNT membranes deliver power densities at 120-130 °C that can be up to 60% larger than those corresponding to the unmodified Nafion membrane. The sustenance of the performance at T ≥ 120 °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, PEMFC having Nafion-trititanate composite membranes present a remarkable behavior. The power density augments with increasing temperature for temperatures within the 80-110 °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 PEMFC have performances at 130 °C that are similar to the ones at 80 °C. This beneficial effect could pave the way for significant enhancements in PEMFC efficiencies at higher temperature. On the other hand, large ohmic drops are observed for membranes with high TNT content, which results in an appreciable decrease of PEMFC performance as compared with pure Nafion membranes at 80 °C. However, this overall decrease in power density can be compensated by e.g. a reduction in the membrane thickness. Finally, it is worth mention that, at operating conditions of high relative humidity and high temperature, a possible contribution to the protonic transport by the trititanate nanotubes may be significant.¹⁶ 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 trititanate nanotubes.

Conclusion

In conclusion, proton exchange membrane fuel cell operating at high temperature using composite electrolytes comprised of Nafion and trititanate nanotubes was demonstrated. The addition of trititanate nanotubes to Nafion resulted in a significant enhancement of proton exchange membrane fuel cells operating up to 130 °C in pure hydrogen. The experimental results suggest that the high specific surface area of nanotubes improves the transport properties of the Nafion composite electrolytes at high temperature.

Acknowledgments

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References

1. Vielstich, W.; Lamm, A.; Gasteiger, H. *Handbook of Fuel Cells: Fundamentals, Technology and Applications*, p.142, Willey, (2003).
2. Alberti, G; Casciola, M. *Annu. Rev. Mater. Res.*, **33**,129 (2003).

3. Mauritz, K.A; Moore, R.B. *Chem. Rev.*, **104**, 4535 (2004).
4. Adjemian, K.T.; Lee, S.J.; Srinivasan, S.; Benziger, J.; Bocarsly, A.B. *J. Electrochem. Soc.*, **149**, A256 (2002).
5. Li, Q.; He, R.; Jensen, J.O.; Bjerrum, N. *Chem. Mater.*, **15**, 4896 (2003).
6. Aricò, A.S.; Baglio, V.; Di Blasi, A.; Modica, E.; Antonucci, P.L.; Antonucci, V. *J. Power Sources*, **128**, 113 (2004).
7. Adjemian, K.T.; Dominey, R.; Krishnan, L.; Ota, H.; Majsztrik, P.; Zhang, T.; Mann, J.; Kirby, B.; Gatto, L.; Velo-Simpson, M.; Leahy, J.; Srinivasan, S.; Benziger, J.B.; Bocarsly, A.B. *Chem. Mater.*, **18**, 2238 (2006).
8. Chalkova, E.; Pague, M.B.; Fedkin, M.V.; Wesolowski, D.J.; Lvov, S.N. *J. Electrochem. Soc.*, **152**, A1035 (2005).
9. Aricò, A.S.; Baglio, V.; Di Blasi, A.; Creti, P.; Antonucci, P.L.; Antonucci, V. *Solid State Ionics*, **161**, 251 (2003).
10. Baglio, V.; Di Blasi, A.; Aricò, A.S.; Antonucci, V.; Antonucci, P.L.; Trakanprapai, C.; Esposito, V.; Licoccia, S.; Traversa, E. *J. Electrochem. Soc.*, **152**, A1373 (2005).
11. Chalkova, E.; Fedkin, M.V.; Wesolowski, D.J.; Lvov, S.N. *J. Electrochem Soc.*, **152**, A1742 (2005).
12. Costamagna, P.; Yang, C.; Bocarsly, A.B.; Srinivasan, S. *Electrochim. Acta*, **47**, 1023 (2002).
13. (a) Kasuga, T.; Hiramatsu, M.; Hoson, A.; Sekino, T.; Niihara, K. *Langmuir*, **14**, 3160 (1998). (b) Kasuga, T.; Hiramatsu, M.; Hoson, A.; Sekino, T.; Niihara, K. *Adv. Mater.*, **11**, 1307 (1999).
14. Bavykin, D.V.; Friedrich, J.M.; Walsh, F.C. *Adv. Mater.*, **18**, 2807 (2006).
15. Thorne A.; Kruth A.; Tunstall D.; Irvine J.T.S.; Zhou W.Z.. *J. Phys. Chem. B*, **109**, 5439 (2005).
16. Yamada, M.; Wei, M.; Honma, I.; Zhou, H. *Electrochem Commun.*, **8**, 1549 (2006).
17. Wang, M.; Guo, D.J.; Li, H.L. *J. Sol. Stat. Chem.*, **178**, 1996 (2005).
18. Moore, R.B.; Martin, C.R. *Anal. Chem.* **58**, 2570 (1986).
19. Saccà, A.; Carbone, A.; Passalacqua, E.; D'Epifanio, A.; Licoccia, S.; Traversa, E.; Sala, E.; Traini, F.; Ornelas, R. *J. Power Sources* **152**, 16 (2005).
20. Saccà, A.; Gatto, I.; Carbone, A.; Pedicini, R.; Passalacqua, E. *J. Power Sources*, **163**, 47 (2006).
21. Tsai C.C.; Teng H. *Chem. Mater.*, **16**, 4352 (2004).
22. Yang, C.; Srinivasan, S.; Bocarsly, A.B.; Tulyani, S.; Benziger, J.B. *J. Memb. Sci.*, **237**, 145 (2004).