



Electrochemical Properties of the Ionic Liquid 1-Ethyl-3-methylimidazolium Difluorophosphate as an Electrolyte for Electric Double-Layer Capacitors

Kazuhiko Matsumoto^{*z} and Rika Hagiwara^{*}

Graduate School of Energy Science, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan

The electrochemical properties of 1-ethyl-3-methylimidazolium difluorophosphate (EMImPO₂F₂) ionic liquid have been investigated as an electrolyte for electric double-layer capacitors using activated carbon electrodes. A two-electrode cell test reveals that the capacitance of EMImPO₂F₂ exhibits a larger voltage dependence than that of a typical ionic liquid electrolyte EMImBF₄. At a charging voltage of 2.5 V, the capacitance obtained for EMImPO₂F₂ is 49 F g⁻¹ and is larger than 44 F g⁻¹ obtained for EMImBF₄. According to the charge–discharge cycle test, the breaking-up voltage of EMImPO₂F₂ is lower than that of EMImBF₄, which may be caused by the lower anodic stability of PO₂F₂⁻ than that of BF₄⁻. The ionization potential of PO₂F₂⁻ was calculated by quantum mechanical calculations to estimate its anodic stability and was compared with those of several anions used in typical electrolytes. The results indicate that the anodic stability of PO₂F₂⁻ is similar to that of ClO₄⁻ and lower than those of BF₄⁻ and PF₆⁻. © 2010 The Electrochemical Society. [DOI: 10.1149/1.3336831] All rights reserved.

Manuscript submitted December 28, 2009; revised manuscript received February 1, 2010. Published April 6, 2010.

Electric double-layer capacitors (EDLCs) are attractive energy storage devices for energy regeneration. High power density and long lifetime are the beneficial points of EDLCs compared to secondary batteries because EDLCs store energy at the interface between the electrode surface and the electrolytic solution (or electrolyte) without faradaic processes.^{1–4} Electrode materials with a high surface area such as the activated carbon are required for this purpose, whereas the capacitance is usually nonlinear to the specific surface area because of the effect of the pore structure.⁵

Although aqueous electrolytes such as sulfuric acid are attractive in terms of their high conductivity, high capacitance, easy handling, and low cost, the low breaking-up voltage (<1 V for a practical cell) limits their available energy density. The temperature range in which the aqueous electrolyte is usable below and above room temperature is not wide due to relatively high freezing and low boiling temperatures of water. Although the high achievable voltage for nonaqueous electrolytes (~3 V) is a great benefit, their low conductivity increases the internal resistance. From the viewpoint of safety, the flammability of the organic electrolytes is another drawback especially for their application to large-scaled capacitors. Ionic liquids composed of only ionic species have some unique properties such as nonflammability, low vapor pressure, and wide liquid-phase temperature range, rendering the construction of safe electrochemical devices operable in a wide temperature range.^{6–10} Their ionic conductivity and electrochemical stability depend on the ionic species, sometimes being comparable to or higher than the organic electrolytes. The use of ionic liquids as electrolytes combined with carbonaceous electrodes in EDLCs has been attempted by many groups, where the fluoroanions [BF₄⁻,^{11–19} PF₆⁻,^{11,16} N(SO₂CF₃)₂⁻,^{11,16,20,21} and N(SO₂F)₂⁻,²² and others^{23,24}] are often used as counteranions. Although the understanding of the double-layer structures in ionic liquids is still undergoing, experimental and theoretical approaches have been made by several research groups.^{25–33}

A series of ionic liquids based on the difluorophosphate anion (PO₂F₂⁻) reported recently exhibits some desirable properties as an electrolyte for EDLCs such as a low melting point, low viscosity, high conductivity, and high hydrolytic stability.³⁴ The effect of the asymmetric structure for PO₂F₂⁻ on capacitance should also be examined in comparison with the other highly symmetric anions such as BF₄⁻ and PF₆⁻. In this study, the electrochemical properties of the ionic liquid 1-ethyl-3-methylimidazolium difluorophosphate (EMImPO₂F₂, Fig. 1) as an electrolyte for EDLCs are reported.

Experimental

Reagents.—The ionic liquid electrolyte EMImBF₄ was purchased from Kanto Kagaku and dried under vacuum (<1 Pa) at 373 K for 2 days. The starting chloride EMImCl was prepared by the reaction of 1-methylimidazole (Aldrich Chemicals, purity >99%) and chloroethane (Wako Chemicals, purity >99%) and was purified by recrystallization from acetonitrile by adding ethylacetate.³⁴ The potassium salt KPO₂F₂ was prepared by the reaction of KPO₃ (Wako Chemicals) and KPF₆ (Aldrich purity >99.5%).³⁴ The difluorophosphate ionic liquid EMImPO₂F₂ was prepared by the reaction of EMImCl and KPO₂F₂ and was purified through the activated alumina column as described in the literature.³⁴ Final drying was performed under vacuum (<1 Pa) at 373 K for 1 week. The Karl–Fischer measurements showed that the typical water contents in these ionic liquids were below 100 ppm.

Measurements.—An electrochemical measurement was performed at 298 K with the aid of an electrochemical measurement system HZ-3000 (Hokuto Denko). The electrochemical window was measured using a vitreous carbon working electrode and a Pt counter electrode. The reference electrode was made of silver wire immersed in EMImBF₄, containing 0.05 M AgBF₄ that was separated from the electrolyte by a window made of porous Vycor glass. The potential was referenced to the ferrocenium/ferrocene (Fc⁺/Fc) redox couple.

A two-electrode cell made of poly(tetrafluoroethylene) (PTFE) was used for the EDLC tests. A pair of activated carbon sheets with a diameter of 10 mm, a thickness of 0.5 mm, and a weight of 0.021 g [85 wt % of activated carbon from phenol resin (surface area, 2050 m² g⁻¹, mean pore diameter, 2.14 nm, and total pore volume, 1.10 cm³ g⁻¹), 10 wt % of PTFE, and 5 wt % of carbon black] were used as electrodes. The electrodes dried under vacuum at 453 K overnight were immersed in the electrolyte and degassed under vacuum before use. The PTFE filter (ADVANTEC H100A013A, 35 μm thickness and 13 mm diameter) was used as a separator. Vitreous carbon disks were used as current collectors. The test cell was charged to a given voltage and discharged at a constant current rate of 5 mA. The capacitance *C* (F g⁻¹) was calculated from the discharge curve using the relationship $C = it/wV$, where *i* is the current, *t* is the time, *V* is the voltage, and *w* is the total weight of a pair of disk electrodes.

Electronic structure calculations.—Geometries were optimized at the HF and PBE1PBE levels of theory combined with the aug-cc-pVTZ basis set using the program Gaussian 03.³⁵ Molecular volumes were calculated using the Monte Carlo method as implemented in Gaussian 03.

* Electrochemical Society Active Member.

^z E-mail: k.matsumoto@ky7.ecs.kyoto-u.ac.jp

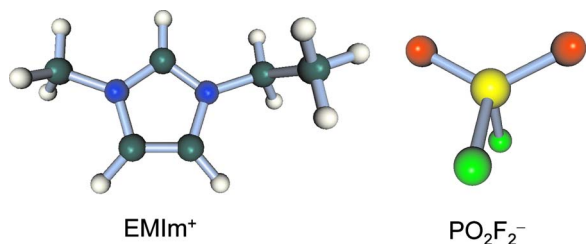


Figure 1. (Color online) Structures of the 1-ethyl-3-methylimidazolium cation (EMIm⁺) and difluorophosphate anion (PO₂F₂⁻).

Results and Discussion

Electric double-layer capacitance.— Table I summarizes the physical properties of EMImPO₂F₂ and EMImBF₄ used in the current study. The melting point of EMImPO₂F₂ (280 K) is slightly lower than that of EMImBF₄ (288 K), and the conductivity and viscosity of EMImPO₂F₂ are comparable to those of EMImBF₄.^{34,36} Figure 2 shows the charge–discharge curves obtained for EMImPO₂F₂, together with those obtained for EMImBF₄ for comparison. In the EMImPO₂F₂, the voltage increase in the charge curve becomes sluggish at a charging voltage of 3.0 V, and the deformation of the discharge curve becomes apparent at a charging voltage of 3.5 V. The charge and discharge curves for EMImPO₂F₂ at a charging voltage of 4.0 V are totally deformed. The deterioration of the electrolyte causes such behavior and results in the increase in the internal resistance, as shown in the increase in the IR drop. Figure 3 shows the voltage dependence of capacitance for the EDLC using EMImPO₂F₂ together with that using EMImBF₄ as the electrolyte for comparison. The charging voltage was increased from 1.0 to 4.0 V by a 0.1 V step. Overall, the capacitance of EMImPO₂F₂ exhibits a higher voltage dependence than that of EMImBF₄, leading to the higher capacitance of EMImPO₂F₂ at the charging voltages above 1.5 V. Although the origin of this behavior is not clear, the asymmetric PO₂F₂⁻ might change the orientation on the electrode at high voltages. The capacitance obtained for EMImPO₂F₂ is 49 F g⁻¹ and is higher than 44 F g⁻¹ for EMImBF₄ when the cell is charged at 2.5 V. The capacitance of EDLCs using activated carbon electrodes and BF₄⁻-based ionic liquids is usually higher than those using other ionic liquids such as PF₆⁻ and N(SO₂CF₃)₂⁻-based ones.^{8,11} The larger capacitance of EMImPO₂F₂ compared to that of EMImBF₄ is considered to arise from the characteristics of PO₂F₂⁻. The obvious difference between PO₂F₂⁻ and BF₄⁻ in terms of molecular geometry is their symmetry. The PO₂F₂⁻ anion has a C_{2v} symmetry with a dipole moment and a more negative charge on the oxygen atoms than the fluorine atoms, while the BF₄⁻ has a higher symmetry of T_d. Such a difference in molecular geometry may affect the structure of the electric double layer and may result in the different voltage dependence of capacitance. According to the quantum mechanical calculation at PBE1PBE/aug-cc-pVTZ, the molecular volume of PO₂F₂⁻ (85 Å³) is between the two popular fluorocomplex anions used for ionic liquid electrolytes, BF₄⁻ (74 Å³) and PF₆⁻ (97 Å³) (Fig. 4). The size of PO₂F₂⁻ may be another factor for its

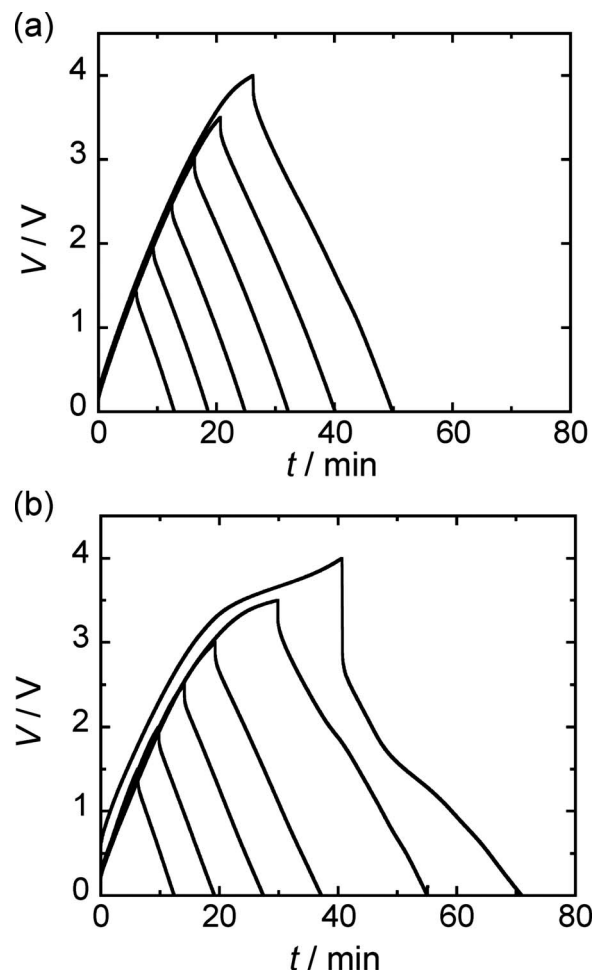


Figure 2. Charge–discharge curves of EDLCs using (a) EMImBF₄ and (b) EMImPO₂F₂.

high capacitance. In the region above the charging voltage of 3.0 V, the capacitance of EMImPO₂F₂ is increased steeply, which is ascribed to the decomposition of the electrolyte, whereas the capacitance of EMImBF₄ exhibits almost a linear increase in this region.

Figure 5 shows the capacitance and coulomb efficiency of the EDLCs using (a) EMImPO₂F₂ and (b) EMImBF₄ as a function of cycle number, where the charging voltage was increased every 50th cycle by 0.5 V from 2.0 to 3.5 V. The capacitance loss during the cycles at 2.0 and 2.5 V is quite small in both the cases of EMImPO₂F₂ and EMImBF₄. The capacitance of EMImPO₂F₂ slightly decreases during the cycles at 3.0 V and significantly drops during the cycles at 3.5 V, whereas the capacitance of EMImBF₄ is constant during the cycles at 3.0 V, and slightly decreases as the cycle proceeds at 3.5 V. The drop in the coulomb efficiency at the high charging voltage is more evident for EMImPO₂F₂ than that for EMImBF₄. These results indicate the lower electrochemical stability

Table I. Physical and thermal properties of the ionic liquids in the current study.

	$T_m(T_g)$ (K)	ρ/g (cm ⁻³)	MV (cm ³ mol ⁻¹)	η (mPa s)	σ (mS cm ⁻¹)	Λ (S cm ² mol ⁻¹)	C (F g ⁻¹)	Ref.
EMImPO ₂ F ₂	280	1.31	161	35	12	1.9	49	34
EMImBF ₄	288 (194)	1.27	156	34	13	2.0	44	36

T_m : melting point, T_g : glass transition temperature, ρ : density at 298 K, MV: molar volume at 298 K, η : viscosity at 298 K, σ : ionic conductivity at 298 K, Λ : molar conductivity at 298 K, and C : capacitance obtained for the present EDLC cell at the charging voltage of 2.5 V.

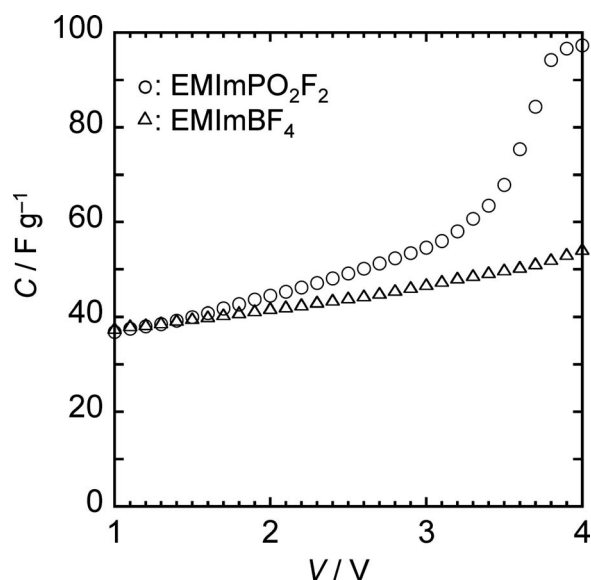


Figure 3. Voltage dependence of capacitance for EMImPO₂F₂ and EMImBF₄.

of EMImPO₂F₂ compared to that of EMImBF₄ in the present EDLC cell. Although there may be several factors on this point including the reaction of the electrolyte and surface functional groups on the activated carbon electrode, the difference in the anodic stability is considered to be one of the possible reasons, as shown below.

Anodic stability of PO₂F₂⁻.— Figure 6 shows the comparison of the electrochemical stability between EMImPO₂F₂ and EMImBF₄ by using the linear sweep voltammetry of a vitreous carbon electrode. The voltammetric curves for the two ionic liquids completely overlap at the cathode limit (-2.5 V vs Fc⁺/Fc, where the current density is 0.5 mA cm⁻²), suggesting the decomposition of the cationic species. The anode limit of EMImPO₂F₂ is lower than that of EMImBF₄ by 0.3 V, which arises from the difference in the stability of the anions against oxidation. The anodic stability of typical anionic species for the electrolytes in the organic solvents and for the ionic liquid electrolytes was experimentally determined on a vitreous carbon electrode,^{37,38} although such anions are often intercalated into graphitized materials at lower potentials.³⁹⁻⁴² Theoretical works to evaluate the anodic stability were performed by calculating the ionization potential of the anions.^{37,43-45} The evaluation using the highest occupied molecular orbital energy (E_{HOMO}) is based on Koopmans' theorem and is valid only at the HF level. The vertical ionization potential (E_v) is also used for this purpose and is calculated from the energy difference between the total energy of the anion and that of the neutral radical without geometry optimization (the same geometry as the optimized geometry for the corresponding anion) based on the Franck-Condon principle. These calcula-

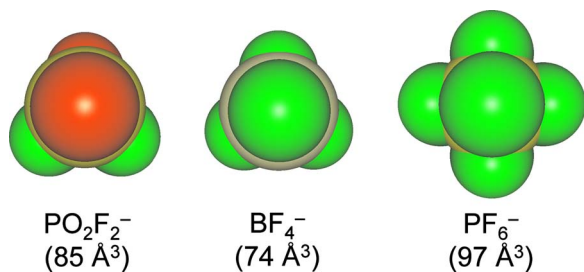


Figure 4. (Color online) Space filling models of PO₂F₂⁻, BF₄⁻, and PF₆⁻. The volumes calculated at PBE1PBE/aug-cc-pVTZ are given in parentheses.

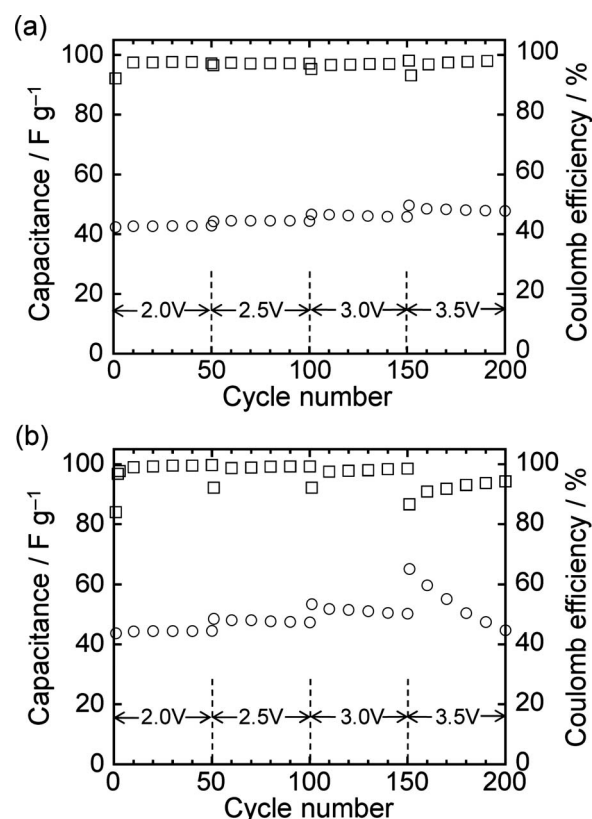


Figure 5. The capacitance (○) and coulomb efficiency (□) of the EDLCs using (a) EMImBF₄ and (b) EMImPO₂F₂ as a function of cycle number, where the charging voltage was increased every 50th cycle by 0.5 V from 2.0 to 3.5 V.

tions provide the order of the anodic stability of the anions. Table II lists E_{HOMO} at HF/aug-cc-pVTZ and E_v at PBE1PBE/aug-cc-pVTZ calculated for PO₂F₂⁻ with the values for PF₆⁻, BF₄⁻, and ClO₄⁻ for

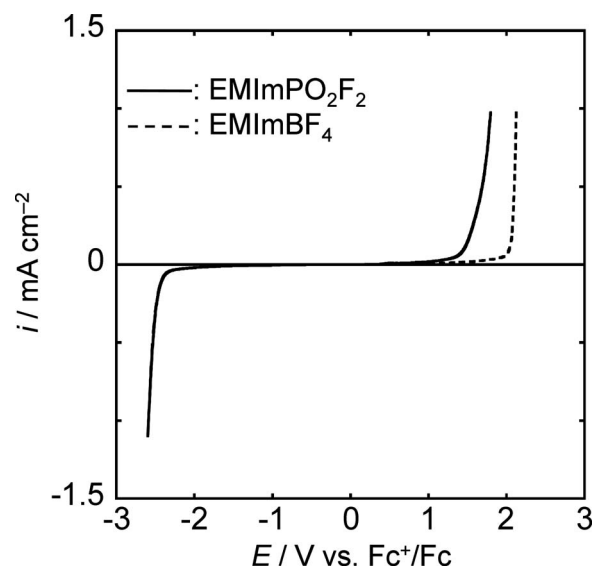


Figure 6. Linear sweep voltammograms of a vitreous carbon electrode in EMImPO₂F₂ and EMImBF₄. Scan rate: 5 mV s⁻¹, counter electrode: Pt wire, and reference electrode: Ag wire immersed in EMImBF₄ containing 0.05 M AgBF₄. The potential is referenced to the redox potential of the Fc⁺/Fc couple.

Table II. E_{HOMO} and E_{v} for PO_2F_2^- , BF_4^- , PF_6^- , and ClO_4^- .

	$E_{\text{HOMO}}^{\text{a}}$ (eV)	E_{v}^{b} (eV)
PO_2F_2^-	-7.3	-5.3
BF_4^-	-10.3	-7.3
PF_6^-	-11.0	-8.0
ClO_4^-	-7.4	-5.5

^a E_{HOMO} was calculated at HF/aug-cc-pVTZ.

^b E_{v} was calculated at PBE1PBE/aug-cc-pVTZ.

comparison. In both the methods, the ionization potentials obtained in this study increases in the order of $\text{PO}_2\text{F}_2^- \approx \text{ClO}_4^- < \text{BF}_4^- < \text{PF}_6^-$. The low stability of ClO_4^- against oxidation compared to the common inorganic fluoroanions was already pointed out in previous studies.^{38,43} The present calculations proved that the anodic stability of PO_2F_2^- is similar to that of ClO_4^- and validated the lower breaking-up voltage of the EDLC using EMIm PO_2F_2^- than that using EMIm BF_4^- .

Conclusion

In this study, the performance of the EDLC using EMIm PO_2F_2^- was measured and compared with that using EMIm BF_4^- . The high capacitance observed for EMIm PO_2F_2^- is attractive in the practical use. The breaking-up voltage of the EDLC using EMIm PO_2F_2^- is lower than 3.0 V, which may be explained by the lower anodic stability of PO_2F_2^- than the typical fluorocomplex anions such as BF_4^- .

Kyoto University assisted in meeting the publication costs of this article.

References

- B. E. Conway, *Electrochemical Supercapacitors*, Kluwer Academic/Plenum, New York (1999).
- A. Burke, *J. Power Sources*, **91**, 37 (2000).
- R. Kötz and M. Carlen, *Electrochim. Acta*, **45**, 2483 (2000).
- S. Sarangapani, B. V. Tilak, and C. P. Chen, *J. Electrochem. Soc.*, **143**, 3791 (1996).
- J. Huang, B. G. Sumpter, and V. Meunier, *Chem.-Eur. J.*, **14**, 6614 (2008).
- H. Ohno, *Electrochemical Aspects of Ionic Liquids*, John Wiley & Sons, Hoboken (2005).
- R. Hagiwara, *Electrochemistry (Tokyo, Jpn.)*, **70**, 130 (2002).
- M. Galinski, A. Lewandowski, and I. Stepniak, *Electrochim. Acta*, **51**, 5567 (2006).
- M. C. Buzzeo, R. G. Evans, and R. G. Compton, *ChemPhysChem*, **5**, 1106 (2004).
- D. R. MacFarlane, M. Forsyth, P. C. Howlett, J. M. Pringle, J. Sun, G. Annat, W. Neil, and E. I. Izgorodina, *Acc. Chem. Res.*, **40**, 1165 (2007).
- K. Yuyama, G. Masuda, H. Yoshida, and T. Sato, *J. Power Sources*, **162**, 1401 (2006).
- S. Shiraishi, T. Miyauchi, R. Sasaki, N. Nishina, A. Oya, and R. Hagiwara, *Electrochemistry (Tokyo, Jpn.)*, **75**, 619 (2007).
- S. Shiraishi, N. Nishina, A. Oya, and R. Hagiwara, *Electrochemistry (Tokyo, Jpn.)*, **73**, 593 (2005).
- I. Murayama, N. Yoshimoto, M. Egashira, M. Morita, Y. Kobayashi, and M. Ishikawa, *Electrochemistry (Tokyo, Jpn.)*, **73**, 600 (2005).
- T. Sato, G. Masuda, and K. Takagi, *Electrochim. Acta*, **49**, 3603 (2004).
- A. Lewandowski and M. Galinski, *J. Phys. Chem. Solids*, **65**, 281 (2004).
- Y. Nagao, Y. Nakayama, H. Oda, and M. Ishikawa, *J. Power Sources*, **166**, 595 (2007).
- Y. J. Kim, Y. Matsuzawa, S. Ozaki, K. C. Park, C. Kim, M. Endo, H. Yoshida, G. Masuda, T. Sato, and M. S. Dresselhaus, *J. Electrochem. Soc.*, **152**, A710 (2005).
- H. Zhang, G. P. Cao, Y. S. Yang, and Z. N. Gu, *J. Electrochem. Soc.*, **155**, K19 (2008).
- M. Lazzari, F. Soavi, and M. Mastragostino, *J. Power Sources*, **178**, 490 (2008).
- T. Katakabe, T. Kaneko, M. Watanabe, T. Fukushima, and T. Aida, *J. Electrochem. Soc.*, **152**, A1913 (2005).
- N. Handa, T. Sugimoto, M. Yamagata, M. Kikuta, M. Kono, and M. Ishikawa, *J. Power Sources*, **185**, 1585 (2008).
- M. Ue, M. Takeda, A. Toriumi, A. Kominato, R. Hagiwara, and Y. Ito, *J. Electrochem. Soc.*, **150**, A499 (2003).
- M. Ue, M. Takeda, T. Takahashi, and M. Takehara, *Electrochem. Solid-State Lett.*, **5**, A119 (2002).
- C. Nanjundiah, S. F. McDevitt, and V. R. Koch, *J. Electrochem. Soc.*, **144**, 3392 (1997).
- K. B. Oldham, *J. Electroanal. Chem.*, **613**, 131 (2008).
- M. V. Fedorov and A. A. Kornyshev, *J. Phys. Chem. B*, **112**, 11868 (2008).
- M. V. Fedorov and A. A. Kornyshev, *Electrochim. Acta*, **53**, 6835 (2008).
- V. Lockett, R. Sedev, J. Ralston, M. Horne, and T. Rodopoulos, *J. Phys. Chem. C*, **112**, 7486 (2008).
- S. Baldelli, *J. Phys. Chem. B*, **109**, 13049 (2005).
- C. Aliaga and S. Baldelli, *J. Phys. Chem. B*, **110**, 18481 (2006).
- M. T. Alam, M. M. Islam, T. Okajima, and T. Ohsaka, *J. Phys. Chem. C*, **111**, 18326 (2007).
- N. Nanbu, Y. Sasaki, and F. Kitamura, *Electrochem. Commun.*, **5**, 383 (2003).
- K. Matsumoto and R. Hagiwara, *Inorg. Chem.*, **48**, 7350 (2009).
- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, et al., Gaussian 03, Revision E.01, Gaussian, Inc., Wallingford, CT (2004).
- J. Ohtsuki, K. Matsumoto, and R. Hagiwara, *Electrochemistry (Tokyo, Jpn.)*, **77**, 624 (2009).
- V. R. Koch, L. A. Dominey, C. Nanjundiah, and M. J. Ondrechen, *J. Electrochem. Soc.*, **143**, 798 (1996).
- M. Ue, M. Takeda, M. Takehara, and S. Mori, *J. Electrochem. Soc.*, **144**, 2684 (1997).
- R. T. Carlin, H. C. De Long, J. Fuller, and P. C. Trulove, *J. Electrochem. Soc.*, **141**, L73 (1994).
- P. W. Ruch, M. Hahn, F. Rosciano, A. Holzapfel, H. Kaiser, W. Scheifele, B. Schmitt, P. Novak, R. Kötz, and A. Wokaun, *Electrochim. Acta*, **53**, 1074 (2007).
- J. A. Seel and J. R. Dahn, *J. Electrochem. Soc.*, **147**, 892 (2000).
- Z. Zhang and M. M. Lerner, *J. Electrochem. Soc.*, **140**, 742 (1993).
- M. Ue, A. Murakami, and S. Nakamura, *J. Electrochem. Soc.*, **149**, A1572 (2002).
- P. Johansson, *J. Phys. Chem. A*, **110**, 12077 (2006).
- J. Scheers, P. Johansson, and P. Jacobsson, *J. Electrochem. Soc.*, **155**, A628 (2008).