THE JOURNAL OF PHYSICAL CHEMISTRY A LETTERS

2006, *110,* 12077−12080
Published on Web 10/12/2006

Intrinsic Anion Oxidation Potentials

Patrik Johansson*

Department of Applied Physics, Chalmers University of Technology, SE-412 96 Göteborg, Sweden

Received: August 17, 2006; In Final Form: October 2, 2006

Anions of lithium battery salts have been investigated by electronic structure calculations with the objective to find a computational measure to correlate with the observed (in)stability of nonaqueous lithium battery electrolytes vs oxidation often encountered in practice. Accurate prediction of intrinsic anion oxidation potentials is here made possible by computing the vertical free energy difference between anion and neutral radical (ΔG_v) and further strengthened by an empirical correction using only the anion volume as a parameter. The 6-311+G(2df,p) basis set, the VSXC functional, and the C-PCM SCRF algorithm were used. The ΔG_v calculations can be performed using any standard computational chemistry software.

Introduction

In rechargeable lithium ion batteries, a nonaqueous electrolyte is the key to the ion conduction, but the electrolyte also imposes several limitations on the overall battery performance. The perhaps most profound limitation is the instability of the electrolyte, often due, directly or indirectly, to the choice of lithium salt.[1] The electrolyte/electrode solid electrolyte interphase (SEI) is critical, often with the lithium salt anion as a major contributor, with a severe impact on the cycle life, useful voltage, and working temperature, etc., of the battery.[2,3] Therefore, at least three different measures of inherent lithium salt stability are of importance for practical use in lithium battery electrolytes: stability vs reduction, stability vs oxidation, and chemical stability. Here, the stability vs oxidation will be addressed for anions of prominent lithium battery salts.

While anion stability vs oxidation can and has been monitored extensively experimentally for electrolytes, we will here advocate for computational chemistry methods. The main reasons are that the limiting oxidation potentials (E_{ox}) obtained by linear sweep voltammetry (LSV) depend heavily on the measurement conditions (e.g., electrode materials) and how the LSV data are evaluated.[4] Therefore, E_{ox} reported from different sources are far from consistent with each other, even qualitatively. Additionally, also the solvent can be oxidized, especially when propylene carbonate (PC) is used; thus, special studies using other solvents have been performed (GLN,[5] EC/DEE,[6] DEE[6]). To further exclude such solvent effects, Koch et al. made measurements using molten salts to get the “intrinsic anodic stability”.[7] However, in general, solvent oxidation may clearly interfere with attempts to reveal the intrinsic anion oxidation potential. Even an accurately experimentally obtained anion oxidation potential is not a unique feature of the anion itself: the counterion affects the obtained values as does the solvent, via dielectric constant shifted oxidation potentials. These effects are also interconnected: a stronger dielectric solvent solvates the cation stronger and thus leaves the anion more independent, and together with the above-mentioned measurement conditions defies any attempt at reaching intrinsic anion oxidation potentials.

In contrast, computational chemistry methods are uniquely defined and (ideally) produce exactly the same results regardless of the choice of program, computer, and laboratory. They also provide information arising only from the species under study. Several groups have used a computational approach to anion oxidation potentials. Ue and co-workers pioneered the field of computed anion oxidation stabilities with combined computational and experimental studies,[5,8,9] e.g., using tetraalkylammonium salts of a set of anions suitable for electrolytes.[5] In their studies, experimental and computed data agree qualitatively within families of anions, but discrepancies remain for different anion chemistries. This may be due either to inherent problems with the computational approaches taken or to the various sources and errors of the experimental data. The available computational resources at the time probably put a limitation on the work by Kita et al.[10] and Barthel et al.[11] The recent work by Xue and Chen,[12] which copies the strategy of Ue, also uses a very limited range of anion chemistry. In addition to the anions covered in the early studies, new anions have now been synthesized and used, and thus, there is a need to complement these studies computationally.

With all of this in mind, three basic computational strategies are applied on a wide range of anion chemistries including also more recently suggested lithium battery anions such as Id$^-$,[13] TADC$^-$,[14,15] and BOB$^-$.[16] A successful computational approach will be an important future tool to predict the oxidative stability of new lithium salts prior to synthesis.

Computational

The anions studied were the following: AsF_6^-, PF_6^-, BF_4^-, $CF_3SO_3^-$ (Tf$^-$), $[(CF_3SO_2)_2N]^-$ (“imide”, TFSI$^-$), $[(CF_3SO_2)_3C]^-$ (“methide”, TriTFSM$^-$), $N_5C_4^-$ (TADC$^-$), $[(C_2O_4)_2B]^-$ (BOB$^-$), $[(1,2\text{-}C_6H_4O_2)_2B]^-$ (BBB$^-$),[17] $[(1,2\text{-}C_6F_4O_2)_2B]^-$ (4F−BBB$^-$),[11] $[(2,3\text{-}C_{10}H_6O_2)_2B]^-$ (BNB$^-$),[11] and $[1,3\text{-}BF_3-(N_2C_3H_3)]^-$ (“imi-

---

* E-mail: patrikj@fy.chalmers.se. Fax: +46-31-7722090.

10.1021/jp0653297 CCC: $33.50

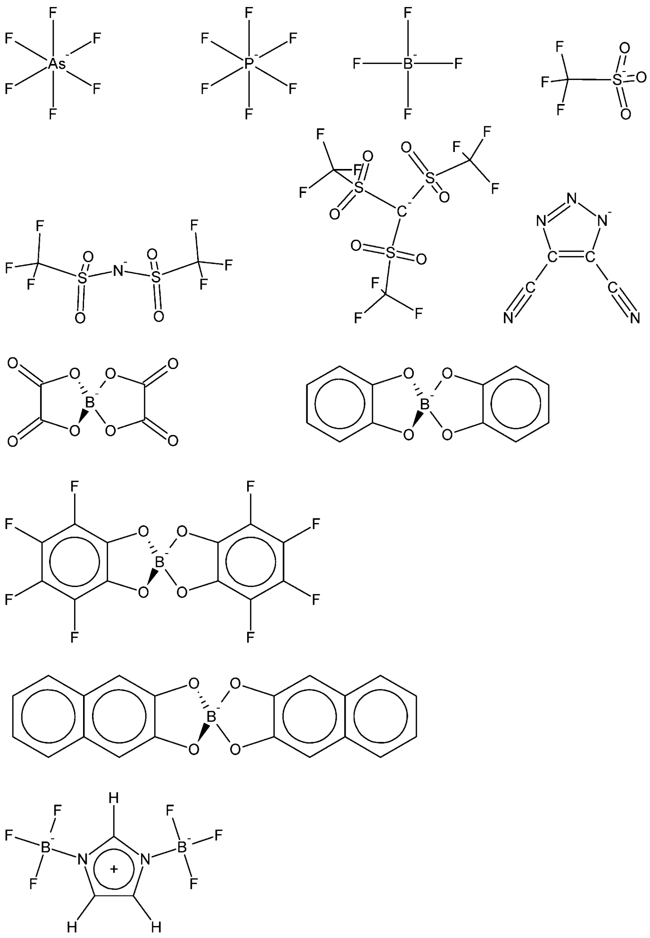

Figure 1. Chemical structures for the anions studied.

dazolide", Id$^-$). The chemical structures of all the anions are found in Figure 1. Literature values of E_{ox} are listed in Table 1.

All anion structures have been fully geometry optimized in the ground state using semiempirical methods (MNDO, AM1), the Hartree−Fock (HF) approximation, and three different density functional theory (DFT) methods: the hybrid functional B3LYP as implemented in Gaussian 03,[18−20] the "nonempirical" exchange-correlation functional of Perdew and co-workers (PBE),[21,22] and van Voorhis and Scuseria's τ-dependent gradient-corrected correlation functional (VSXC).[23] The less common VSXC functional was included due to its reported excellent accuracy with respect to ionization potentials (IPs).[24]

Four different Pople type basis sets were tested: 6-31G* (only for HF with the purpose of direct literature comparison), 6-311+G* ("**a**"), 6-311+G(2df,p) ("**b**"), and 6-311++G(3df,3pd) ("**c**"). Geometry optimizations were done cumulatively. DFT calculations are often quoted to converge more rapidly with basis set size, and here, the basis set convergence for HF and two of the functionals was estimated by the **a** to **c** average deviation in (i) highest occupied molecular orbital (HOMO) energies (eV)—HF, 0.15; B3LYP, 0.11; PBE, 0.12—and (ii) anion electronic energies (eV)—HF, 3.61; B3LYP, 2.91; PBE, 2.75. Thus, the DFT methods are considerably more converged than the HF method. As there are only minute changes from **b** to **c**, all reported data is for basis set **b** due to the lower resource demand, unless where otherwise stated.

As a first measure of anion stability, the highest occupied molecular orbital (HOMO) energies (HF) and the Kohn−Sham HOMO (KS-HOMO) energies (DFT) were extracted (E_{HOMO}). The significance of using E_{HOMO} from HF calculations for comparison with LSV data is generally accepted and is based on Koopmans' theorem connecting the negative of the HOMO energy with the IP.[25] At the same time, it is often stated that the KS-HOMO energy values cannot be used the same way. However, there are suggestions that the KS eigenvalues and orbitals are intrinsically better, as they are true one-electron level based.[26,27] Henceforth, the E_{HOMO} values from both HOMO and KS-HOMO are used without bias.

As the second measure, the vertical transition energy (ΔE_v) was calculated as the electronic energy difference between the anion and the corresponding unrelaxed neutral radical, performed as an additional single-point calculation, i.e., assuming no geometry change during the ionization (the Franck−Condon principle). This corresponds to the IP without zero-point energy (ZPE) correction (which would affect the IP by no more than 0.02−0.1 eV,[9] while adding a significant amount of computational overhead).

However, both the IPs and the calculated ΔE_v are by definition gas phase values. To simulate condensed phase systems, as in battery electrolytes, the different solvation free energies (ΔG_{solv}) of the anions and corresponding radicals should be considered to obtain the vertical free energy change (ΔG_v) (by electrochemical definition, the free electron always is a gas phase species). This was made by additional single-point calculations using a self-consistent reaction field (SCRF) strategy via the C-PCM algorithm.[28] C-PCM offers a ΔG_{solv} accuracy of ~0.1 eV for charged species.[29] For the C-PCM calculations, the default value for water was used to mimic a strong dielectric solvent ($\epsilon = 78.39$) (as often is the case in lithium ion battery electrolytes). To avoid numerical convergence problems, the OFAC and RMIN parameters for C-PCM were set to 0.8 and 0.5, respectively.

All energy changes were converted to electrochemical potentials, and by correcting for the Li^+/Li^0 electrode (−3.04 V[30]), values directly comparable to E_{ox} were obtained.

TABLE 1

			E_{HOMO} vs Li^+/Li^0 (V)						ΔE_v vs Li^+/Li^0 (V)					
anion	E_{ox} vs Li^+/Li^0 (V)	ref	MNDO	AM1	HF	B3LYP	PBE	VSXC	MNDO	AM1	HF	B3LYP	PBE	VSXC
AsF_6^-	6.5−6.8	5,9	n/a	n/a	−8.63	−2.76	−3.02	−1.24	n/a	n/a	7.19	5.30	5.35	4.47
PF_6^-	6.3−6.8	5,9	−6.61	−5.73	−8.05	−2.22	−2.47	−0.70	6.17	5.78	6.58	4.89	4.91	4.07
BF_4^-	6.2−6.6	5,9	−5.52	−4.18	−7.27	−1.47	−1.73	0.06	5.15	3.76	5.94	4.30	4.33	3.64
TFSI$^-$	6.1−6.3,5.3	5,9,10	−5.20	−4.66	−5.30	−1.27	−1.47	−0.27	3.67	4.33	3.20	3.82	3.78	2.94
TriTFSM$^-$	6.1,5.5	9,10	−5.65	−5.57	−4.90	−1.58	−1.76	−0.59	3.81	5.07	2.62	3.29	3.25	2.99
Tf$^-$	5.9−6.0,5.0	5,9,10	−3.91	−3.31	−4.24	0.14	−0.05	1.36	3.51	2.87	3.60	2.36	3.24	2.02
Id$^-$	4.9	13	−3.42	−3.00	−3.25	−0.88	−1.05	−0.05	2.93	2.47	1.83	3.15	3.08	3.00
BOB$^-$	>4.5	16	−4.37	−4.45	−5.52	−1.29	−1.49	−0.08	4.24	4.30	4.80	3.14	3.20	2.47
4F−BBB$^-$	4.1	33	−3.20	−2.98	−2.52	−0.11	−0.20	0.77	2.86	2.63	1.88	1.63	1.59	1.21
TADC$^-$	>4.0	15	−2.38	−2.46	−2.77	−0.39	−0.59	0.51	3.59	3.59	0.90	2.40	2.39	2.14
BNB$^-$	3.9	33	−1.59	−1.69	−0.76	0.97	0.82	1.68	1.12	1.24	0.13	0.19	0.23	−0.15
BBB$^-$	3.7	33	−1.66	−1.77	−1.27	0.93	0.77	1.76	1.33	1.43	0.03	0.73	0.80	0.21

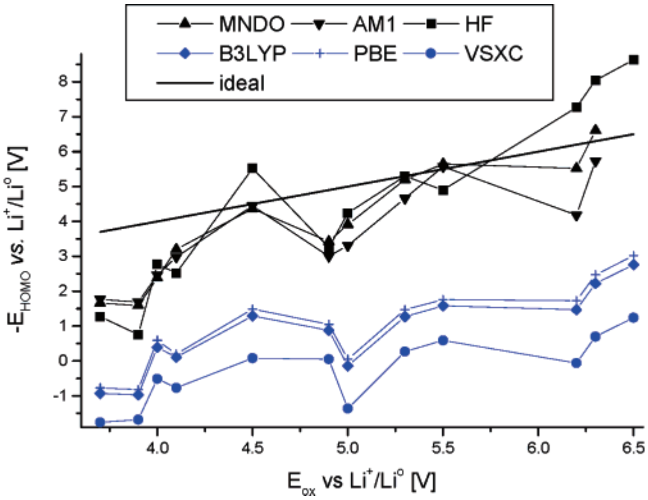

Figure 2. $-E_{HOMO}$ vs E_{ox} for different computational levels.

Anion volumes were obtained from a forthcoming study[31] using MP2(full)/6-31G(d) and a Monte Carlo based algorithm and a 0.001 e•bohr^{-3} electron density cutoff. All calculations were performed using the Gaussian 03 program package.[32]

Results and Discussion

A. E_{HOMO}. The first approach used is based on Koopmans' theorem, and in Table 1, our obtained E_{HOMO} results are shown. At large, the trends found for the very fast semiempirical methods MNDO and AM1 remain for the computationally much more expensive HF and DFT methods. For all computational levels, the small traditional weakly coordinating inorganic fluorinated octahedral anions (YF_6^-) are the most stable, while the larger organic anions with boron centers are the least stable, in agreement with experimental observations. However, for all methods except VSXC, we find BNB$^-$ to be less stable than BBB$^-$, in contrast with experimental results.[33,34] VSXC on the other hand is the only method for which BF_4^- is less stable than both TFSI$^-$ and Id$^-$. Remarkably, the value of −3.541 eV for BNB$^-$ at HF/6-31G* (not shown) is at odds with an earlier computational study using the same method (−4.507 eV[9]).

As shown in Figure 2, there is absolutely not a satisfactory quantitative or qualitative agreement of $-E_{HOMO}$ for any of the methods used toward the literature minimum E_{ox} values. Thus, there is plenty of room for questioning the practical use of anion E_{HOMO} values to accurately estimate anion stabilities, especially for the less stable anions. The method will, however, probably work qualitatively or even quantitatively for similar anions, e.g., the fluorination series of Barthel et al. (BBB$^-$ and 4F−BBB$^-$).

B. ΔE_v. The second approach used is the vertical electronic energy difference between an anion and its neutral radical (ΔE_v). In contrast to Ue et al.,[5,8,9] we use the ΔE_v measure of IPs also for the semiempirical and HF methods. All of the resulting ΔE_v values are found in Table 1 and Figure 3. The absolute values are clearly much better on average than those for the E_{HOMO} measure, but large uncertainties remain. Similar to the previous section, the HF and DFT methods show the most stable anions to be the inorganic fluorinated anions. In contrast to the E_{HOMO} results, however, there is now a clear method dependency for the relative stability of the BBB$^-$ and BNB$^-$ anions—all of the DFT methods suggest BBB$^-$ to be more stable. Surprisingly, the most accurate functional for IPs,[24] VSXC, shows much too low absolute values for all anions. However, the computed IPs via ΔE_v may be perfectly correct but are by definition gas phase values and may thus not be directly comparable with the observed E_{ox}.

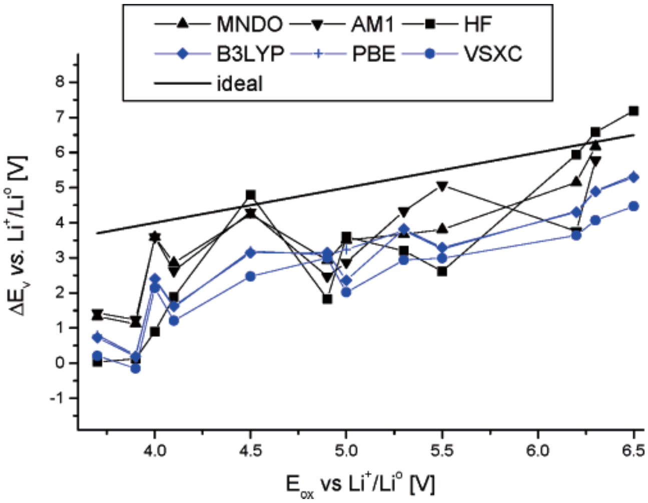

Figure 3. ΔE_v vs E_{ox} for different computational levels.

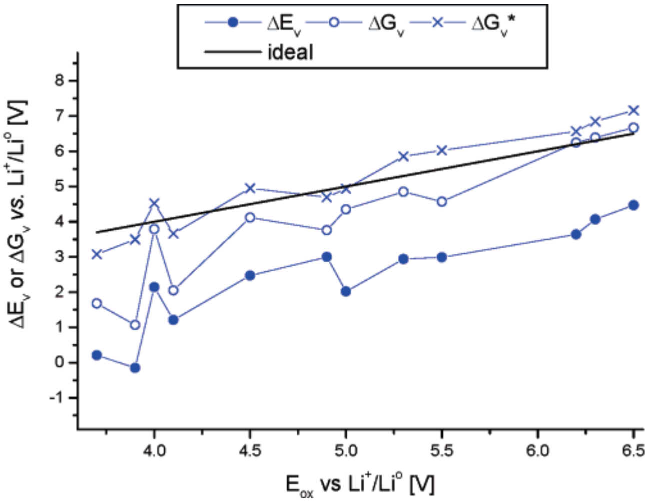

Figure 4. ΔE_v and ΔG_v vs E_{ox} using the VSXC functional including also corrected ΔG_v*.

C. ΔG_v. As outlined in the computational section, the issue of gas phase IPs vs condensed phase E_{ox} is here attacked by using a continuum solvent approach to obtain the vertical free energy change (ΔG_v). ΔG_v is obtained as $\Delta E_v + \Delta G_{solv}$, where the latter is a sum of two main contributions: an electrostatic contribution (ΔG_{el}) based on the polarization of the solute by the continuum solvent and a nonelectrostatic (ΔG_{nonel}) contribution made from three terms—a term based on the cavity to be created for the solute (ΔG_{cav}), a term based on the dispersion interaction (ΔG_{disp}), and a term for the repulsion (ΔG_{rep}). As the physical extent of the anion and the radical are the same, the electrostatic difference between the negatively charged anion and the neutral radical dominates. In Supporting Information Table 1S and Figure 4, the separate contributions to ΔG_{solv} and the final ΔG_v are shown. These data were obtained using the VSXC functional due to its reported accuracy with respect to IPs.[24] It is also clear from the ΔE_v values together with the size of the ΔG_{solv} correction that, e.g., HF would result in a much worse quantitative agreement vs E_{ox}, especially for the most stable anions. From Figure 4, an excellent quantitative agreement is found using ΔG_v for the AsF_6^-, PF_6^-, BF_4^-, BOB$^-$, and TADC$^-$ anions. Still, however, the overall agreement for the least stable anions is far from perfect, but the relative agreement can be excellent within the same family of less stable anions: the E_{ox} difference between BBB and 4F−BBB is 0.4 V, and the obtained difference in ΔG_v is 0.37 V.

Examining the ΔG_v data more carefully, it is clear that the larger the anion, the larger the error vs E_{ox}. This can probably be explained by the way the C-PCM algorithm works: the reaction field potential (V_{PCM}) is obtained iteratively by evaluating the surface charges on the boundary between the solute and the solvent. The boundary surface is based on the vdW radii of the solute atoms, and thus, V_{PCM} is a function of the anion volume. This volume is also dependent on the choice of solvent, and here, the very small water molecule creates a large boundary surface. To correct for the observed error in the volume dependence, we fit our data using $E_{ox} = \Delta G_v + k^*V_{anion}$ and use the resulting k value (0.005 47 ± 0.000 67) to obtain a new, corrected ΔG_v* values (Figure 4). The anion volumes used are listed in Supporting Information Table 1S. As seen (Figure 4), the data are now in excellent agreement with the experimental data for the entire range of reported E_{ox} values. The average error (($E_{ox} - \Delta G_v$*)/E_{ox}) is less than 10%. Changing to the maximum literature E_{ox} values as reference, k becomes 0.006 45 ± 0.000 60 and the error less than 7%. Altogether, these errors should be seen in the light of the sometimes vastly different and uncertain E_{ox} values reported for the same anion.

Conclusions

As previously shown by many others, but perhaps not emphasized enough, both the usual measures of E_{HOMO} and ΔE_v fail to accurately reproduce E_{ox}. In contrast, here, a method that also involves the important solvation behavior and the associated free energy changes is shown to be able to provide quantitative values of anion oxidation potentials. This ΔG_v approach is then strengthened by an empirical correction using only the anion volume as a parameter to predict E_{ox} (as ΔG_v*) across very differently sized anions and anion chemistries. This stands in clear contrast to earlier computational approaches where different fits have had to be made for each type of anion chemistry; cf. Figure 6 in ref 9.

The method is fast and simple and can be applied using any standard computational chemistry software to screen new lithium salts for battery electrolytes with respect to stability vs oxidation.

Acknowledgment. The Swedish Research Council (VR) supported this work. The calculations were performed on the local CMP Linux-cluster and at the Centre for Parallel Computing (PDC) provided through a grant by the Swedish National Allocations Committee (SNAC).

Supporting Information Available: Table showing ΔG_v components and anion volumes. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Tarascon, J. M.; Armand, M. *Nature* **2001**, *414*, 359.
(2) Andersson, A. M.; Herstedt, M.; Bishop, A. G.; Edström, K. *Electrochim. Acta* **2002**, *47*, 1885.
(3) Peled, E.; Golodnitsky, D.; Menachem, C.; Bar-Tow, D. *J. Electrochem. Soc.* **1998**, *145*, 3482.
(4) Xu, K. *Chem. Rev.* **2004**, *104*, 4303.
(5) Ue, M.; Takeda, M.; Takehara, M.; Mori, S. *J. Electrochem. Soc.* **1997**, *144*, 2684.
(6) Guyomard, D.; Tarascon, J. M. *J. Power Sources* **1995**, *54*, 92.
(7) Koch, V. R.; Dominey, L. A.; Nanjundiah, C.; Ondrechen, M. J. *J. Electrochem. Soc.* **1996**, *143*, 798.
(8) Ue, M.; Ida, K.; Mori, S. *J. Electrochem. Soc.* **1994**, *141*, 2989.
(9) Ue, M.; Murakami, A.; Nakamura, S. *J. Electrochem. Soc.* **2002**, *149*, A1572.
(10) Kita, F.; Kawakami, A.; Sonoda, T.; Kobayashi, H. In *New Sealed Rechargeable Batteries and Supercapacitors*; Barnett, B. M., Dowgiallo, E., Halpert, G., Matsuda, Y., Takehara, Z., Eds.; The Electrochemical Society Proceedings Series; Electrochemical Society: Pennington, NJ, 1993; PV 93-23, p 321.
(11) Barthel, J.; Buestrich, R.; Carl, E.; Gores, H. J. *J. Electrochem. Soc.* **1996**, *143*, 3572.
(12) Xue, Z. M.; Chen, C. H. *Electrochim. Acta* **2004**, *49*, 5167.
(13) Barbarich, T. J.; Driscoll, P. F. *Electrochem. Solid-State Lett.* **2003**, *6*, A113.
(14) Johansson, P.; Béranger, S.; Armand, M.; Nilsson, H.; Jacobsson, P. *Solid State Ionics* **2003**, *156*, 129.
(15) Egashira, M.; Scrosati, B.; Armand, M.; Béranger, S.; Michot, C. *Electrochem. Solid-State Lett.* **2003**, *6*, A71.
(16) (a) Lischka, U.; Wietelmann, U.; Wegner, M. Ger. DE 19829030 C1, 1999. (b) Xu, W.; Angell, C. A. *Electrochem. Solid-State. Lett.* **2001**, *4*, E1.
(17) Barthel, J.; Wühr, M.; Buestrich, R.; Gores, H. J. *J. Electrochem. Soc.* **1995**, *142*, 2527.
(18) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
(19) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
(20) Vosko, S. H.; Wilks, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.
(21) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.
(22) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1997**, *78*, 1396.
(23) van Voorhis, T.; Scuseria, G. E. *J. Chem. Phys.* **1998**, *109*, 400.
(24) Cramer, C. J. *Essentials of Computational Chemistry*; John Wiley & Sons: Chichester, U.K., 2002; Table 8.4.
(25) Koopmans, T. *Physica* **1934**, *1*, 104.
(26) Stowasser, R.; Hoffmann, R. *J. Am. Chem. Soc.* **1999**, *121*, 3414.
(27) Baerends, E. J. *Theor. Chem. Acc.* **2000**, *103*, 265.
(28) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995.
(29) Winget, P.; Cramer, C. J.; Truhlar, D. G. *Theor. Chem. Acc.* **2004**, *112*, 217.
(30) Aylward, G.; Findlay, T. *SI Chemical Data*, 3rd ed.; John Wiley & Sons: Brisbane, 1994; Table 21.
(31) Johansson, P. *Phys. Chem. Chem. Phys.* **2007**, in press.
(32) Frisch, M. J.; et al. *Gaussian 03*, revision C.02; Gaussian, Inc.: Pittsburgh, PA, 2003.
(33) Nolan, B. G.; Strauss, S. H. *J. Electrochem. Soc.* **2003**, *150*, A1726.
(34) Barthel, J.; Gores, H. J.; Neueder, R.; Schmid, A. *Pure Appl. Chem.* **1999**, *71*, 1705.