468 *J. Chem. Eng. Data* **2009,** *54,* 468–471

Investigation of the Hydrolysis of Lithium Bis[1,2-oxalato(2-)-*O*,*O′*] Borate (LiBOB) in Water and Acetonitrile by Conductivity and NMR Measurements in Comparison to Some Other Borates[†]

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The hydrolysis of lithium bis[1,2-oxalato(2-)-*O*,*O′*] borate (LiBOB) was investigated in pure water and in solutions of acetonitrile at low water content. The reaction in pure water can easily be observed by time-dependent conductivity measurements as protons are generated in the first step of hydrolysis. The results of these measurements can be evaluated according to a reaction of pseudo first order. Hydrolysis of other lithium borates in water was also studied for comparison. In acetonitrile as solvent, hydrolysis is much more complicated. NMR studies show a very slow reaction of LiBOB with water resulting in equilibria, depending on the water content of acetonitrile. Temperatures of 60 °C and water contents of several percent are necessary to achieve observable effects.

Introduction

Water is known as one of the major impurities in lithium-ion batteries impairing battery performance. It not only decomposes at the potentials of a lithium-ion cell but also reacts with the anions of the electrolyte. Especially the state of the art conducting salt lithium hexafluorophosphate ($LiPF_6$) is prone to react with water to form hydrogen fluoride (HF).[1] The hydrolysis of $LiPF_6$ has been investigated in pure water and in a solution of ethylene carbonate/diethyl carbonate (EC/DEC) comparable to a battery electrolyte.[2] Density functional theory and molecular dynamics studies were used to explain the reaction mechanism in typical battery solvents.[3] The new conducting salt lithium bis[1,2-oxalato(2-)-*O*,*O′*] borate (LiBOB, CAS-No. 244761-29-3) has the advantage of being free of fluorine inherently preventing the unwanted formation of HF. On the other hand, only little is known about its hydrolysis. Xu and Angell state a slow decomposition yielding lithium metaborate $LiBO_2$ and monolithiumoxalate.[4]

LiBOB can decompose in reversal of one of its formation reactions

$$LiOH + 2H_2C_2O_4 + H_3BO_3 \rightarrow Li[B(C_2O_4)_2] + 4H_2O \quad (1)$$

which can be carried out in water as solvent.[5] The first step of hydrolysis is probably the opening of one of the chelate rings followed by formation of monolithium oxalate. In water, this step sets free protons dominating the conductivity of the solution due to their high single ion conductivity. To break all four B−O bonds of the BOB anion, 4 equiv of water is necessary (compare eq 1). The hydrolysis of LiBOB was studied in two different ways. The first approach is to dissolve LiBOB in a very small amount of acetonitrile (AN) and inject the resulting solution into a large amount of water. The second one is to use a solution of LiBOB in AN that is mixed with a small amount of water. This approach is more similar to the situation of a lithium-ion cell contaminated with water.

Experimental

The storage of chemicals and the preparation of the required solutions were done in an Ar-filled glovebox (MBraun, Melsungen, type MB150BG, $\omega(H_2O) < 1 \cdot 10^{-6}$). All glassware was dried for 24 h at 65 °C and 0.1 mbar before use. LiBOB (battery grade) was obtained from Chemetall GmbH, Frankfurt, and acetonitrile (selectipur) from Merck KGaA, Darmstadt. Acetonitrile-d_3, HDO + D_2O < 0.05 %, 99.8 % D, was obtained from Euriso-Top GmbH, Saarbrücken, and $LiBF_4$ was obtained from Stella Chemifa Corp., Osaka, Tokio (battery grade). All other electrolytes were synthesized in our laboratory of purity in excess of 99.5 %. For their synthesis, analysis, and characterization see refs 6, 7, 8, and 9 and the literature cited therein. To observe hydrolysis of lithium tetrafluoroborate ($LiBF_4$), lithium difluoromono[1,2-oxalato(2-)-*O*,*O′*] borate (LiF_2OB), lithium bisoxalatoborate (LiBOB), lithium bis[1,2-benzenediolato(2-)-*O*,*O′*] borate (LiBBDB), lithium bis[monofluoro-1,2-benzenediolato(2-)-*O*,*O′*] borate (LiBFBDB), and lithium bis[3,4,5,6-tetrafluoro-1,2-benzenediolato(2-)-*O*,*O′*] borate ($LiBF_4BDB$), in an excess of water (approach 1), concentrations of acetonitrile solutions were adjusted so that by adding 1000 μL of these solutions a total cell concentration of $1 \cdot 10^{-2}$ mol·L^{-1} in excess water was realized. Previous to addition of the AN-based solutions, the measurement cell was flushed with nitrogen, filled with 50 mL of H_2O (Millipore), and thermostatted by a thermostat (RK8 KP Lauda) at (25.0 ± 0.1) °C. Conductivity measurements were recorded by a WTW LF597 conductometer in an in-house built cell (Pt-electrodes, cell constant of approximately 42 cm^{-1}). Some conductivity measurements at 25 °C where also done in a setup recently designed for recording phase diagrams.[10] Conductivity measurements at 60 °C were performed with an in-house built cell (Pt-electrodes, cell constant of approx. 35 cm^{-1}) that was stirred by a magnetic stir bar and thermostatted within 0.1 K. Again, a WTW LF597 conductometer connected to a PC was used for data acquisition. ^{11}B and ^{7}Li NMR spectra were measured with a Bruker Avance 400 at 128.4 MHz (^{11}B) and at 155.5 MHz (^{7}Li), and ^{1}H and ^{13}C NMR

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[†] Part of the special issue “Robin H. Stokes Festschrift”.

10.1021/je800473h CCC: $40.75

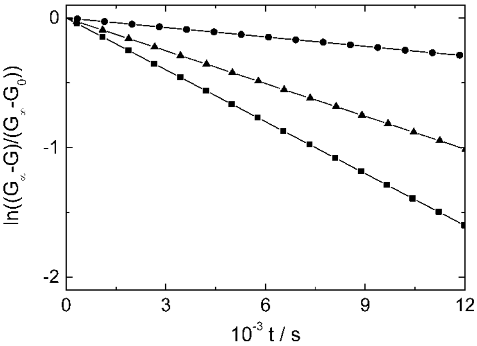

Figure 1. Fit of conductivity data according to eq 2 showing the influence of fluorination of ligands. From top to bottom: LiF_4 (circles), LiF_2OB (triangles), LiBOB (squares).

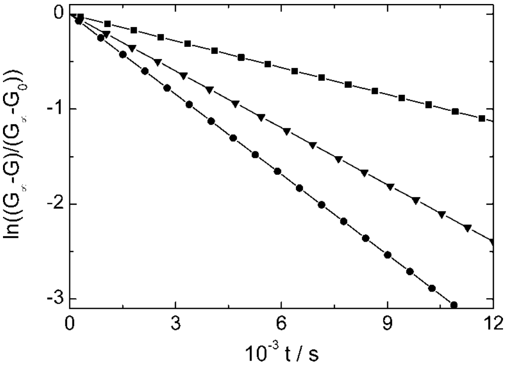

Figure 2. Fit of conductivity data according to eq 2 showing influence of electron-withdrawing ligands. From top to bottom: LiBBDB (squares), LiBFBDB (triangles), and $LiBF_4BDB$ (circles).

spectra were measured with a Bruker Avance 300 at 300.1 MHz (^1H) and at 75.5 MHz ($^{13}C\{^1H\}$), respectively.

Results and Discussion

Hydrolysis in Water. Concerning aqueous solutions, the major part of conductivity derives from protons because of their high single ion conductivity λ_{H+}.[11] The anions of the educts and the ones formed during hydrolysis do scarcely differ in dimensions and charge, so they are, as well as liberated fluoride, not taken into account. So, for analysis of total hydrolysis, a pseudo first order kinetics is supposed. The respective integral time law is

$$\ln \frac{G_\infty - G}{G_\infty - G_0} = -kt \qquad (2)$$

where G is the conductivity at any time t; G_∞ is the conductivity at $t = \infty$; and G_0 is the conductivity at the beginning of the experiment. Received data were fitted (Origin 6.0, Microcalc) to the $G(t)$ function presented in eq 2, yielding a linear function as expected. Figure 1 shows such a linear plot according to eq 2.

It is obvious that hydrolysis kinetics is different for measured salts. The rate constants show the sequence $LiBF_4 < LiBF_2OB < LiBOB$, increasing with decreasing fluorination of boron. A possible reason for this observation is the hydrophobic behavior of fluorine ligands.

Figure 2 shows that another influence on rate constant is observable by exchange of organic ligands by more electron-withdrawing ones. It was found that liability to hydrolyze increases by lithium bis[1,2-benzenediolato(2-)-*O*,*O*′] borate (LiBDB), lithium bis[3-fluoro-1,2-benzenediolato(2-)*O*,*O*′] borate (LiBFBDB), and lithium bis[3,4,5,6-tetrafluoro-1,2-benzenediolato(2-)-*O*,*O*′] borate ($LiBF_4BDB$) with cumulative grade of fluorination of the ligand (see also Table 1). The result is in line with the conception of charge delocalization by electron-withdrawing ligands at boron. This effect involves a dislocation of charge from boron to bridging oxygen, the resulting decrease of charge density facilitating the attack of water in the first step. Table 1 shows the rate constants for hydrolysis of lithium borates in water along with errors obtained for linear least-squares fitting.

Table 1. Measured Rate Constants *k* of Some Borates in Water

salt	acronym	$10^5k/s^{-1}$
$LiBF_4$	–	2.431 ± 0.003
$Li[BF_2(C_2O_4)]$	LiF_2OB	8.428 ± 0.013
$Li[B(C_2O_4)_2]$	LiBOB	13.346 ± 0.003
$Li[B(C_6H_4O_2)_2]$	LiBBDB	9.396 ± 0.009
$Li[B(C_6H_3FO_2)_2]$	LiBFBDB	19.937 ± 0.127
$Li[B(C_6F_4O_2)_2]$	$LiBF_4BDB$	28.123 ± 0.052

Table 2. Changes of Conductivity *G* of 0.097 mol·kg^{-1} LiBOB in AN after 244 000 s at Given Water Contents[a]

$\omega(H_2O)/10^{-6}$	$n(H_2O)/n(LiBOB)$	$G(t = 0)$ / mS	$G(t_{Addition})$ / mS	$G(t = 244\,000$ s) / mS	ΔG/%
490	0.286	10.89	10.45	10.58	+1.2
1100	0.642	9.29	8.26	8.44	+2.2
2920	1.70	7.95	7.59	7.77	+2.4
4990	2.91	8.50	7.96	8.12	+2.0
6840	4.00	8.41	8.40	7.95	−5.4
9260	5.39	12.62	12.16	11.57	−4.9

[a] Temperature for all experiments was 25 °C. $G(t = 0)$ denotes conductivity of dry solution; $G(t_{Addition})$ is conductivity after water addition; and $G(t = 244\,000$ s) is conductivity at the end of the measurement. Due to the use of cells with different cell constants, absolute conductivities differ. As we are only interested in relative changes of conductivity, cell constants were not determined.

Hydrolysis at Small Water Contents. The large excess of water in the experiments described up to now does not reflect the situation in a real battery. Here, the conducting salt, e.g., LiBOB, is dissolved in some organic solvents, and small amounts of water are present as contamination. The following measurements try to model this situation. Experiments with water mass fractions below $5 \cdot 10^{-4}$ did not show any observable effects, so the water content was increased. The measurements were done at 25 °C with the setup mentioned above[10] and are summarized in Table 2. To handle the small amounts of water, standard solutions with $\omega(H_2O) = 5.58 \cdot 10^{-3}$ and $\omega(H_2O) = 5.40 \cdot 10^{-2}$ water in AN were injected. The mole ratio of water and LiBOB for each experiment is given in the column $n(H_2O)/n(LiBOB)$. The additions of water were chosen so that LiBOB is in excess at water mass fractions up to $\omega(H_2O) = 4.99 \cdot 10^{-3}$. At $\omega(H_2O) = 6.84 \cdot 10^{-3}$, the assumed stoichiometry of 4:1 is reached, whereas at $\omega(H_2O) = 9.26 \cdot 10^{-3}$, water is in excess.

Apart from fluctuations during the injection phase of water, no significant change of conductivity can be detected. The changes of conductivity after 244 000 s are given in Table 2. Water contents up to $\omega(H_2O) = 4.99 \cdot 10^{-3}$ result in a slight increase in conductivity probably due to solvation effects, whereas at higher water contents, a slight decrease is observed, which can be attributed to the starting hydrolysis of LiBOB. To achieve a distinct effect during reasonable measurement time, water and also LiBOB contents were increased in the following experiments. However, with an up to 49-fold excess of water, this was not the case. So temperature was increased to 60 °C using the in-house built cell and the WTW conductometer. The conductivity curves of additions of 2.19 % ($n(H_2O)/n(LiBOB) = 12.7$) and 4.67

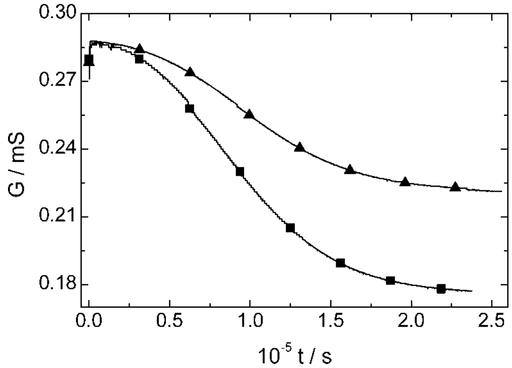

Figure 3. Conductivity during hydrolysis of 0.09 mol·kg^{-1} LiBOB in AN at 60 °C. Triangles denote $\omega(H_2O) = 2.19 \cdot 10^{-2}$ and squares denote $\omega(H_2O) = 4.67 \cdot 10^{-2}$. Conductivity of dry solution before addition of H_2O is 0.28 mS.

Table 3. Water Contents Determined by ^{1}H NMR during Reaction of 0.249 mol·kg^{-1} LiBOB with 0.530 mol·kg^{-1} Water

sample	t/s	G/mS	$b(H_2O, NMR)/(mol \cdot kg^{-1})$
1	345	0.779	0.699
2	75331	0.754	0.585
3	122716	0.741	0.581
4	162321	0.739	0.581

% ($n(H_2O)/n$(LiBOB) = 29.1) water to a solution of 0.09 mol·kg^{-1} LiBOB in AN are shown in Figure 3. As the proton does not show a dominating single ion conductivity in AN, the contribution of educts and products to overall conductivity cannot be neglected. This complicates numerical evaluation as all occurring species have to be taken into account.

During the reaction, a solid precipitate appeared that was collected at the end of the measurement. The precipitate was washed with AN and dried in vacuum. It was soluble neither in methanol nor in dimethyl sulfoxide but only soluble in water. Adding AN to a solution in water precipitates the solid again. A ^{11}B NMR recorded in D_2O showed no boron signals but a peak at 165.57 ppm in the ^{13}C NMR that can be attributed to oxalic acid.[12] ^{7}Li NMR shows a singulett at 0.035 ppm originating from solvated Li^+. ^{1}H NMR shows only a singulett at 4.7 ppm caused by traces of water.

To get more information about the species appearing and their concentration, ^{11}B NMR spectroscopy was applied. Samples were drawn during the reaction monitored by conductivity and stored at −18 °C under a dry nitrogen atmosphere. As the experiments at 25 °C have shown, this should slow down the reaction so far that further changes of the sample during storage are negligible. At the end of the experiment, spectra of all samples were recorded. All spectra show a peak at 8.08 ppm that can be clearly attributed to the BOB anion. During the reaction, a second peak appears at 20.5 ppm indicating trivalent boron bound to three oxygen atoms.[13] The integral of this peak gradually increases to 13 % of the BOB peak but does not exceed this value, although conductivity shows no change in conversion anymore.

The change of water content during the reaction is investigated by a technique developed originally to determine the water content of LiBOB.[14] Because of the limited dynamic range of NMR spectrometers, this method requires deuterated AN as solvent. The solution used for the experiment contained 0.236 mol·kg^{-1} ethylene carbonate as proton standard. LiBOB content was 0.249 mol·kg^{-1}, and 0.530 mol·kg^{-1} water was added. Considering the stoichiometry of 4:1, this is a 2-fold excess of LiBOB, so all water should be consumed during reaction.

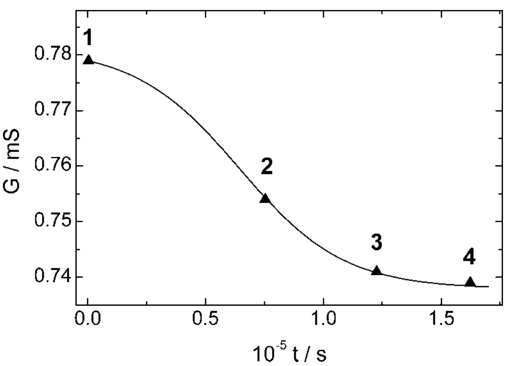

Figure 4. Conductivity and samples taken for ^{1}H NMR. 0.249 mol·kg^{-1} LiBOB in AN with 0.530 mol·kg^{-1} water. Numbers over the triangles denote sample numbers.

Table 3 gives an overview over the four samples drawn during reaction, which was again monitored by conductivity as shown in Figure 4. Sample 1 was taken directly after injecting water into the solution so the value determined by NMR should conform to the value of 0.530 mol·kg^{-1} calculated from masses. The deviation of +33 % matches the results published for this method.[14] Sample 2 was taken near the inflection point of conductivity showing only slightly reduced water content. Although the conductivity at samples 3 and 4 shows no significant change anymore, water content is still considerably high. This indicates that the reaction is running into an equilibrium on the side of the educts. Adding additional amounts of water at this point produces similar conductivity curves as shown in Figure 4, while the system is running into the new equilibrium.

Conclusion

Hydrolysis of LiBOB in a large excess of water has been investigated by conductivity measurements which can be interpreted as kinetics of pseudo first order. The hydrolysis of other borates was studied for comparison. In the sequence $LiBF_4$, LiF_2OB, and LiBOB, rate constants increase reflecting an easier splitting of B−O when compared to B−F bonds. In contrast, for benzenediolatoborates, increasing rate constants are observed with increasing fluorination, k(LiBBDB) < k(LiBFBDB) < $k(LiBF_4BDB)$, showing the increasing ability of fluorinated ligands to leave boron.

As a simple model system for the situation in a lithium-ion cell, hydrolysis was also studied in acetonitrile. At 25 °C, water contents up to 30 % did not show observable effects during measurement time. At 60 °C and water contents of several percent, sigmoid conductivity curves were obtained in the time scale of 100 000 s. Analysis of the solution by ^{11}B and ^{1}H NMR indicated equilibria on the side of the educts which can be shifted by repeated additions of water. During reaction, a solid precipitated which contains oxalate.

Compared to $LiPF_6$, LiBOB not only has the advantage of benign decomposition products but also shows higher stability against water. This may be a valuable property of LiBOB for its use in lithium-ion cells.

Acknowledgment

We thank R. H. Stokes, who paved the way for us to understand electrolyte solutions, and D. Moosbauer for editing.

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Received for review June 26, 2008. Accepted September 8, 2008. The corresponding author thanks our sponsors, the DFG-Forschungsinitiative: Funktionsmaterialien and Materialanalytik zu Lithium-Hochleistungsbatterein (contract # 544243), Chemetall GmbH (Frankfurt), and Merck KGaA (Darmstadt).

JE800473H