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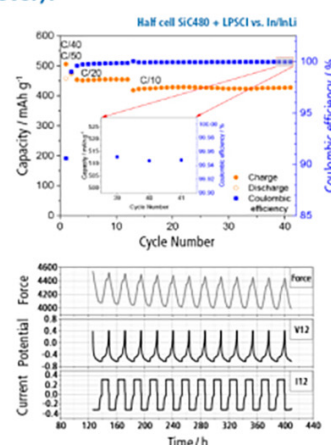
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Some Effects of Intentionally Added Water on LiCoO₂/Graphite Pouch Cells

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LiCoO₂/graphite pouch cells with 1 M LiPF₆ in EC:DEC (1:2 v/v) (control electrolyte) containing selected additives and different amounts of intentionally added water were studied. Archimedes principle was used to track gas evolution while an automated storage system, electrochemical impedance spectroscopy and cell cycling experiments were used to study electrochemical properties imparted by the addition of water. Water was added from 125 to 2000 ppm to control electrolyte and to electrolyte with 2% vinylene carbonate (VC) and/or 2% lithium bis(trifluoromethane sulfonyl imide) (LiTFSI). The addition of water to either VC or VC + LiTFSI-containing electrolyte resulted in minimal or no changes in voltage drop and charge transfer resistance during storage while both added water and LiTFSI actually decreased swelling during storage. Added water to control electrolyte or VC-containing electrolyte did not impair cell cycling performance at 55°C. Solution nuclear magnetic resonance (SNMR), in-situ gas measurements, gas chromatography coupled with a thermal conductivity detector (GC-TCD), and X-ray photoelectron spectroscopy (XPS) were employed to understand why added water did not affect cell performance.

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Lithium-ion batteries are generally used in power tools and portable electronics applications. Li-ion battery packs for electrified vehicles and grid energy storage need even longer lived and, preferably, less expensive cells. Water is commonly regarded as being detrimental to cell performance, because HF generated from water and LiPF₆ (widely used in lithium-ion batteries) can react with SEI components and corrode positive materials causing transition metal dissolution.^{1,2} Therefore, Li-ion cell manufacturers generally lower water contents in electrolyte solvents and electrolytes to less than 50 ppm.³

Stringent water content specifications lead to increased manufacturing cost. Recently, Burns et al.⁴⁻⁶ found that water (up to 1000 ppm) added intentionally to the electrolyte of Li-ion prismatic cells with LiCoO₂ (LCO) or LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ (NMC) positive electrodes and graphite or LTO negative electrodes did not have a detrimental effect on cell performance. In some cases, the addition of water was even beneficial in terms of coulombic efficiency, cell impedance and voltage drop during storage. They found that the added water caused cell swelling during the first cycle and generally the more water that was added the larger expansion the cells experienced. The swelling of cells can lead to mechanical stress of the devices containing the cells. Pouch cells are widely used in the Li-ion industry and are an excellent cell format to study gas evolution due to their flexible packaging.^{7,8} In addition, pouch cells are degassed after the first formation step so any initial gases produced by the presence of water can be removed.

In this study, pouch cells were chosen to study the impact of intentionally added water on their electrochemical properties and gas evolution. Various experimental techniques were used to study the gas compositions, the electrolyte evolution and surface chemistry changes due to the added water to gain insights into why added water does not greatly impair cell performance.

Experimental

Dry 323036-size LiCoO₂ (LCO)/graphite (320 mAh) pouch cells without electrolyte were received from BAK Co. (Shenzhen, China). The cells were vacuum sealed in a dry room in China and then shipped to Canada for filling with electrolyte. Cells to be filled with 1 M LiPF₆ in EC:DEC (BASF, USA, water content of the EC:DEC < 20 ppm, water content of the LiPF₆ < 50 ppm) (1:2 v/v) (called control electrolyte here) + 0, 125, 250, 500, 1000, 2000 ppm water or/and 2%

vinylene carbonate (VC) (99.97% BASF, USA) were not dried again in a vacuum oven before filling. However, cells with to be filled with control electrolyte + 2% LiTFSI (>99%, 3 M, USA) + 0, 125, 250, 500, 1000, 2000 ppm water and/or 2% VC were cut open below the seal and dried in a vacuum oven at 110°C for 14 hours prior to filling. The pouch cells were filled with electrolyte in an argon-filled glove box and two cells of each type were made to ensure repeatability of the measurements. In rare cases, only one cell was available. After adding 1.00 g of electrolyte, cells were vacuum sealed at 94% vacuum using a vacuum sealer (MTI Corporation, MSK-115A). A centrifugal wetting (50 g-force for 20 min) procedure and a 24 h hold at 40.0 ± 0.1°C and 1.5 V were used to ensure complete wetting of the cell coil.

The first charge-discharge cycle (called the formation cycle here) involved charging at 2 mA (corresponding to C/160) for 10 hours and then at 15 mA (~C/20) to 4.2 V followed by a discharge to 3.8 V at 15 mA. After the formation cycle, cells were degassed in the glove box and vacuum sealed again. The total volumes of gas generated in the cells after the formation cycle were measured using Archimedes' principle by weighing the cells while submerged in nano-pure water and comparing the weight before and after formation. After degassing, cells were transferred to a Biologic VMP3 for electrochemical impedance spectroscopy (EIS) measurements between 100 kHz and 10 mHz at 10 ± 0.1°C. After EIS was completed, the cells were moved to a 40°C temperature box and the cells were charged to 4.2 V at 25 mA and then held at 4.2 V until the current dropped to the corresponding C/1000 current. The cells were then moved to a storage system to measure voltage versus time for a 500 h storage period at 40°C.⁹ After the storage period, Archimedes' principle was again used to determine the gas generation during storage and then the cells were moved into the glove box, degassed and sealed again. Finally, cells were moved to the same charger system to be discharged to 3.8 V at 25 mA and held until the current dropped down to the corresponding C/1000 rate and EIS spectra were measured again. Several cells were selected for long term cycling at 55°C using a 15 mA charge/discharge current (around C/20) between 2.8 and 4.2 V. Cells were cycled without physical pressure, i.e. unclamped.

In-situ gas measurements for water-containing cells.—Two cells with 0.84 g of control electrolyte + 1750 ppm water or 0.79 g of control electrolyte + 1750 ppm water + 2% VC were held at 1.5 V for 45 h then 1.9 V for 10 h while the volume of gas generated was measured in-situ versus time using novel equipment.⁸

Analysis of gas compositions for water-free and water-containing cells.—Four cells with 0.9 g of control electrolyte or

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control electrolyte + 1500 ppm water were held at 1.5 V for 24 h. The gas produced in these cells was then extracted following the method described by Petibon et al.¹⁰ The extracted gas was then injected in the GC-TCD. The GC-TCD used consisted of a Bruker 436 GC equipped with a splitless injector (270°C) and a Bruker thermal conductivity detector equipped with a custom-made capillary column. The column consisted of 5 A molecular sieve column (Bruker, 10 m, 0.32 mm ID, 30 μ m coating), in parallel with a Q-LOT column (Bruker, 50 m, 0.53 mm ID, 20 μ m coating). This custom column allows for permanent gases (H_2 , O_2 , N_2 , CO) and light hydrocarbons (CH_4 , C_2H_6 , C_2H_4 , etc) and CO_2 to well be separated in a single injection. Argon was as carrier gas at a flow rate of 9 mL min⁻¹. In order to maximize the sensitivity of the detector, the reference cell flow rate of the TCD was set at 30 mL/min and the make-up flow rate of the analytical cell was set to 5 mL/min. The TCD temperature was set to 230°C while the filament temperature was set to 370°C. A custom gas mixture of known composition was obtained from Praxair. This gas mixture was used for retention time determination and signal calibration.

X-ray photoelectron spectroscopy (XPS) for surface analysis and scanning electron microscope (SEM) study of the separator surface.—XPS was used for surface analysis of the surfaces of graphite and LCO electrodes from pouch cells with and without 2000 ppm water. These pouch cells were either only held at 1.5 V for 24 h or charged to 3.8 V at C/20 after a 24 h potential hold at 1.5 V. The sample preparation procedure followed that the one described by Madec et al.¹¹ XPS was performed on a SPECS spectrometer equipped with a Phoibos 150 hemispherical energy analyzer and using Mg K α radiation ($h\nu = 1253.6$ eV). The analyzed sample area was $\sim 2 \times 3$ mm² which gives results representative of the whole electrode. Core electron spectra were recorded in the fixed analyzer transmission (FAT) mode with a 20 eV pass energy at an operating pressure $< 2 \times 10^{-9}$ mbar. Short acquisition time spectra were first recorded as reference to follow any possible sample degradation during the analysis. Data treatment was performed using CasaXPS software. The binding energy scale was calibrated from the C1s peak at 285 eV (C-C/C-H) and the O1s peak at 529.6 eV (O^{2-} anion from the NMC) for the graphite and NMC electrodes respectively. Nonlinear Shirley-type background¹² was used for core peaks analysis while 70% Gaussian - 30% Lorentzian Voigt peak-shape profiles and full width at half-maximum (fwhm) constraint ranges were selected to optimized areas and peak positions. The surface of the separator taken from a fresh LCO/graphite pouch cell was investigated using a NanoScience Phenom Pro G2 Desktop SEM. The separator was coated with a ~ 10 nm gold layer before analysis.

Solution nuclear magnetic resonance (SNMR) for analysis of the by-products created by water added to electrolytes.—SNMR was used to identify how added water reacts with electrolytes especially within the cell. ¹⁹F-NMR and ³¹P-NMR spectra were collected at room temperature using a Bruker AC-250 (5.9 T) NMR spectrometer. Chemical shifts are reported in ppm relative to external reference standards (³¹P-NMR, 85% H_3PO_4 and ¹⁹F-NMR, 0.5% $CF_3C_6H_5$). Since HF generated from the hydrolysis of $LiPF_6$ can react with typical NMR tubes, a thin wall fluoro-ethylene propylene (FEP) liner with a polytetrafluoroethylene (PTFE) plug (Sigma) inserted into a normal glass NMR tube was used to prevent this reaction.

The NMR samples were either collected from water-containing electrolyte which was stored in a sealed container in an argon-filled glove box for 5 days or from cells filled with water-containing electrolyte which were held at 1.5 V for 24 h. In order to investigate if the cell components (separator, fresh graphite or the LCO electrode) react with the byproducts from hydrolysis of $LiPF_6$, the water-containing electrolyte was also mixed with cell components and stored in separate sealed containers under the same conditions. Enough electrolyte could not simply be removed from the cells for NMR experiments since the electrolyte was evenly distributed in jelly roll. In order to extract enough electrolyte from the cells, EMC was added into the cells after the cells were cut open in the glove box. After squeez-

ing the cells several times to mix the EMC with the electrolyte, an appropriate amount of the mixture was extracted from the cells and injected directly into the special NMR tube. The samples were not further mixed with any deuterated or non-deuterated solvent.

Results and Discussion

Figure 1 shows the volume (mL) of gas generated during the formation cycle as a function of the amount of added water to control electrolyte, VC-containing, LiTFSI-containing and VC + LiTFSI-containing electrolyte. The pouch cells have an initial volume of about 2.5 mL. This gas volume was measured using Archimedes' principle at 21°C using deionized water. The gas volume increased when more water was added to any of the electrolytes. The slope of the gas volume versus water content curve for cells without VC is roughly the same as that for cells with VC. This may suggest that the gas generation mechanism due to added water is the same whether the cells contain VC or not. VC has been shown to limit gas generation in cells without water by presumably changing the distribution of products of electrolyte reduction from gases to liquids or polymers.⁸ The experimental slopes of the data in Figure 1 are between the expected slope based on one mole of water producing one mole of hydrogen and the expected slope based on one mole of water producing a half mole of hydrogen.

Figure 2 shows the gas volume measured using Archimedes' principle (water, 21°C) after the 500 h storage period. Some cells containing LiTFSI had small negative volume changes. Since the measurements were taken at almost the same voltage, contraction of the electrodes cannot be the reason for this phenomenon. We believe that a small portion of gas was not extracted from the pouch during the degassing process (second vacuum sealing) since the cells were not pumped to full vacuum during vacuum sealing. This remaining gas could then be consumed at either the positive electrode or the negative electrode during the 500 h storage period leading to a small decrease in cell volume.¹³ The cells containing control + H_2O electrolyte have smaller gas evolution during the storage period than the control cells. It seems that the more water was added the less gas was produced during storage. Furthermore, the cells containing control + H_2O produced less gas than those containing control + VC + H_2O . The introduction

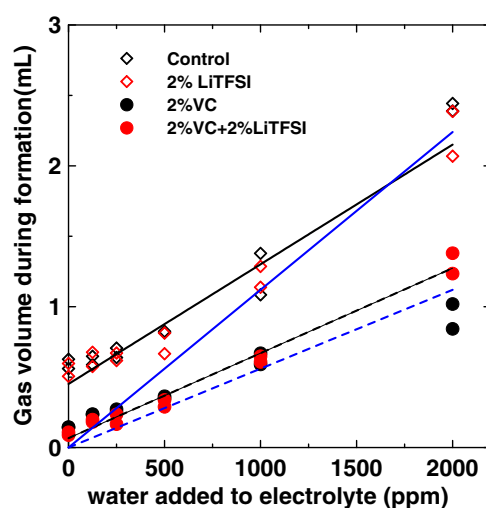


Figure 1. The gas volume during formation at 40°C for cells with control electrolyte + different amounts of added water (black diamonds), control + 2% VC + different amounts of water (black circles), control + 2% LiTFSI + different amounts of added water (red diamonds) and control + 2% VC + 2% LiTFSI + different amounts of added water (red circles). The dashed and solid black lines were fitted to the data for cells with and without VC, respectively. The solid and dashed blue lines were calculated with slopes that correspond to one mole of water producing one mole of hydrogen or one mole of water producing a half mole of hydrogen, respectively.

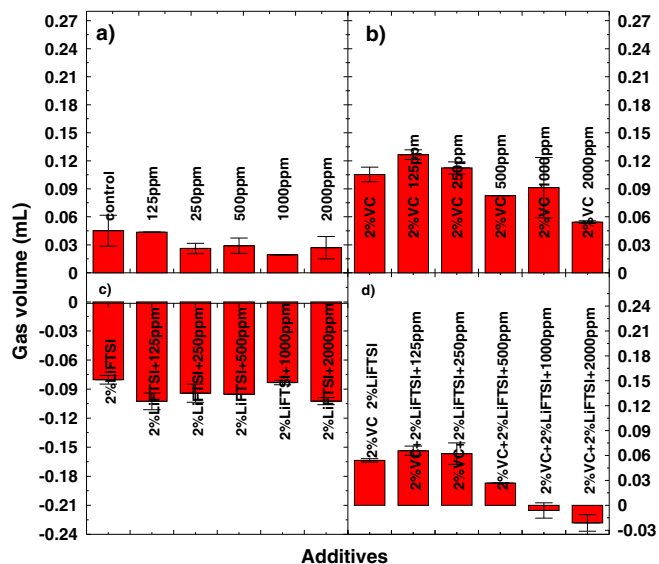


Figure 2. The amount of gas evolved after the 500 h storage period at 40°C for cells having initial voltage of 4.2 V with: control + different amounts of added water (a); control + 2% VC + different amounts of added water (b); control + 2% LiTFSI + different amounts of added water (c); and control + 2% VC + 2% LiTFSI + different amounts of added water (d).

of LiTFSI suppressed gas evolution, which is consistent with the findings of Burns et al.⁵ This suggests that LiTFSI may suppress gassing mainly during cell use rather than during the formation cycle.

Figure 3 shows the charge transfer impedance (the real impedance difference between the low and high frequency minima) after the formation cycle (3a, 3c, 3e and 3g) and after the 500 hour storage

period (3b, 3d, 3f and 3h). After 500 h of storage, all cells had larger charge transfer impedance than after the formation cycle. This could be caused by solid-electrolyte interphase (SEI) growth during storage. For all water-containing cells, the impedance did not differ significantly compared to the corresponding water-free cells (the difference was around 10 Ohm.cm²). This means that added water did not affect the cell impedance significantly during this relatively short storage period. Petibon et al. found that the added water generally affected the charge transfer impedance of the positive electrode and did not greatly affect the charge transfer impedance of the graphite electrode.⁶ Those electrodes were taken from prismatic cells experiencing more than one-year automated storage at 40°C. The water-containing cells used here may experience a larger impedance growth than the water-free cells if they were stored for a longer period of time.^{14,15}

Figure 4 shows the open circuit voltage versus time during storage at 40°C. The cells containing 2% VC + water and 2% VC + 2% LiTFSI + water have expanded scales in panels b) and d) for clarity. As discussed by Sinha et al.,⁹ the voltage drop during storage is caused by electrolyte oxidation or transition metal dissolution at the positive electrode. Panel a) shows that cells containing 125, 250, 500, 1000 and 2000 ppm water show smaller voltage drop than those with control electrolyte. This may mean that some species from the added water reacted in some way to make a more stable SEI on the positive electrode. For cells with either 2% LiTFSI and/or 2% VC + water there is a minimal difference in voltage drop. This suggests that adding water in the presence of VC and/or LiTFSI has a small influence on the reactivity of the positive electrode with the electrolyte.

Figure 5 shows long-term cycling data collected at 55°C for 2000 ppm water-containing cells and water-free cells between 2.8 and 4.2 V at 15 mA (~C/20). The VC-containing cells had much better capacity retention than those without VC since VC has positive effects on both the negative and positive electrodes.¹⁶ The cells with control + 2000 ppm water experienced a smaller capacity fade rate than those with control electrolyte. The cells containing control + 2% VC + 2000 ppm water had a similar capacity retention as those with control + 2% VC.

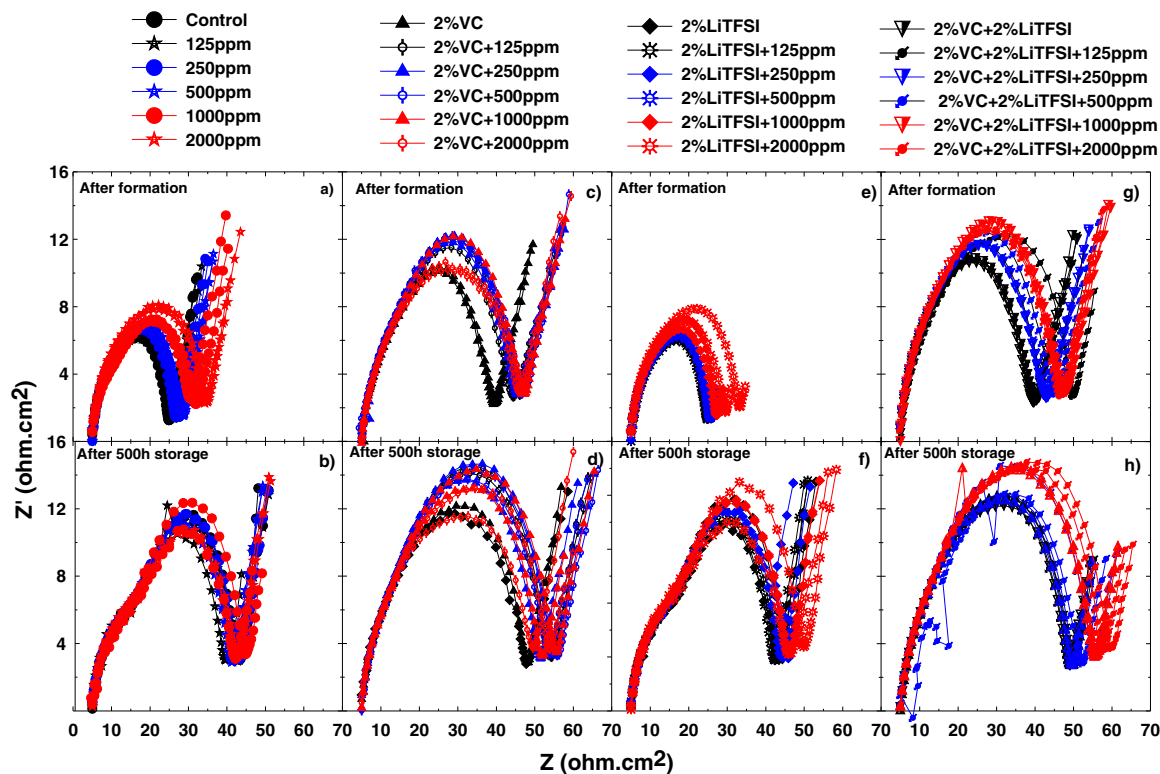


Figure 3. Impedance spectra collected at 3.8 V and 10°C before storage (a, c, e, g) and after storage (500 h and 40°C) (b, d, f, h) for: control + different amounts of added water (a, b); control + 2% VC + different amounts of added water (c, d); control + 2% LiTFSI + different amounts of added water (e, f); and control + 2% VC + 2% LiTFSI + different amounts of water (g, h).

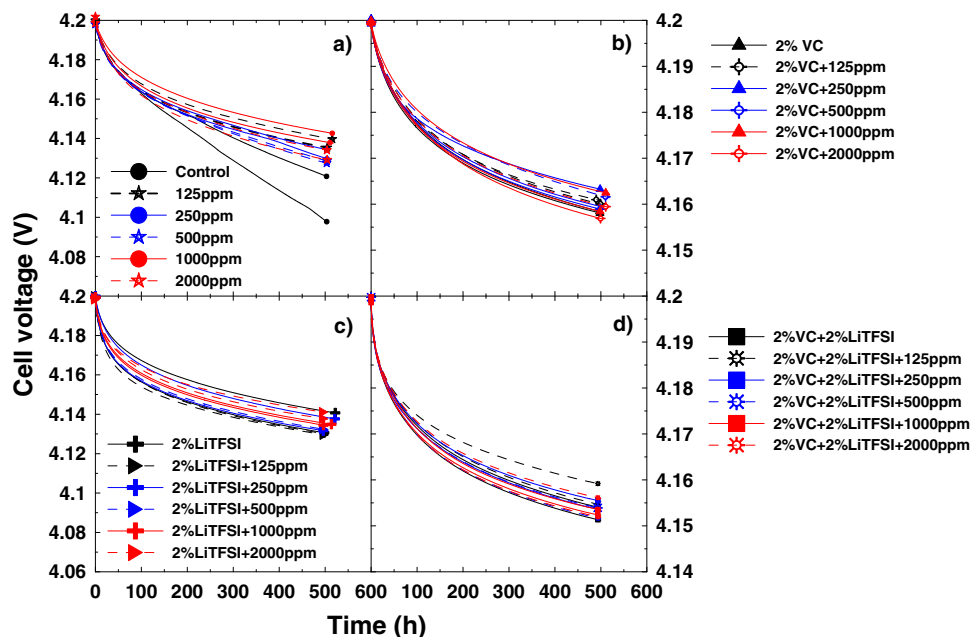


Figure 4. Open circuit voltage versus time during storage at 40°C for: control + different amounts of added water (a); control + 2% VC + different amounts of added water (b); control + 2% LiTFSI + different amounts of added water (c); and control + 2% VC + 2% LiTFSI + different amounts of water (d). The cells were charged to 4.2 V and held until the current decreased to the corresponding C/1000 current before going into open circuit storage.

These results demonstrate that the added water does not impair the cell cycling performance in these cells. It is worth mentioning that the low rate testing in these experiments took 7 months. Testing of 18650-size LCO/graphite cells under a low rate C/24 condition for 10 months showed a capacity loss of 10%, much less than observed here.¹⁷ The electrolyte additives in the cells tested by Smith et al. are unknown and, in addition, the pouch cells tested here were cycled without clamps. A large volume expansion (about 1 mL) of the pouch

cells which had 2% VC and 2% VC + 2000 ppm water at the end of testing was observed.

Figure 6 shows gas compositions in cells with and without 1500 ppm water after the 1.5 V potential hold for 24 h using both the GC-MS method and Archimedes principle. Figure 6 shows that the total gas volume measured using the GC-MS method is roughly the same as that from Archimedes principle for cells with 1500 ppm

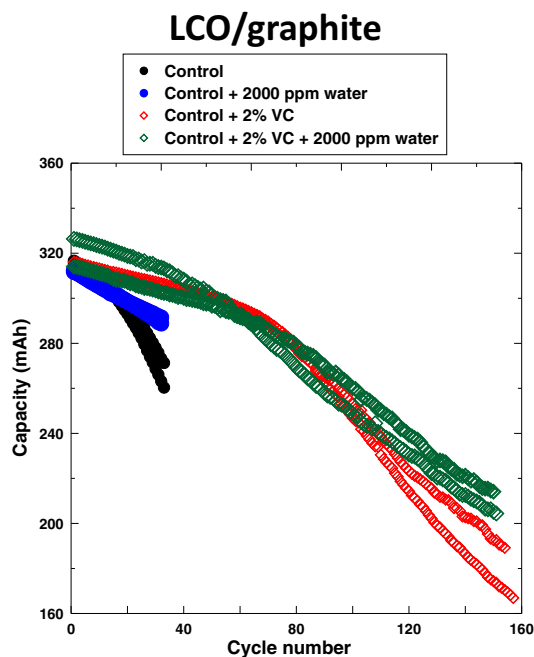


Figure 5. Capacity versus cycle number for cells with control (black circle), control + 2000 ppm water (blue circle), control + 2% VC (red diamond) and control + 2% VC + 2000 ppm water (green diamond). These cells were cycled at 15 mA at 55°C between 2.8 and 4.2 V.

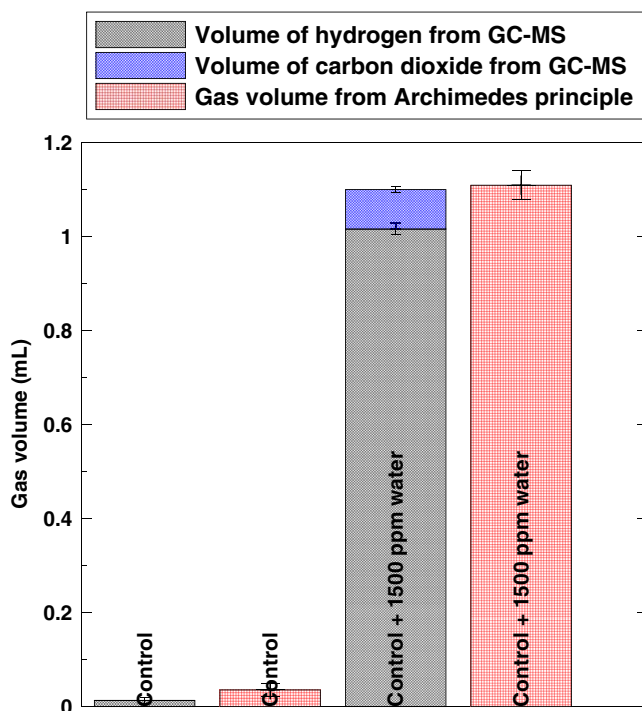


Figure 6. Gas volumes and compositions for cells with control electrolyte and control + 1500 ppm water held at 1.5 V for 24 h period at 40°C measured using the GC-MS method and Archimedes principle.

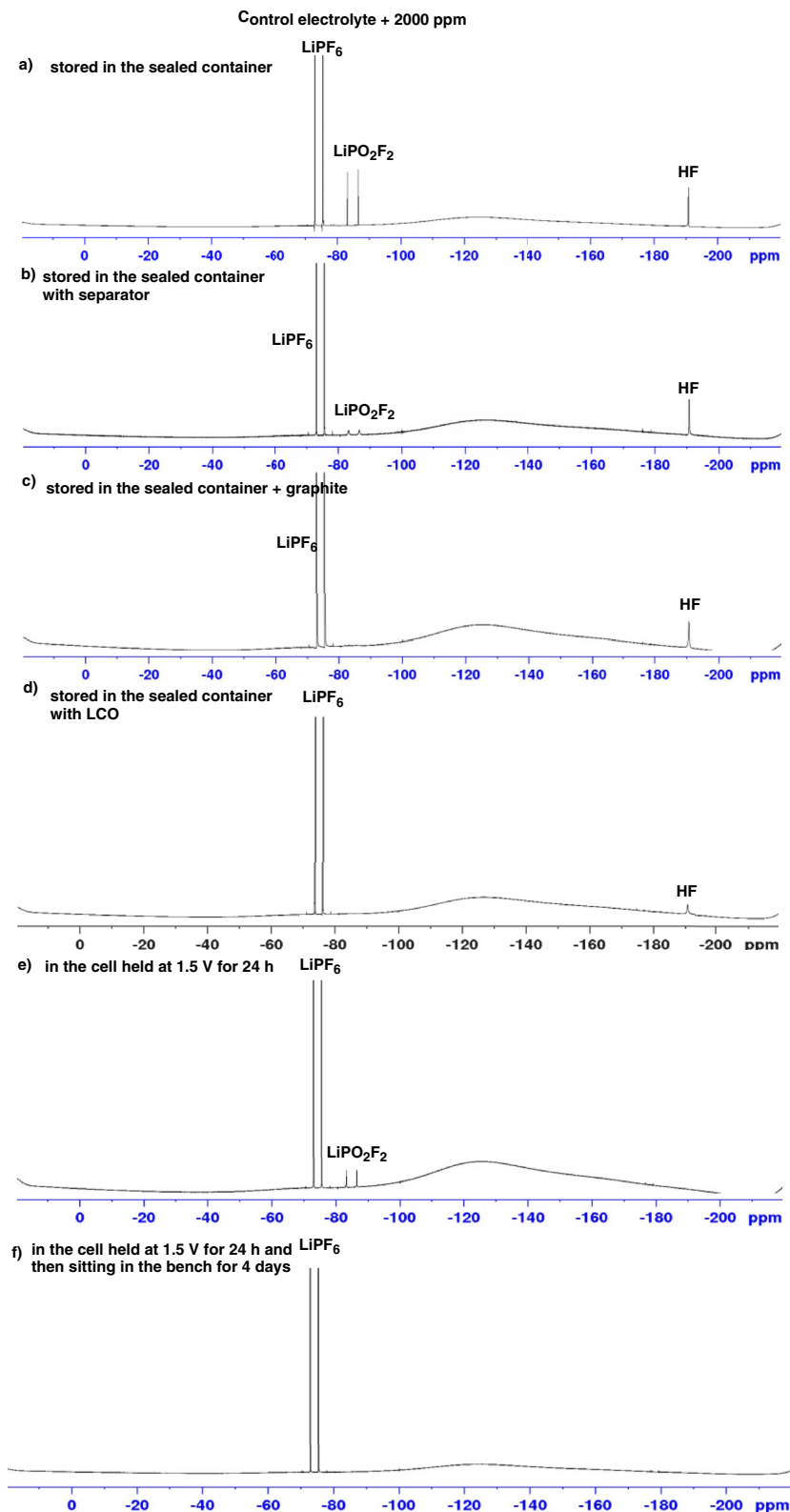


Figure 7. ^{19}F NMR spectra for control electrolyte + 2000 ppm water (a), control electrolyte + 2000 ppm water + separator (b), control electrolyte + 2000 ppm water + fresh graphite electrode (c), control electrolyte + 2000 ppm water + fresh LCO electrode (d), control electrolyte + 2000 ppm water harvested from a cell held at 1.5 V for 24 h (e), control electrolyte + 2000 ppm water harvested from a cell held at 1.5 V for 24 h and then stored at room temperature for 4 days (f).

water. Hydrogen was the most abundant gas in the cells with 1500 ppm water. This suggests that the solubility of hydrogen in the organic carbonate electrolyte solution at room temperature is small. Figure 6 shows that no hydrogen was detected in the water-free cells; however, a small amount of CO_2 was detected. A small amount of OH^- from the reduction of trace amounts of water could react with EC to produce CO_2 and carbonate oligomers.¹⁸ Given that cells prepared

with 1500 ppm water produced more CO_2 than the water-free cells, this additional CO_2 in the water-containing cells may be attributed to higher content of OH^- produced.¹⁸

Figure 7 shows the ^{19}F NMR spectra for control electrolyte containing 2000 ppm water. These water-containing electrolytes were either stored for 24 h in a sealed container with or without cell components (separator, graphite and LCO electrode) or experienced a 24 h

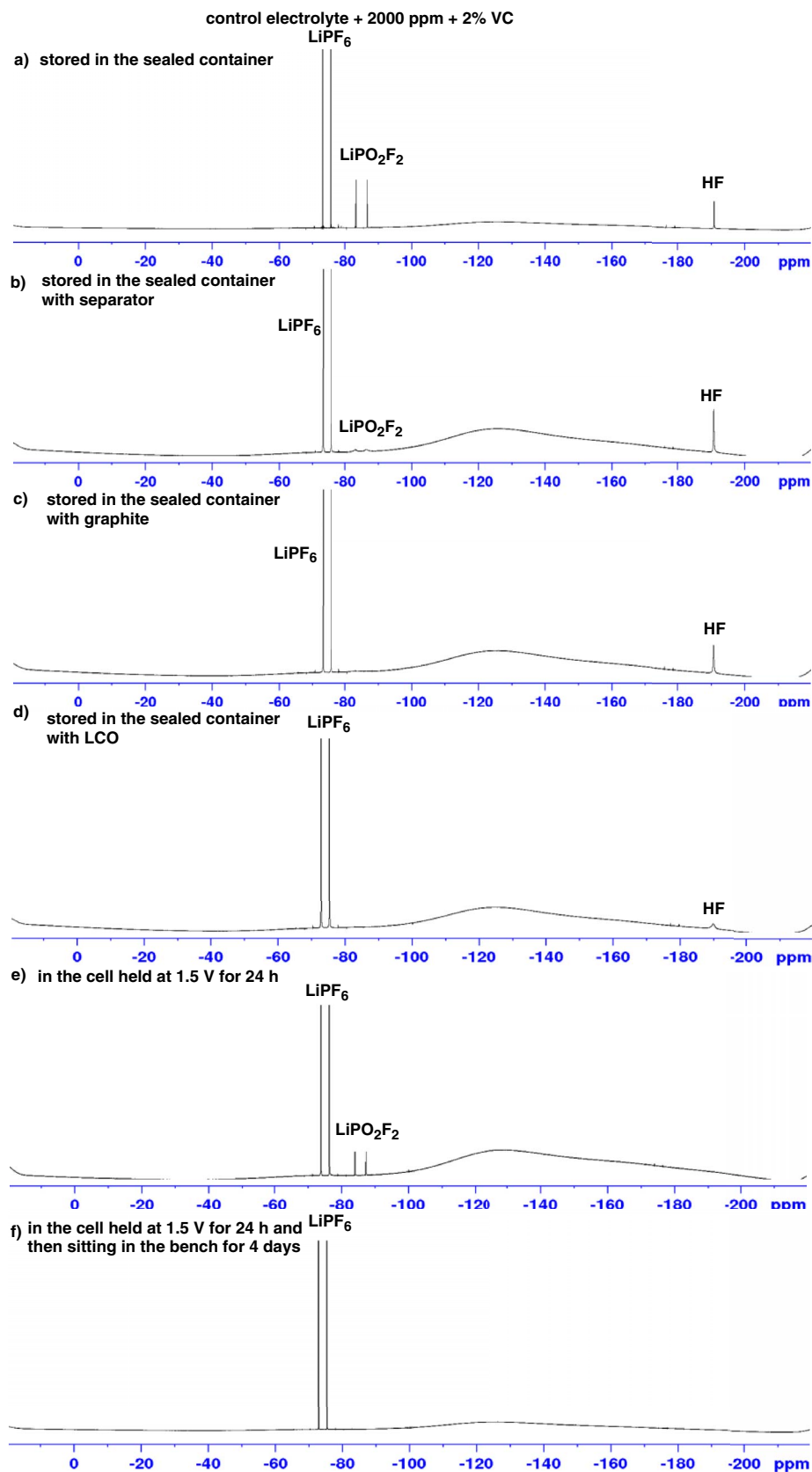
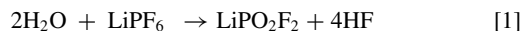


Figure 8. ^{19}F NMR spectra for control electrolyte + 2000 ppm water + 2% VC (a), control electrolyte + 2000 ppm water + 2% VC + separator (b), control electrolyte + 2000 ppm water + 2% VC + fresh graphite electrode (c), control electrolyte + 2000 ppm water + 2% VC + fresh LCO electrode (d), control electrolyte + 2000 ppm water + 2% VC harvested from a cell held at 1.5 V for 24 h (e), control electrolyte + 2000 ppm water + 2% VC harvested from a cell held at 1.5 V for 24 h and then stored at room temperature for 4 days (f).

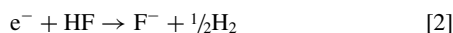
potential hold at 1.5 V in a cell. Figure 7a shows that the added water produces HF and LiPO_2F_2 from reactions with LiPF_6 . The stoichiometry of this reaction is generally agreed upon and may be written as:



The F^- anion was observed as an HF singlet at -190 ppm, which is consistent with the findings of Markevich et al.¹⁹ The PO_2F_2^- anions show as a triplet in ^{31}P NMR as shown in the supporting information (Figures S1 and S2) and as a doublet in ^{19}F NMR. The ^{31}P - ^{19}F coupling constant is approximately 942 Hz. The PF_6^- anions show as a septet in ^{19}F NMR and as a doublet in ^{31}P NMR (Figures S1 and S2) demonstrated in the supporting information.

Figures 7c and 7d show that no LiPO_2F_2 is detected in water-containing electrolyte plus graphite or LCO electrodes. This suggests that LiPO_2F_2 reacts with both the graphite and the LCO electrodes by mechanisms unknown. Moreover, Figure 7b shows that the ratio between LiPO_2F_2 and HF for water-containing electrolyte plus separator taken out of the pouch cell is much less than that for water-containing electrolyte without cell components (Figure 7a). This may indicate that some of the LiPO_2F_2 has been consumed. SEM studies showed that some electrode particles are attached to the separator demonstrated in the supporting information. These attached electrode particles at the separator may be the cause of LiPO_2F_2 consumption. Figures 7b, 7c and 7d show that HF is still detected in all the water-containing electrolyte plus cell component samples. The peak corresponding to HF is relatively less intense and broadened in Figure 7d, which may indicate a slow reaction or some other interaction between HF and the LCO material. Nevertheless, the results in Figure 7 demonstrate that HF is not removed from the solution by any of the cell components.

Figure 7e shows that only LiPO_2F_2 is detected in the water-containing cell that was held at 1.5 V for 24 h. The presence of LiPO_2F_2 indicates that Reaction 1 occurred and that the HF was subsequently removed via another reaction. The presence of HF in the solution in Figures 7a–7d demonstrated that HF is chemically stable in the electrolyte solution and in the presence of any of the electrode components. Therefore, the absence of an HF signal in Figure 7e, i.e., the absence of HF in a cell that was held at 1.5 V for 24 h, suggests that HF is removed from the solution electrochemically, rather than chemically. This is proposed to occur via the following reduction:



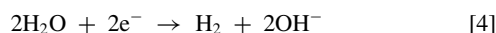
The potential at the graphite surface during the potential hold step is $E_{\text{neg}} \sim 2.3$ V vs. Li/Li^+ . Figure 7f shows that neither LiPO_2F_2 nor HF is present when cells are left at open circuit, at room temperature for 4 days after the 24 h hold at 1.5 V. Therefore, LiPO_2F_2 is consumed completely by chemical reaction with the electrode materials over time even if cells are not charged and discharged. The absence of an HF signal in Figure 7f may indicate that most of the water was removed from the solution during the 1.5 V hold.

The experiment was repeated for solutions that contained 2000 ppm water + 2% VC, shown in Figure 8. The same findings were obtained as in Figure 7. This suggests that there is no significant chemical interaction between VC and LiPF_6 , LiPO_2F_2 , or HF at these concentrations. Moreover, VC does not inhibit or prevent the reactivity of LiPO_2F_2 with the electrode materials, or the reduction of HF at 1.5 V in a full cell.

Reactions 1 and 2 compose a two-step scheme for the reduction of water in Li-ion cells. Overall, this may be written as:



This overall reaction predicts that for every mole of water introduced into the cell, a mole of hydrogen gas will be produced. However, it was demonstrated in Figure 1 that the hydrogen-to-water ratio is between 0.5–1.0. Therefore, it is here proposed that reactions 1 and 2 compete kinetically with the direct reduction of water at the negative electrode:



This reaction, which has a water-to-hydrogen molar ratio of 2:1 has been suggested previously for cells prepared with added water in

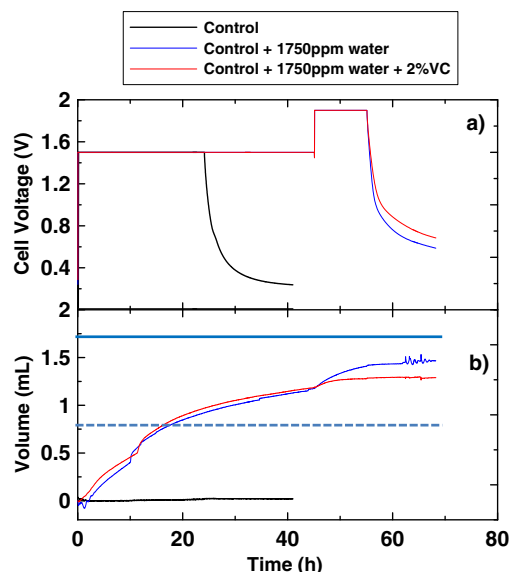


Figure 9. Cell potential held at 1.5 V for 45 h and then at 1.9 V for 10 h (what temperature? (a); Gas volume versus time for the cells indicated during the two-step potential hold (b). The dashed blue line and the solid blue line indicate the calculated gas volumes based on one mole of water producing one mole of hydrogen and one mole of water producing a half mole of hydrogen, respectively.

LiTFSI electrolyte.²⁰ However, it is only the competition of Reactions 3 and 4 that is consistent with the experimental slopes in Figure 1. Moreover, the Reaction 4 predicts the formation of hydroxide anions. This is in agreement with the production of carbon dioxide in water-containing cells (Figure 6) via decomposition of EC by reaction with hydroxide species.

In order to test this theory, that there is a kinetic competition between Reactions 3 and 4, in situ volumetric measurements were performed. This allows the gas evolution to be monitored in real-time, rather than following an entire formation cycle. Figure 9 shows gas evolution versus time for cells with and without VC in the presence of added water. Figure 9 shows that the gas volume gradually increased during the two-step potential hold at 1.5 V ($E_{\text{neg}} \sim 2.3$ V vs. Li/Li^+) and 1.9 V ($E_{\text{neg}} \sim 1.9$ V vs. Li/Li^+) where no electrolyte reduction or oxidation is thought to occur. For comparison, the standard potential of Reaction 4 in aqueous media is $E^0 = 3.0$ V vs. Li/Li^+ . After the two-step potential hold, the additional gas volume from added water in both electrolytes is within the predicted hydrogen-to-water range of 0.5–1.0. This supports the hypothesis that added water reacts through both the one-step (4) and two-step [(1) and (2)] reactions concurrently.

Figure 10 shows the C 1s (a), O 1s (b), F 1s (c) and P 2p (d) XPS core spectra of the graphite electrodes as well as the O 1s XPS core spectra of the LCO electrodes (e) taken from LCO/graphite pouch cells with control and 2000 ppm water-containing electrolytes held at 1.5 V for 24 h and then charged to 3.8 V. The core electron assignment shown in Figure 10 is justified in Reference 11 described by Madec et al.¹¹ Figure 10a shows that the water-containing cells after the formation cycle have a similar C 1s spectrum compared to water-free cells. The intensity of the graphite peak decreased slightly for water-containing cells indicating a slightly thicker SEI film at the graphite surface. More CO-like species at 287.5 eV were detected in the water-containing cells than in the water-free cells. This supports the occurrence of one-step Reaction 4, followed by the reaction of the hydroxide anions with ethylene carbonate to produce insoluble alkyl-carbonate oligomers.²⁰ Figure 10b shows that the O content in the SEI on the graphite electrode for water-containing cells is about two times larger than for the water-free cells, which is consistent with the C 1s spectrum. Figure 10c shows that the cells with 2000 ppm water contained less LiF than the cells with control electrolyte. Figure 10d shows that there are more P_xO_y and $\text{Li}_x\text{PO}_y\text{F}_z$ species on the

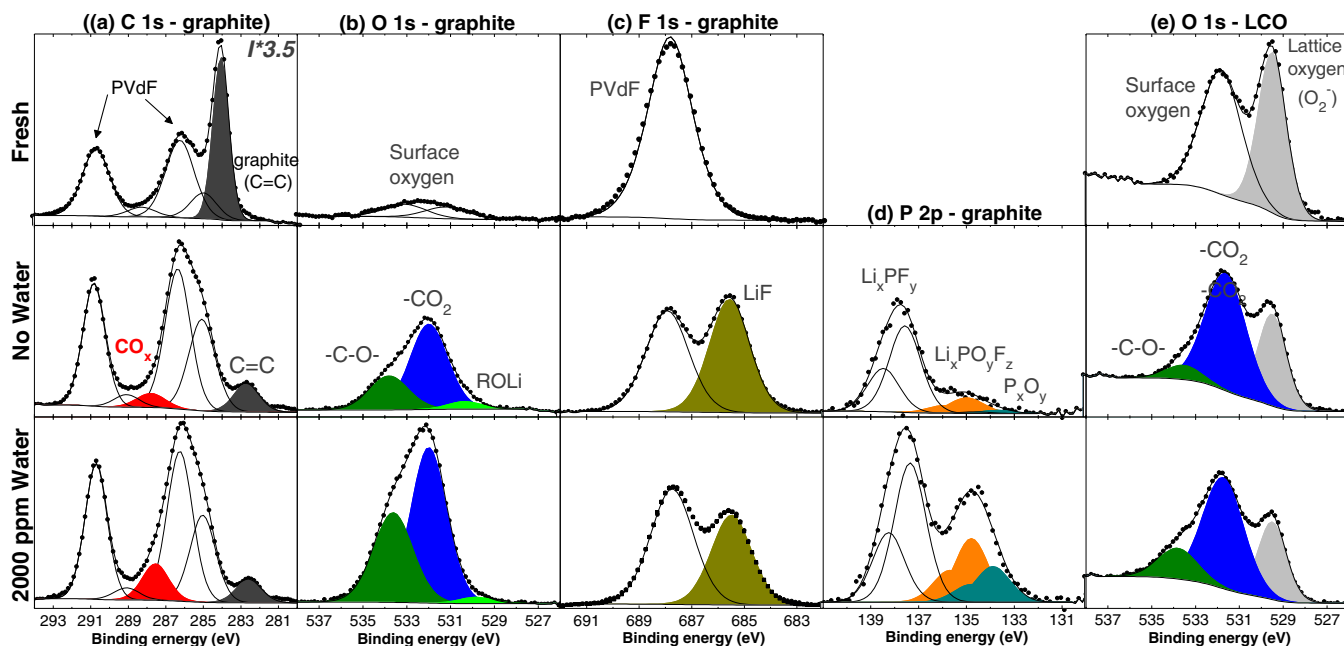


Figure 10. C 1s (a), O 1s (b), F 1s (c), P 2p (d) XPS core spectra for graphite electrodes and O 1s XPS core spectra for LCO electrodes (e) taken from fresh (uncycled) cells, cells without water and cells with control + 2000 ppm water which were first held at 40°C for 24 h and then charged to 3.8 V at C/20 at 40°C.

negative electrode surface in the water-containing cells than in the water-free cells. This result is in agreement with the production of LiPO_2F_2 in solution via Reaction 1.

Conclusions

A study of the impact of intentionally added water to the electrolyte of $\text{LiCoO}_2/\text{graphite}$ pouch cells with and without VC and LiTFSI has been reported here. In terms of gas evolution (during storage), impedance growth and voltage drop during storage, the added water did not negatively affect cell performance. In fact, in some cases it was found to be beneficial. This is consistent with the findings of Burns et al. for prismatic cells with LCO or NMC positive electrodes and graphite or LTO negative electrodes.^{4,5} The added water apparently can react in the electrolyte through a one-step (Equation 4) and through two step reactions (Equations 1 and 2) simultaneously. The generated HF is removed electrochemically during a low voltage potential hold or during cell formation. The SEI compositions for water-containing cells, as measured using XPS, are roughly the same as those for those of the water-free cells. This may be the main reason why less than 2000 ppm water in the cells does not impair cell electrochemical performance.

This report suggests that the strict specifications for water content in electrolytes for Li-ion cells can be relaxed, which could reduce the cost of Li-ion cell manufacturing without causing a decrease in cell performance. However, prudence should be exercised in taking this step as this report did not examine the impact on long term cycling behavior at room temperature, for example.

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References

1. S. S. Zhang, *J. Power Sources*, **162**, 1379 (2006).
2. K. Xu, *Chem. Rev.*, **104**, 4303 (2004).
3. <http://www.targray.com/documents/DMMP-Electrolyte-Solution.pdf>.
4. J. C. Burns, N. N. Sinha, G. Jain, H. Ye, C. M. VanElzen, E. Scott, A. Xiao, W. M. Lamanna, and J. R. Dahn, *J. Electrochem. Soc.*, **161**, A247 (2014).
5. J. C. Burns, N. N. Sinha, G. Jain, H. Ye, C. M. VanElzen, E. Scott, A. Xiao, W. M. Lamanna, and J. R. Dahn, *J. Electrochem. Soc.*, **160**, A2281 (2013).
6. R. Petibon, N. N. Sinha, J. C. Burns, C. P. Aiken, H. Ye, C. M. VanElzen, G. Jain, S. Trussler, and J. R. Dahn, *J. Power Sources*, **251**, 187 (2014).
7. J. Xia, N. N. Sinha, L. P. Chen, G. Y. Kim, D. J. Xiong, and J. R. Dahn, *J. Electrochem. Soc.*, **161**, A84 (2014).
8. C. P. Aiken, J. Xia, D. Y. Wang, D. A. Stevens, S. Trussler, and J. R. Dahn, *J. Electrochem. Soc.*, **161**, A1548 (2014).
9. N. N. Sinha, A. J. Smith, J. C. Burns, G. Jain, K. W. Eberman, E. Scott, J. P. Gardner, and J. R. Dahn, *J. Electrochem. Soc.*, **158**, A1194 (2011).
10. R. Petibon, L. M. Rotermond, and J. R. Dahn, *J. Power Sources*, **287**, 184 (2015).
11. L. Madec, J. Xia, R. Petibon, K. J. Nelson, J.-P. Sun, I. G. Hill, and J. R. Dahn, *J. Phys. Chem. C*, **118**, 29608 (2014).
12. D. A. Shirley, *Phys. Rev. B*, **5**, 4709 (1972).
13. J. Self, C. P. Aiken, R. Petibon, and J. R. Dahn, *J. Electrochem. Soc.*, **162**, A796 (2015).
14. J. C. Burns, A. Kassam, N. N. Sinha, L. E. Downie, L. Solnickova, B. M. Way, and J. R. Dahn, *J. Electrochem. Soc.*, **160**, A1451 (2013).
15. J. Vetter, P. Novák, M. R. Wagner, C. Veit, K.-C. Möller, J. O. Besenhard, M. Winter, M. Wohlfahrt-Mehrens, C. Vogler, and A. Hammouche, *J. Power Sources*, **147**, 269 (2005).
16. D. Xiong, J. C. Burns, A. J. Smith, N. Sinha, and J. R. Dahn, *J. Electrochem. Soc.*, **158**, A1431 (2011).
17. A. J. Smith, H. M. Dahn, J. C. Burns, and J. R. Dahn, *J. Electrochem. Soc.*, **159**, A705 (2012).
18. R. Bernhard, M. Metzger, and H. A. Gasteiger, *J. Electrochem. Soc.*, **162**, A1984 (2015).
19. E. Markevich, K. Fridman, R. Sharabi, R. Elazari, G. Salitra, H. E. Gottlieb, G. Gershinsky, A. Garsuch, G. Semrau, M. A. Schmidt, and D. Aurbach, *J. Electrochem. Soc.*, **160**, A1824 (2013).
20. R. Bernhard, S. Meini, and H. A. Gasteiger, *J. Electrochem. Soc.*, **161**, A497 (2014).