# Li-Ion Battery Performance in a Convection Cell Configuration

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*The convection battery forces flow of electrolyte through the cathode, anode, and the separator between them, unlike a flow battery where electrolyte cannot cross the separator. The goal is to increase ion fluxes (A/cm$^2$) to realize the benefit of thicker electrodes, lower cost batteries, and reduced charge times. A pump that circulates electrolyte was turned off to create a diffusion control to which the performance of the convection battery was compared. Based on performance at 1.1 V overpotential (based on a 3.1 V open circuit) and similar capacity utilization, the convection battery provided a 5.6-fold increase in ion flux for these initial studies, increasing flux from 1.6 to 8–10 A/cm$^2$. Little capacity fade was observed on the measured discharge cycles (10 cycles). These studies provided an important milestone in the research, development, and validation of a new battery design including cycling studies with lithium iron phosphate chemistry.* © 2012 American Institute of Chemical Engineers *AIChE J,* 59: 1774–1779, 2013

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## Introduction

Large-scale batteries can be used in conjunction with green energy sources to satisfy rising energy demands in both electric utility and transportation applications in a sustainable manner. Batteries can be used for grid-energy storage to match electricity demand to the output of intermittent energy sources such as wind and solar and constant energy sources like nuclear. Furthermore, batteries can provide a mode of emission-free transportation. In order for these applications to come to fruition, large-scale batteries must be made lighter and more cost effective.

A new type of cell, termed a convection cell or convection battery, is being investigated that is aimed at decreasing the cost and mass of large-scale batteries. In the convection cell, electrolyte is pumped through porous electrodes as pictured in Figure 1 to decrease diffusion or concentration overpotential losses and make the potential more uniform throughout the electrode.

In electrochemical reactors, flow-through electrodes can be used for electrowinning,[1] electro-organic synthesis,[2] and removal of metals from wastewater streams.[3,4] For these reactors, flow may be necessary to fully utilize the high surface area of porous electrodes; flow-through porous electrodes allow operation at fairly high rates while maintaining selectivity.

Flow-through porous electrodes are frequently used in flow batteries; but with the exception of the convection battery, flow-through separators are not used in commercial or research batteries. In flow batteries, either flow-through or flow-by porous electrodes are utilized to distribute active reagents in a liquid electrolyte to the electrodes where reaction occurs.[5]

A key difference between the convection battery and flow batteries (including air batteries) is that the same electrolyte is used in both the anode and the cathode in the convection cell. The flow battery requires two separate electrolytes, because active species are dissolved in the electrolyte(s)—flow-through separator would mix reactive species outside the desired half-cell scheme.[6] Flow of electrolyte between electrodes in the convection battery is not only allowed, but also it can lead to decreased concentration gradients across the separator (at sufficiently high loads). Having one electrolyte also eliminates the need for an ion-selective membrane, which is required in the flow batteries to prevent mixing of electrolytes.

Scientific literature describes several different flow cells. Just as with flow reactors, flow patterns and dynamics in flow cells can have a major impact on performance. As described in the previous paragraphs, the convection battery of this article is unique in design, fluid dynamics, and performance improvements.

A major benefit of the convection battery is compatibility with most commonly used and researched battery chemistries—chemistries that use a single electrolyte. When the convection battery is understood sufficiently, new and improved battery chemistries could be easily incorporated into the convection cell configuration to realize the performance advantages of flow-through separators.

In a convection cell, the flow of electrolyte allows the use of thicker electrodes. At sufficiently high currents, in a battery without flow, an inhomogeneous distribution of local current density will develop due to ionic diffusion limitations.[7] This will lead to a lower overall cell potential and a loss of capacity due to side reactions. Traditional batteries are made with thin electrodes to mitigate these effects. In a convection cell, the flow reduces the diffusion limitations, resulting in a higher and more uniform potential throughout the electrode at a given current density.[8] This allows the use of thicker electrodes, which is recognized as a primary

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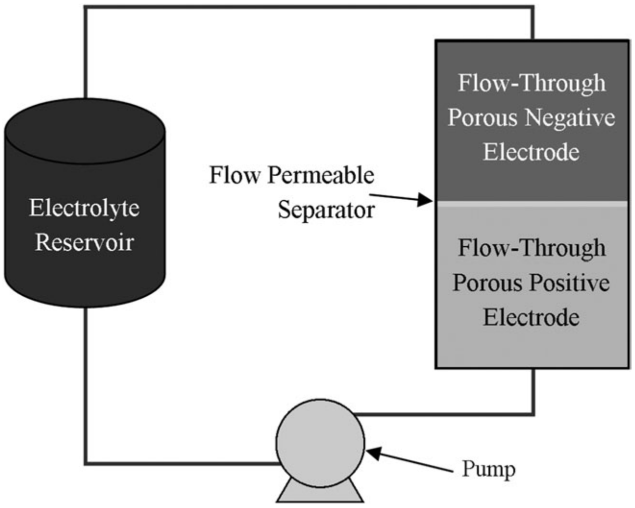

**Figure 1. A schematic of the convection cell.**

means to reduce battery costs.[9–11] Thicker electrodes result in the use of less separator and current collector materials, which lowers material and manufacturing costs while also reducing the mass and volume of the cell. This translates into higher specific capacity and energy density.

The convection battery is pursued due to advantages that could include:

- Better use of thicker electrodes due to a more-uniform distribution of potential in the electrodes.
- Reduced separator and current collector materials, which results in lower-cost and higher-energy-density batteries.
- Mitigation of dendrite formation through multiple mechanisms including shear forces from flow that can inhibit single-crystal growth.
- Elimination of drying of electrodes through replenishing of electrolyte.
- Easy temperature management by flow of electrolyte through heat exchangers.
- Ability to routinely drain electrolyte from cells during nonuse to increase cell life.
- Ability to increase electrode separation distance due to decreased concentration gradients across the separator.
- Ability to implement measures that will better-allow use of metallic lithium.
- Wide applicability to present and future battery chemistries that use the same electrolyte in both electrodes.

In previous work, the authors have demonstrated the convection battery in primary cell applications with zinc-alkaline chemistry.[12,13] The purpose of this article is to present data that validates performance of secondary convection cells using lithium iron phosphate chemistry. $LiFePO_4$ was selected for study, because it is a lithium-ion battery technology widely regarded as having a good combination of high energy density, good cyclability, safety benefits, and reasonable cost.[14]

The energy and weight required to pump the electrolyte through the convection cell are not addressed at this time, because the design parameters to reduce battery system costs are different than those parameters that optimize the performance of the convection battery. As with the vast amount of flow battery research, pumping costs, in both energy and weight, are real; but at the same time, they are not pertinent to the immediate advancement of the science and technology. In addition, pump operation is only needed during high load operation, and actual energy costs are a degree of freedom in the overall cell design. As with flow battery technology, pumping costs are a complex function of many variables that are substantially a distraction during fundamental studies such as those reported in this article. A recent review on vanadium flow batteries[15] states that the pump consumes about 8–15% of the overall energy in standard designs. The energy cost for the convection cell is expected to be lower than this, because the convection cell can operate without the pump for extended periods of time when the current density is low. The pump is only necessary at high loads to increase efficiency. With this pumping requirement, it is likely that the benefits of the convection battery will outweigh the pump costs in a scaled up cell, but this cannot be determined until the convection battery is more fully understood.

## Experimental

The negative electrode paste used in the cells tested consisted of 62.5 wt % 250–425 $\mu$m graphite and 37.5 wt % binder solution. Acros Organics graphite from Fisher was used and sieved to obtain the desired particle size. The binder was a 6 wt % solution of polyvinylidene fluoride powder (PVDF) in anhydrous *n*-methyl-2-pyrrolidone, both from Sigma–Aldrich. The positive electrode paste consisted of 50 wt % 250–425 $\mu$m graphite, 33.3 wt % binder solution, and 16.7% $LiFePO_4$ powder obtained from MTI Corporation. The electrolyte was a 1 molar solution of $LiPF_6$ in a 1:1:1 mixture by volume of ethylene carbonate, dimethyl carbonate, and diethyl carbonate with a vinylene carbonate additive. The premixed electrolyte was also obtained from MTI Corporation.

The convection cell used in these studies is shown in Figure 2. This is also the "diffusion" or "control" cell when operated without flow. It consists of two stainless steel pistons fitted with hose barbs to facilitate electrolyte entry/exit, two 1.1 cm inside diameter stainless steel tubes for the positive and negative electrodes, a high-density polyethylene (HDPE) separation coupling, and two compression plates that are held together with screws and threaded nylon spacers. All work was done in a dry argon-filled glove box until the cell was fully assembled and sealed.

The first step in assembling the cell is to dry the electrode pastes in the electrode tubes for the positive and negative electrodes. This is done by using drying pistons (pictured in Figure 2 center) that are the same length as the electrode tube. When the piston is inserted into the electrode tubes, there is no open volume. Spacers are added between the piston and the bottom of the tube. By doing this, the height of the electrode is determined by the height of the spacers. An electrode thickness of 6 mm was used in these studies. The electrode tubes are then filled with paste and scraped flush with the top of the tubes. The pistons are then placed on a hot plate in the glove box and allowed to fully dry.

After the electrodes are dry, the cell is assembled. The two electrode tubes with the electrodes are inserted into the HDPE coupling and are separated by three pieces of 1.27-cm diameter Fisher P8 filter paper. The sides of the tubes that are flush with the electrode material face the filter paper, so the separation thickness is equal to the thickness of the filter paper. Buna-N O-rings are used to seal between the electrode tubes and the coupling. The two compression plates are then placed on the outsides of the tubes and screwed together with screws from each side with a threaded nylon coupler in the middle to maintain electrical isolation.

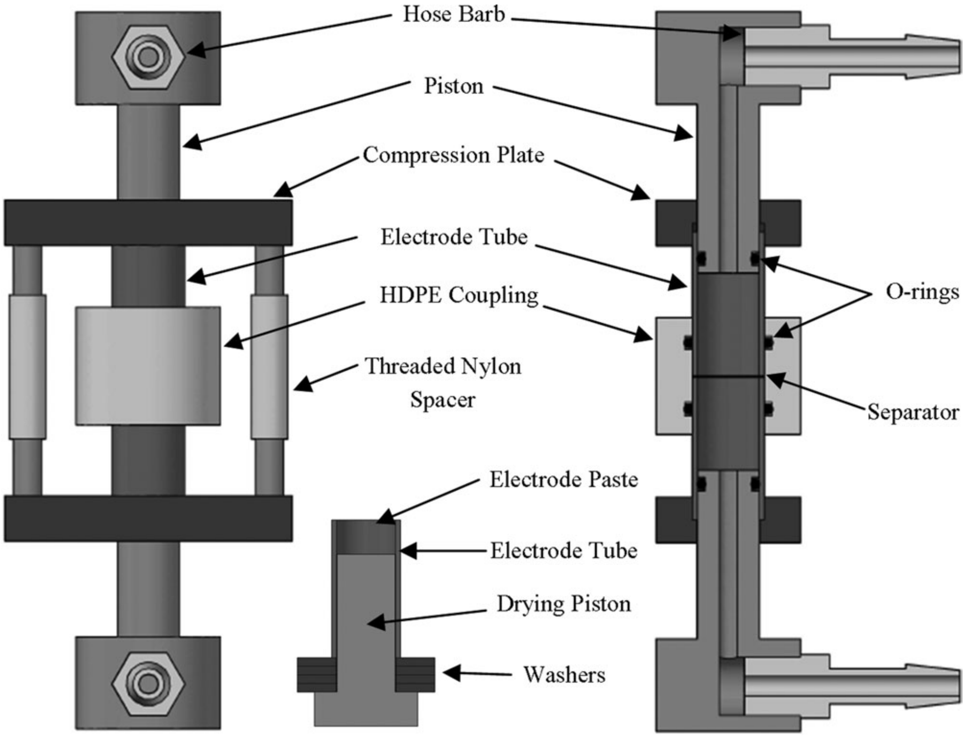

**Figure 2. Schematic of the test cell for the convection battery and drying piston; front view (left), rotated cutaway view (right), and cutaway view of the drying piston (center).**

The pistons are then fitted with O-rings and HDPE hose barbs. They are then inserted into the electrode tubes. Next the tubing is attached to the hose barb in each piston and the electrolyte reservoir. Prior to fully connecting the tubes, 10 mL of electrolyte is added to saturate the cell and fill the reservoir. A 10-mL glass volumetric pipette with part of each end cut off was used as a reservoir. A Masterflex L/S high-performance pump head was used with L/S 16HP Norprene tubing to circulate the electrolyte through the convection cells. The flow rate was 0.9 mL/min from the positive electrode on the bottom to the negative electrode on top. A pressure of 1200 kPa was applied to the electrodes by adding weights on the top piston.

The test cells were assembled as described earlier and then connected to an external cycling circuit with switch automation for opening and closing the circuits and controlling the pump. Voltage measurement and automated switch signals were provided by National Instruments LabVIEW software (using custom created virtual instrument files) through a National Instruments PCI-6229 data acquisition card connected to a National Instruments SCB-68 shielded connector block.

For all of the studies of this work, the cells were operated for 30 min at open circuit and then cycled. The cells were cycled between 2 and 4 V using a constant current charge and a constant resistance discharge. The voltage was recorded over the test, so that current and resistance could be calculated for the discharges and charges, respectively. For the convection cells, the pump was turned on for all of the cycles. For the control cell, the pump was turned off for the discharge steps and could be turned on or off for the charging steps depending on the experiment.

The coefficient of permeability was tested for the electrodes and electrode materials using a falling head permeameter according to ASTM test method D5856-95.[16] A pressure of 1200 kPa was applied to the samples to test the coefficient of permeability. The electrodes were made in the same manner as mentioned earlier and placed in the permeameter for testing.

## Results and Discussion

The convection battery requires the use of electrodes with good permeabilities to allow flow. As summarized in Table 1, powders such as lithium iron phosphate powder are substantially impermeable to flow. To further exasperate this problem, preliminary studies showed that while packed-bed electrodes worked in primary-cell applications, charging of a depleted cell failed in the absences of a binder like PVDF. This binder tended to further decrease the flow-permeability of the powders.

A solution to this problem was attained through the use of large-particle graphite, 250–425 $\mu$m, which has an acceptable permeability of 4 Darcy. By mixing lithium iron phosphate

**Table 1. Permeabilities and Compositions of Dry Electrodes and Electrode Powder Materials Under a Pressure of 1200 kPa**

| Description | $LiFePO_4$ | Graphite | PVDF Binder | Permeability [Darcy] | Standard Deviation |
|---|---|---|---|---|---|
| Graphite powder | N/A | 100% | N/A | 4 | 2 |
| $LiFePO_4$ powder | 100% | N/A | N/A | <0.001 | N/A |
| Negative electrode | N/A | 97% | 3% | 0.8 | 0.4 |
| Positive electrode | 24.3% | 72.8% | 2.9% | 0.13 | 0.09 |

The graphite is large-particle graphite with 250- to 425-$\mu$m particle sizes.

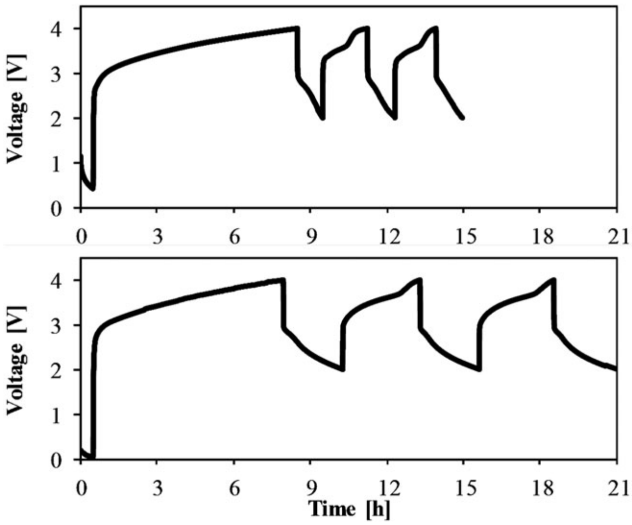

**Figure 3. Voltage profiles of a convection cell with flow (bottom) and a control cell without flow (top) at a constant discharge resistance of 990 Ω.**

**The initial 30 min is an open circuit of the discharged cell, followed by subsequent charge and discharge cycles. For the diffusion control studies, the pump was on during charging to ensure that the state of charge at the start of each discharge was the same as the convection cell.**

powder with 250–425 $\mu$m graphite and binder, acceptable permeabilities of 0.1 Darcy were attained for the positive electrode. The addition of binder significantly reduces the permeability of the graphite powder, but the negative electrode still has a relatively good permeability of 0.8 Darcy.

Convection cells were assembled using the two electrode compositions summarized in Table 1. Example cycling data for a convection cell, and the diffusion control to which it was compared, are summarized in Figure 3. In Figure 3, there is a 30-min open circuit followed by subsequent charge and discharge cycles. For the diffusion control cell, the pump was used during each charging step to assure the same degree of charge as the convection cell; the pump was off during discharge.

As can be seen by these cycling studies, the convection cell realized a higher discharge time and an associated increased utilization of the electrode reagents. By integrating the voltage divided by the resistance as a function of time (and dividing by the mass of $LiFeO_4$), the specific capacities were calculated as summarized in Figure 4.

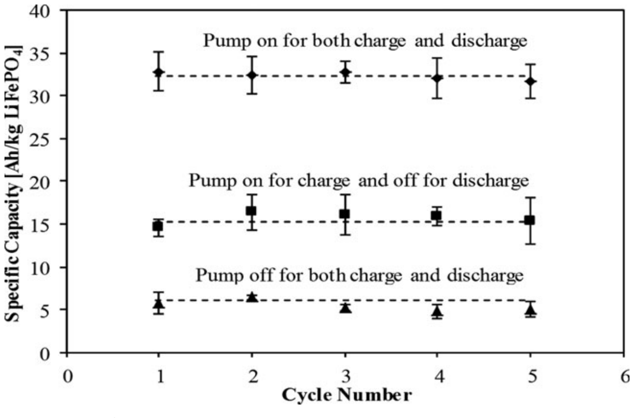

**Figure 4. Specific capacity upon discharge vs. cycle number at a constant resistance discharge of 990 Ω for a convection cell and two control cells.**

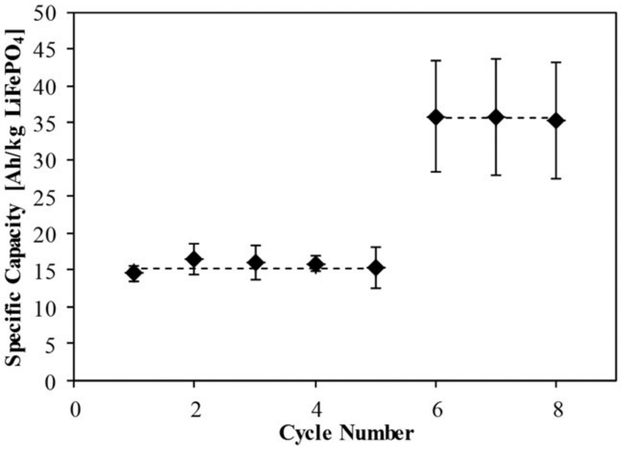

**Figure 5. Specific discharge capacity vs. cycle number for a cell without convection during the first five discharge cycles and with convection for the last three cycles at a constant resistance discharge of 990 Ω.**

The specific capacities summarized in Figure 4 indicate that the convection cell provides consistently higher specific utilization of the active materials. The performances showed little fade with good repeatability. When the pump is turned off during charging as well as discharging, the diffusion control showed even poorer performance.

Performance with the pump on during charging and off during discharging was between the other two performances, which is consistent with expectations—it is a further point of validation of benefits of convection. These data show that convection from the cathode (discharge mode) to the anode benefits both charge and discharge; or stated differently, convection assists the transfer of lithium cations to the cathode even when this transfer is against the direction of flow. The author's previous work[13] summarized a mechanism through which it occurs. This observation has important ramifications in regard to the associated fundamental mechanisms and accurate modeling.

To answer the question of whether the benefits of the convection battery (pumping of electrolyte) are influenced by the history of the cell, studies were conducted with the pump off during discharge for the first five cycles whereafter the pump was on for both charge and discharge (see Figure 5). The specific capacities in the convection cell mode of operation (last three cycles of Figure 5) were substantially the same as those summarized in Figure 4—providing evidence of good reproducibility that is substantially independent of the cell history.

Studies were repeated at several resistances to obtain cell performance curves as summarized in Figure 6. For the test cell, that had 6-mm-thick electrodes, the utilization of active reagents decreased with increasing load (i.e., lower resistance). The convection cell systematically performed better than the diffusion control. It is anticipated that at higher resistances, the gap in performance would diminish, and the two performance curves would asymptotically approach each other. Higher resistances were not studied, because the length of time for five cycles would exceed a week.

Comparing the values of the performance curves of Figure 6 at similar utilized capacities is substantially equivalent to comparing performance at the same overpotentials, because

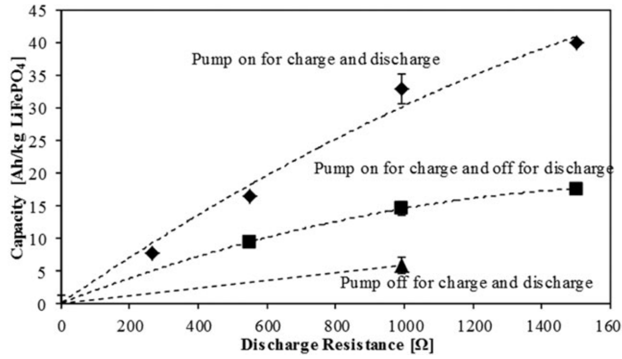

Figure 6. Specific discharge capacity vs. discharge resistance for the first cycle of convection cells and control cells.

all cells were evaluated until an overpotential of 1.1 V out of an open circuit voltage of 3.1 V. The convection battery provided about a 5.6-fold increase in ion flux for these initial studies at the capacity of 5 A h/kg. For the convection battery, the ion flux was 8–10 A/cm$^2$ as compared to 1.6 A/cm$^2$ for the diffusion control.

To further exemplify the difference in performances at different loads and overpotentials seen in Figure 6, voltage profiles at several loads are summarized in Figure 7. These curves provide more information than the total specific capacity—it allows performances to be compared at several different overpotentials. This comparison shows that the convection cells consistently are able to utilize more capacity over a range of loads. The convection cell is able to sustain longer operation due to the improved ion mass transfer from convective flow.

These studies were performed with 6-mm-thick electrodes—these lithium-ion electrodes are 60–200 times thicker than those commercialized with slurry-coating technologies. The maximum utilization observed was about 25% of the theoretical capacity of 170 A h/kg based on the loading of lithium-iron-phosphate in the cathode (discharge mode) during cell assembly. While 25% of theoretical is less than desired, it substantiates an absolute capacity far greater than that of cells with electrode thicknesses of about 0.05 mm, as is typical for commercial lithium-ion batteries. The authors believe that while convection decreases the concentration overpotential, increasing the electrode thickness can increase other overpotentials that affect the cell performance. Therefore, there should be optimal thickness between 0.05 and 6 mm that can provide greater utilization with the use of convection. The optimal thickness can be highly dependent on material properties and other factors specific to design constraints.

The data substantiate a significant improvement in performance of the convection battery vs. the diffusion control. The advantages of flow-through vs. flow-by separators in batteries remains a topic of further investigation. One advantage of flow-through membranes is the reduced travel path between electrodes and associated frictional losses from flow. For example, a simple exercise in geometry reveals that the mean travel path over a 1-m$^2$ separator to a single 1-cm$^2$ orifice through the separator is about 0.36 m. For a 1-m$^2$ separator with 4 0.25-cm$^2$ orifices, the mean travel path can be reduced to 0.18 m; the mean travel path being cut in half each time the number of orifices (with the same cumulative area) is quadrupled. This trend continues, until the distance between orifices approaches the thickness of the electrode; hence, the transition from flow-by to flow-through separators is a continuous transition with at least one definitive advantage associated with flow-through separators.

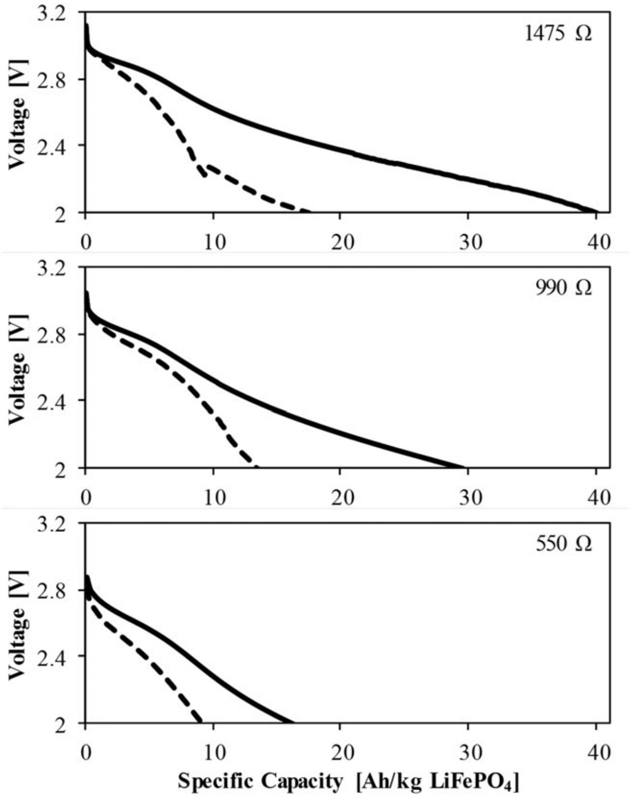

Figure 7. Comparison of discharge voltage profiles at several different constant discharge resistances.

Solid lines represent convection cells and dashed lines represent the control diffusion cells.

The improvement in performance due to the convection is attributed to a reduction in the concentration overpotential, $U_{\mathrm{conc}}$, which is approximated by Eq. 1 in a dilute binary electrolyte, which is derived from the Nernst–Planck equation.[17]

$$U_{\mathrm{conc}} = \frac{z_+ - (z_+ - z_-)t_+}{z_+ z_-} \frac{RT}{F} \ln \frac{c_{\mathrm{I}}}{c_{\mathrm{II}}} \tag{1}$$

where $z$ is the charge number of the respective ion, $t_+$ is the transference number for the positive ion, $F$ is Faraday's constant, $R$ is the universal gas constant, $T$ is the absolute temperature, and $c_{\mathrm{I}}$ and $c_{\mathrm{II}}$ are the salt concentrations at two different points within the electrolyte. In a cell without convection, large concentration differences can develop in the electrolyte resulting in concentration overpotentials described by the above equation.

It is important to recognize that these are only initial, validating studies. Comparison of the overall convection cell performance, including the costs of pumping, to a standard Li-ion cell is of little value at this point in the research. A host of future studies needs to be performed to increase capacity utilization, identify the best match of materials with the needs of the convection battery, better distinguish between advantages of flow-by vs. flow-through separators, and generally optimize performance.

## Conclusions

The convection battery has been demonstrated with an important lithium-ion chemistry with cycling. Benefits of the convection battery include increased utilization of capacity and reduced overpotentials. When considered in combination with previous studies using zinc-alkaline chemistry; the convection battery approach is concluded to be generally applicable to battery chemistries that use the same electrolyte in both electrodes.

Substantially increased ion fluxes (A/cm$^2$) through the separator and respective increases in current were observed for the convection battery as compared to the diffusion control at similar utilization of the active components. These increased ion fluxes can be used to reduce separator areas in batteries and increase thickness of electrodes; leading to improved combinations of higher power/energy ratios and lower costs.

The 6-mm-thick electrodes were a bit ambitious for these initial studies; however, evidence indicates that there is an optimum electrode thickness between 0.05 and 6 mm where good utilization is very attainable and a significant increase in performance can be obtained compared to standard cells with electrode thicknesses of about 0.05 mm. As the optimal materials to achieve the advantages of the convection battery remain yet to be identified, increased fluxes and increased electrode thickness are likely attainable.

Mechanistically, these studies showed that convection assists both charge and discharge—independent of direction of flow. Solid–liquid interfaces likely play a key role in promoting counter-ion counter-diffusion and the stabilization of ion concentration gradients, which is vital to the performance advantages of the convection battery, and the lack of sensitivity to flow direction.

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