Advancements in Water-based Processing for Large Format Lithium Ion Cells

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The performance, cost and safety of batteries can very often make or break an application. Nowhere is this more true than in the transportation and stationary power markets. As electric vehicles and the smart grid transform their respective industries, the role and significance of Lithium-Ion batteries continues to increase. Hybrid Electric Vehicles (HEV), Plug in Hybrid Electric Vehicles (PHEV) and Electric Vehicles (EV) are increasingly turning to Li-ion batteries for their next generation vehicles. In the utility industry, battery based energy storage is being deployed throughout the grid ranging from MWhr trailer systems for frequency regulation to 50-100KWh systems for community energy storage.

Historically, the science underlying the battery technology has often been criticized for its slow growth when compared with Moore's law in the semiconductor industry and rapid innovation in the computer industry. Recently, advancements in Li-ion technology have brought considerable improvement in energy and power performance to meet the demand of next generation vehicles and utility smart grid applications. However, the widespread adoption of Li-ion batteries in

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commercial vehicles is still limited because of its cost and inherent safety. As such, research and development efforts are continuing to reduce Li-ion battery costs by introducing alternative materials and processes. A significant advancement has been made with water-based processing aimed at reducing battery costs and protecting the environment at the same time.

Manufacturing Alternatives

Li-ion cells consist of a positive and negative electrode separated by an electrolyte solution. The electrodes consist of active materials, a binder (predominantly PVdF) and additives that enhance the electronic conductivity of the active materials. Traditionally, Li-ion electrodes are made using a slurry based process which uses large amounts of organic solvents to homogeneously mix the components mentioned above. The solvent predominantly used in the Li-ion industry is N–Methylpyrrolidone (NMP). However, the use of organic solvents is undesirable because of the high cost associated with environmentally compliant handling and disposal, the added material and capital cost for the manufacturing process and the toxicity of the solvent.

Figure 1. Open air water-based coating process equipment

The additional manufacturing costs and environmental concerns associated with the solvent-based process may limit the potential to drive the manufacturing cost down to the level required for widespread adoption in many applications. At International Battery, the focus is on manufacturing Li-ion cells using a water soluble binder (WSB) based process for both the cathode and anode. By eliminating the solvent from the manufacturing process, the material cost and capital investment cost can be reduced considerably. The WSB process has shown not to add any material cost to manufacturing[1] and water is abundantly available. The WSB process uses water as a medium to dissolve and disperse the binders and the electrode materials respectively (Figure 1). For the solvent-based process, additional recovery equipment, hoods and precautions are necessary.

A recent analysis performed by International Battery compared the capital costs, operating costs and environmental factors for building and operating a battery manufacturing facility. One scenario involved energy based applications (1MWh bulk storage for utilities) and assumed usage of large format 160Ah Lithium Iron Phosphate (LFP) cells (Figure 2). The other scenario involved hybrid vehicle applications using a “smaller” cell in the 40-60 Ahr range.

Figure 2. 160 Ahr Lithium Iron Phosphate Cell. 7.2” L x 2.8” W x 11” H

The results of the energy scenario are summarized below. Compared to a traditional solvent-based process, the water-based process resulted in the following advantages:

- 10% reduction in capital costs
- 85% reduction in waste management expenses

- 65% reduction in solvent costs
- 10% reduction in cost per Whr

Additionally, building a facility with a water-based process results in:

- A radical reduction in volatile organic compound (VOC) emissions
- Lower energy consumption
- Easier siting and permitting

Performance Comparisons

It is well known in the battery industry that water and Li-ion cells do not like each other. As such, there is a perception that a WSB process may potentially limit the performance of the Li-ion cell's cycle life, shelf life and other performance related processes. Several research studies have been published about the satisfactory switch from a solvent-based process to a water-based process for the graphite[1,2,3,4,5]. However, very limited information is available about the cathode materials used in the Li-ion industry. Research and development work at International Battery has focused on addressing the stability of the cathode materials in an aqueous media. $LiFePO_4$ has a tendency to absorb moisture while stored at ambient temperature. K. Zaghib et al. reported that $LiFePO_4$ stored at 25 C, 50% humidity, the capacity fade is significant and it is not reversible[6].

To address the stability of the $LiFePO_4$ cathode in a WSB process, electrodes were made using a $LiFePO_4$ cathode and a Graphite anode using a WSB binder (propriety binder). Electrodes were also made with a PVdF binder with NMP solvent. Lithium half-cells were built for $LiFePO_4$ cathode made using the WSB process and the solvent-based process. The electrodes were thick for both WSB and PVdF electrodes. The lithium half-cells were cycled at C/26 rate to test for capacity. The cells with the water soluble binder and PVdF based solvent binder delivered similar capacity. The WSB electrode had a first charge capacity of 140 mAh/g and a first discharge capacity of 125mAh/g. The solvent-based electrode had a first charge capacity of 137mAh/g and a first discharge capacity of 123mAh/g. Cells were charged to 3.6V at C/26 rate constant current charging and allowed to rest for twenty minutes before discharge. The cells did not go through constant voltage charge. There was no difference between the water-based process and solvent-based process. The WSB cells and solvent-based cells specific capacity show minimal increase during second cycle (Figure 3, A&B). The capacity trend for thick electrodes matches well with the earlier results reported in the literature for the water soluble binder and PVdF solvent binder electrodes[7,8].

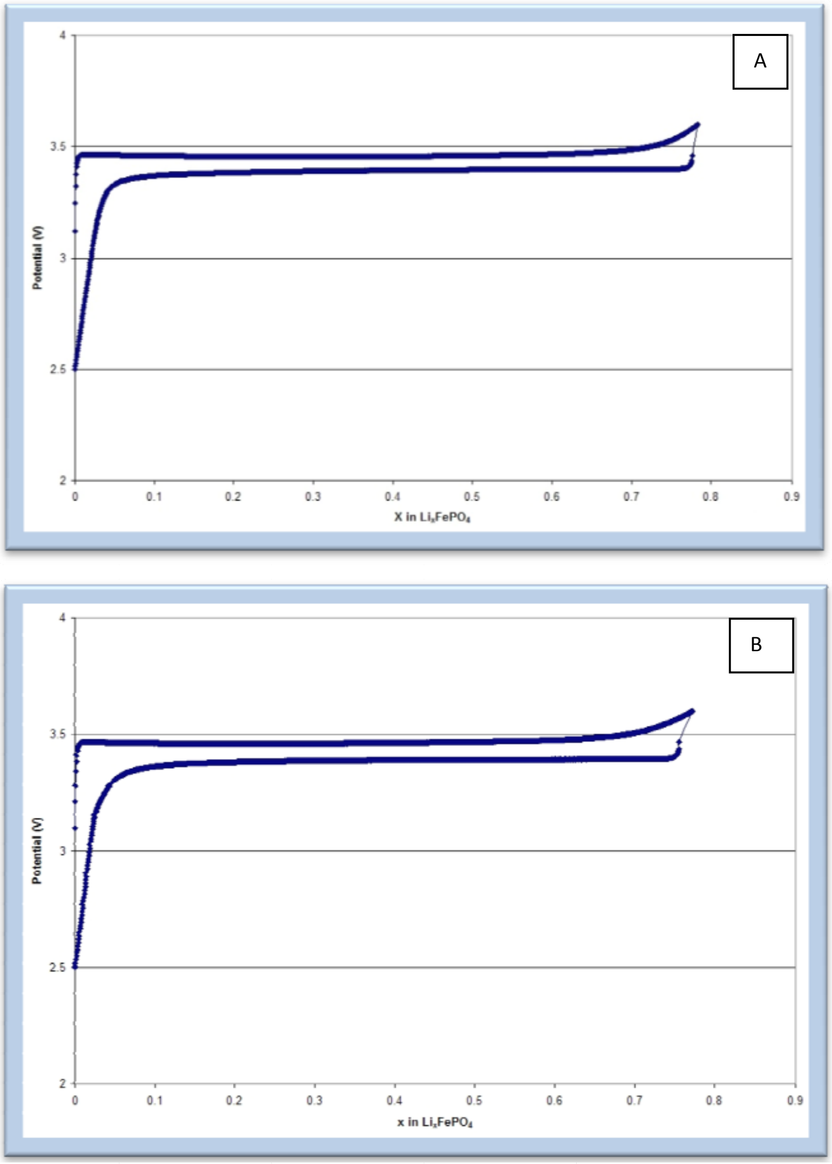

Figure 3, A&B. Second cycle charge/discharge curves for (A) WSB process and (B) PVdF solvent-based process. The charge/discharge curve is for second cycle. The cells were charged and discharged at C/26 rate for capacity determination. Cell configuration (Lithium metal/electrolyte/LiFePO$_4$ cathode)

The charge discharge curves for WSB process and solvent process are shown in Figure 3. Figure 3 shows that there is no additional electrochemical contribution except for the theoretical voltage plateau of the $LiFePO_4/FePO_4$ redox couple. The dq/dv plots for $LiFePO_4$ lithium half-cells also did not show any difference in the electrochemical behavior between the WSB process and the solvent-based process. Large format cells were made using the WSB process and the capacity of the cell is around 160 Ah. The cells were cycled at C/3 rate at room temperature (Figure. 4). The cells were cycled for about 520 cycles and the cells show very minimal capacity fade (Cycle life tests are continuing to validate the cycle life). The rate performance of the cells was tested at different temperatures and the cells show excellent capacity at low temperature and also at high temperatures (Figure. 5, A&B). The test results show that the water-based Li-ion cell should perform well for long shelf life and cycle life.

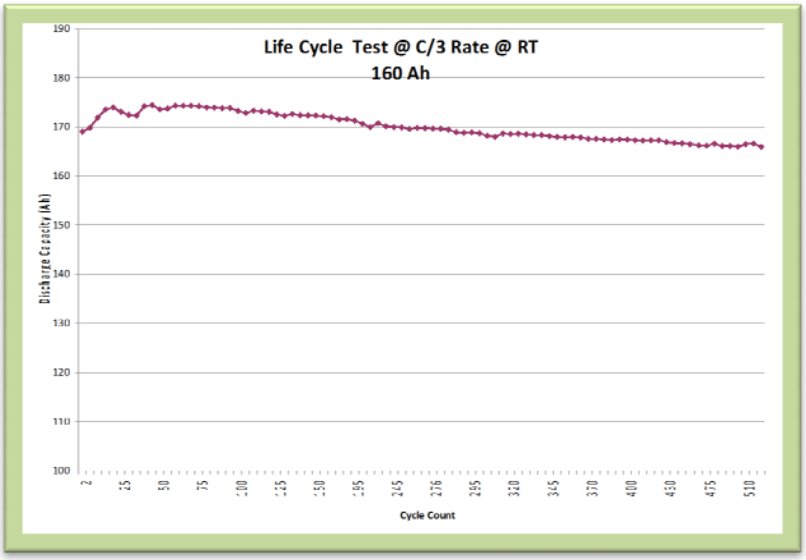

Figure 4. Cycle life room temperature at C/3 rate. Charge cut-off voltage 4.V and discharge cut-off voltage 2.5V. Percent capacity fade 1.61 over last 213 cycles.

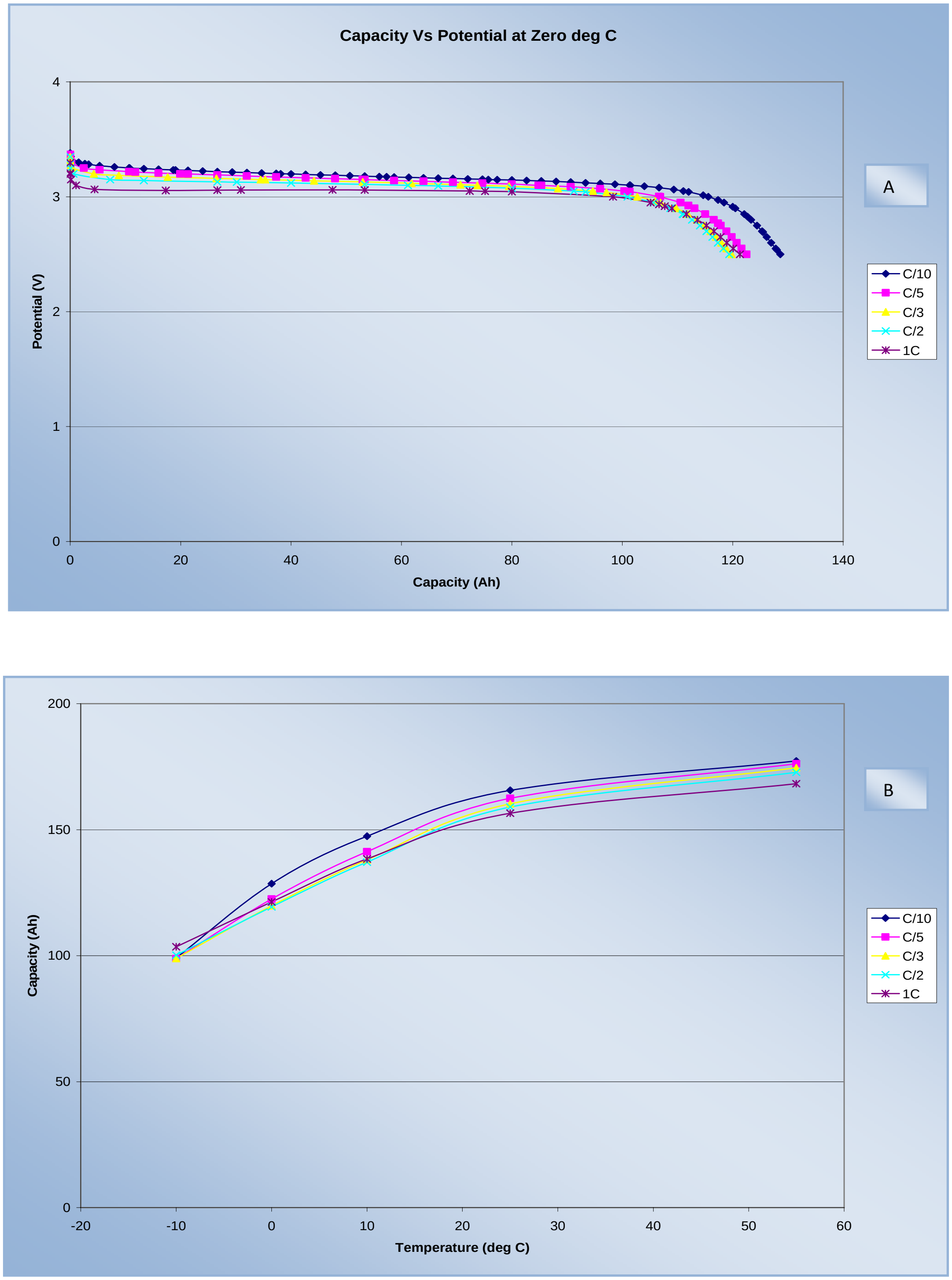

Figure 5, A&B. Rate performance of the 160Ah LFP cells (A) cell discharged at different rate at zero deg. C. and charged at C/3 (const current and const. voltage).
(B) Rate performance at different temperatures and at different rates.

Applications and Deployment

Large format Li-ion cells are now being manufactured and deployed using this well tested and proven process saving both money and the environment. Applications currently using or testing large format cells include:

- Distributed energy storage and bulk energy storage for utilities
- Heavy hybrid vehicles and large scale trucks and buses
- Military vehicles on silent watch
- Backup power for critical NASA ground operations, autonomous ground vehicles and forklifts looking to replace lead acid batteries
- Backup power for telecommunications
- Specialty medical and industrial applications

In several applications, large format cells have been deployed in the field for several years.

Conclusion

Performance results and cost analyses by International Battery indicate that water-based processing and new large format form factors are now available to help drive widespread Li-ion adoption in many key industries. Customer adoption and deployment of large format cells continues to increase and new applications are being identified to utilize the technology. In particular, as the energy content for electric vehicles and smart grid applications continues to increase, lower cost and environmentally friendly manufacturing processes will be pivotal for those industries going forward.

Authors

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