Advanced Electrode Designs of Battery Systems
towards Expanded Applications on the Energy Storage

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SUMMARY

The batteries are approaching a larger share portion of the energy storage demands nowadays. These new sustainable participants are gradually replacing the traditional fossil resource to power the world with their carry-on capability and eco-friendly nature. Among the diverse developments, there exist two attractive trends of electrode designs, which are lowering the cost per unit and providing superior properties. The former one facilitates the usage of batteries toward a larger scale of usage, while the latter one contributes more to sophisticated application platforms such as electronics and electrical vehicles (EVs). For a comprehensive study, here we discussed two design schemes based on each trend, which are a low-cost flow battery system and high-performance electrodes fabricated through powder additive manufacturing. In the first part, a novel flow-able battery system is discussed based on Zn/Ni chemistry. While the capability of conventional Redox flow batteries is limited by the solubility of applied active couple, our Zinc Nickel Flow Battery (ZNFB) model utilizes flow-able slurry electrodes to functionalize the solid-state Zn/Ni reactions in a fuel cell layout, in which way achieves a much higher loading concentration of the active materials and therefore improved electrochemical properties. In the second part, we adopted a remarkable 3D dry powder spraying technology to precisely control the fabrication of electrodes for lithium-ion batteries with different designs of microstructure. This one particularly relates advanced designs to the actual production because of the dominant role of lithium ion batteries in the market now. Demonstrations of both methods are provided, and resultant properties are analyzed as well. This work combines the
consideration of battery designs in two ways: an exploratory study of potential candidates in the future, and practical optimizations on the existing system.
CHAPTER 1. INTRODUCTION

1.1 Redox Flow battery (RFBs)

The escalation of power system promotes the development of battery technologies with its huge application market. Redox flow batteries (RFBs) are very attractive to customers in the energy grid system, and their noticeable technological innovations in the past decades have driven them to gradually replace the conventional energy storage methods under certain circumstance. Portable batteries used in electronics and fully electric vehicles ought to be designed to fulfill the growing desires on supplying energy quicker and longer. Therefore, many significant improvements have been achieved on battery manufacture and mechanism optimization.

An RFB, as shown in Figure 1\(^1\), is an energy-storage device that can store and provide electricity through conversing to chemical energy. Unlike traditional batteries that store energy in electrode materials, RFBs typically store energy in two soluble redox couples contained in separate tanks. When electrolyte flowing through electrodes in a cell stack, the conversion between electrical energy and chemical (or electrochemical) energy occurs. The electrolytes flowing through the cathode is called as catholyte, and the one flowing through anode is called as anolyte, respectively. Between the two electrodes is an ion-conduct membrane that prevents the electrolytes from mixing while allowing the ions transport to maintain electrical neutrality. The earliest work on the RFBs was undertaken at NSA’s Lawrence Laboratories by Thaller in the early to mid-1970s. The possibility of creating a vanadium flow battery was explored variously by Pissoort in 1930's, NASA researchers in the 1970s, and Pelligrni and Spaziante in the 1970s, but none of them were
successful in demonstrating the technology, until the all-Vanadium redox flow battery designed by Prof. Skyllas-kazacos and their following works.[2]

Figure 1 Configuration of flow battery

Nowadays, the development of sustainable energy resource is achieving more and more interest. Among the available renewable energy sources, solar and wind are probably the most abundant and readily accessible, characteristics that are increasingly being recognized as essential components of future global energy production. Globally, a total of 74.3 GW and 94 GW of wind power generation capacity were installed in 2006 and 2007, respectively[3] The World Energy Council estimates that new wind power capacity worldwide will total up to 474 GW by 2020.[4] Likewise, the expansion of photovoltaic module installations currently is increasing by 40% per year worldwide. Therefore, with the need to integrate more renewable energy, the electricity grid system is developing to an intelligent and efficient power system. In this trend, the energy storage systems, are predicted to play a more prominent role to provide a supplemental energy management,
which will lead to a clean sustainable future in grid reliability and utilization. Among all the Energy storage methods, RFBs provide a well-balanced solution for current challenges.

A vanadium redox flow battery (VRFB) consists of an assembly of electrochemical cells, each consisting of two half-cells. Separate reactions occur in each half-cell. During discharge, electrons are produced in the reaction in the negative half-cell and are consumed in the reaction in the positive half-cell, forming the basis for an electric current. The original generation of VRFB proves the following function species as:

**Catholyte:**

\[
\text{VO}^{2+} + 2H^+ \leftrightarrow \text{VO}_2^+ + H_2O - e^- , E_0 = 1.00 \text{ V } \text{vs. SHE}
\]

**Anolyte:**

\[
V^{3+} + e^- \leftrightarrow V^{2+} , E_0 = -0.26 \text{ V } \text{vs. SHE}
\]

During the initial charging, the following redox reactions take place:

- **Positive electrode:** \(V(IV) \rightarrow V(V) + e\)
- **Negative electrode:** \(V(IV) + 2e \rightarrow V(II)\)

Subsequent charge-discharge reactions, however, would be:

- **Positive electrode:** \(V(IV) \leftrightarrow V(V) + e\)
- **Negative electrode:** \(V(III) + e \leftrightarrow V(II)\)

The unique working mechanism of the RFB provides several desirable features. It has two main advantages over the conventional storage battery:
There aren’t any solid-state reactions or accompanying morphological changes at the electrodes, which lead to an unlimited theoretical cycle life. In conventional solid-state batteries, shape changes of electrodes always lead to the capacity losses and finally the failures of the system.

The design of flow battery is quiet flexible compared including the configuration of system, the capacity, and the power output. Because the electrolyte and electroactive materials stored externally, the scale of the RFB capacity are not coupled. In an RFB, the system capacity is controlled by the size of the tanks, while the size of the stack dictates the system power capability.

The flexible modular design allows the RFB to be sized for a wide spectrum of power and energy storage, starting from utility-scale storage (MWh) such as substation to a private application such as house emergency power supplier (kWh). In an RFB system, the role of the electrode is designed to provide active surface for the redox reaction, which protect the RFB electrodes from physical damage during cycling. In contrast, the electrode in a solid-state battery often involve many kind of morphology alterations and finally lead to the failure of the system. With this characteristic, RFBs are often approved for their long service life. Other advantages of RFBs over conventional battery systems includes their safety and thermal management. Also, the mechanism of the RFB simply divides its manufacturing into stacks production, storing system, plumb systems, and electrical systems. Therefore, it bypasses several expensive, and complicated, manufacture steps of solid-state battery.
Compared with conventional batteries, RFBs are attractive to certain customers because of their unique characteristics, such as the decoupled power and energy capacity and their design flexibility. They use the same material (in liquid form) in both half-cells, which eliminates cross contamination problem and resulting in a theoretical unlimited running life. With a relatively low energy density, VRFBs are always chosen for the large stationary energy storage applications, which don’t have a limitation on volume and weight. They include Uninterruptible power supply (UPS), electrical peak shaving and load levelling, and renewable energies grid system (e.g. wind and solar), which are usually in conjunction with the electricity grid system as a supplemental power management. Most suited for utility-scale power systems in the 100 kW to 10 MW size range in applications having low power/energy ratios (long discharge durations). Transmission and distribution applications with these characteristics include:

- Peak Shaving

- Spinning Reserve

- Wind Farm Stabilization & Dispatch
As shown in the Figure 2, RFB can also be used in other energy storage applications, such as backup power. 5 kW units has been available for backup power applications, particularly in telecom, substation, and UPS applications. Using more RFB in the grid system will benefit the economics of the industry. For example, dispatching in peak times would reduce the power requirements from generation sites, thus reducing generation costs. In this example, the economic benefits of the two applications can be combined. Generally, an energy storage option requires it to meet multiple requirements of different applications and modes, which fulfill the flexibility of RFB systems. Also, as shown in the figure, when the power resource locates isolated, RFB is a very good choice on gridding the electricity and powering the nearby town with a certain capacity setting of the RFB system.

As shown in the figure 3, here we list the market for RFB and its competitors. The stationary energy storage is a key factor for smart gridding and for exploring more
intermittent renewable energy sources such as solar and wind. RFB maintains a balancing position among these competitors.

Figure 3 Existing energy storage technology for different applications[6]

The Electricity Storage Association (ESA; http://www.electricitystorage.org) sorted the energy storage methods into four types as mechanically, electrically, chemically, and electrochemically. Dr. Grigori L. Soloveichik concluded them into table 1[7] as shown below, which can provide the brief sense of these technologies and a straightforward view of their applications. And examples of pumped hydro, and compressed air energy storage (CAES), and regenerative fuel cells.

Table 1 Conclusion of different methods[7]
<table>
<thead>
<tr>
<th>Technology</th>
<th>Typical power, MW</th>
<th>Discharge time</th>
<th>Storage capacity cost, $ \text{kWh}^{-1}$</th>
<th>Life time, cycle/years</th>
<th>Efficiency, %</th>
<th>Drawbacks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flywheels</td>
<td>1</td>
<td>&lt;5 min</td>
<td>1,000–2,000</td>
<td>100,000/&gt;10</td>
<td>&gt;90</td>
<td>Cost, power applications</td>
</tr>
<tr>
<td>Compressed air energy storage (CAES)</td>
<td>2,700</td>
<td>2–10 h</td>
<td>90–200</td>
<td>&gt;5,000/&gt;10</td>
<td>50</td>
<td>Site specific, storage and transmission cost</td>
</tr>
<tr>
<td>Pumped-storage hydroelectricity (pumped hydro)</td>
<td>4,000 (up to 22,500)</td>
<td>4–12 h</td>
<td>75–100</td>
<td>&gt;10,000/&gt;25</td>
<td>75–80</td>
<td>Site specific, transmission cost, environment</td>
</tr>
<tr>
<td>Supercapacitors</td>
<td>0.25</td>
<td>&lt;1 min</td>
<td>500–3,000</td>
<td>500,000/20</td>
<td>&gt;90</td>
<td>Explosion hazard, low energy density, cost</td>
</tr>
<tr>
<td>Superconductive electromagnetic storage (SMES)</td>
<td>$10^4$</td>
<td>1–30 min</td>
<td>2,000–10,000</td>
<td>100,000/20</td>
<td>97</td>
<td>High capital cost, cryogenics</td>
</tr>
<tr>
<td>Chemical (hydrogen)</td>
<td>$10^4$</td>
<td>&gt;5 h</td>
<td>13</td>
<td>40–50</td>
<td>Low density storage, high cost, safety</td>
<td></td>
</tr>
<tr>
<td>Secondary batteries (lead-acid, Li-ion, NAS)</td>
<td>0.5–1</td>
<td>1–8 h</td>
<td>250–3,500</td>
<td>1,000–4,500/7–20</td>
<td>75–80</td>
<td>High cost, low cycle life</td>
</tr>
<tr>
<td>Flow battery (vanadium redox battery)</td>
<td>12</td>
<td>10 h</td>
<td>150–2,500</td>
<td>500–2,000/10</td>
<td>70</td>
<td>Low energy density</td>
</tr>
</tbody>
</table>

When the prior scientists defined the RFBs, they were supposed to be inexpensive and possess many features that provide for long life, high reliability, and low maintenance and operation costs. However, before the new All-Vanadium Redox Flow Cell by Dr. M. Skyllas-Kazacos, the development of this technology was not so successful, and was still far from commercialization, and was not so attractive to the academia and energy storage industry. Iron/chromium (Fe/Cr) one was firstly developed by NASA in 1970s as a model of RFB. It contains an aqueous solution of ferric–ferrous (Fe$^{2+}$/Fe$^{3+}$) redox couple in positive reactant and a solution of chromous–chromic redox couple acidified with hydrochloric acid in negative reactant. However, it had the issue of low output voltage and efficiency, and contaminations between iron and chromium ion. Then, Weber et al. proposed a hybrid redox flow battery, which was called as zinc/bromine technology (ZBB). In the ZBB technology, zinc is solid in the charged state and dissolved during the discharge, whereas the bromine is always dissolved in the aqueous electrolyte.$^{[8-9]}$ However, the
technology have to use an ion exchange membrane as the separator, which was a high cost but low durability technique at that time. Also, bromine is highly dangerous for the environment \cite{10} and will cause problems associated with material deterioration.

The use of a single-metal system for both halves of the cell has been proposed to overcome the problem of cross-contamination as well as any limitations resulting from the use of pre-mixed solutions. Thus, leaded by NASA, many other redox couple including Co(III)/Co(II), Ti$^{3+}$/TiO$^{2+}$, and the V(III)/V(II) were investigated to use in a RFB. However, none of them had internal shortage to be used as chemical species at that time.\cite{11-17} The Vanadium Flow battery was first patented in 1978 by Pellegrini and Spaziante, which involves solely vanadium species in both half-cells at different valence states.

Prof. Skyllas-Kazacos and her team continued their study on the VRFB, and consistently extended their investigation of VRFB. Their interests include the VRFB reaction kinetics and mechanisms, screening and building the prototype of VRFB, the system components optimization (mainly on electrode materials, membrane materials and electrolytes), electrochemical performance improvement, technique commercialization, branding and scaling-up, and then working on finding new redox couples of VRFB.\cite{2, 18-58}

After the commercialization of the VRFB, it becomes one of the alternatives for traditional energy storage methods. However, there exists still several disadvantages of VRFB that constraints its applications, such as low energy density, relatively low efficiency and high cost. These aspects became the development trend of RFB and make a significant influence on nowadays RFB techniques. Other than optimizing the conventional
all-vanadium Redox Flow Battery, more RFB options were proposed and grew up diversely and quickly.

Chiang’s group at the Massachusetts Institute of Technology demonstrated a semi-solid lithium rechargeable flow battery in which the traditional Li-ion battery electrode solid materials (LiCoO$_2$ and Li$_4$Ti$_5$O$_{12}$) were suspended in a conductive gel circulating through each of the half-cells, which were separated by an Li-ion battery microporous separator. The LiCoO$_2$-Li$_4$Ti$_5$O$_{12}$ full-cell test produced an average 2.35 V discharge voltage with 397 Wh L$^{-1}$ of energy density. Presumably, other Li-ion battery intercalation chemistry compounds can be used by the same mechanism. The combination of high concentration and high voltage yields significant increases in energy density. The novelty in this approach is the use of particulates of a redox-active compound in suspensions rather than solutions. As a result, the energy density of the electrolyte is no longer constrained by the solubility limitation, but rather the allowed fraction of active material solids in the flowable suspension. In achieving the electronic charge transfer between the active materials particles and the current collector, another intriguing concept of “flow-able electrodes” was developed, in which the particulate active materials and conductive additives (Ketjen black) were dispersed in a typical Li-ion battery electrolyte solution to form a percolation nanoscale conductor network, as shown in Figure 4a. The fractal-like network formed by the nanoscale conductor thus renders the electrolyte decent electronic conductivity. Figure 4b shows the voltage profile of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ and Li$_4$Ti$_5$O$_{12}$ suspension achieved in a flow-able form. In doing so, the charge transfer is no longer confined on the local surface area of the electrode; rather, it is extended to the whole electrolyte volume, which could be a revolutionary development for the RFB electrode. Although it is difficult to suspend the
conductive particles in the aqueous RFB electrolyte because of the strong acidic environment, the approach potentially can be expanded to other non-aqueous RFBs with the help of surface functional groups and the use of the surfactant.

**Figure 4 Semi-flow lithium ion battery**

Given the current trend towards reducing greenhouse gas emissions and increasing the penetration of renewable energy, along with demands of high-quality power and implementation of smart grids, there appears to be general agreement on the need for EESs in the electrical grid. The demand for stationary energy storage has rapidly changed the worldwide landscape of energy system research, which recently brought the RFB technology into the spotlight. The growing interest and worldwide R&D activities suggest a bright outlook for developing improved RFB technologies for the future electric grid. A recent surge in research activities on semi-flow RFB system reiterates a high level of
interest in high-energy-density systems. Although in the initial stage, these approaches open extraordinary new research avenues to adopt redox flow concepts onto other chemistries holding great promise to multiply the energy density of RFBs potentially for transportation applications. The hybrid nature of these new systems will require an interdisciplinary approach to successfully leverage our knowledge of existing battery chemistries with unique redox flow technologies.

Therefore, SSFC is an attractive design scheme for the redox flow batteries (RFBs). While the capability of conventional RFBs is limited by the solubility of its active couple, the SSFC model utilizes a flow-able slurry to functionalize the solid-state reactions in a fuel cell layout, in which way achieves a much higher loading concentration of the active material and therefore advanced electrochemical properties. Through mixing carbon additives into the electrolyte, electron transfer and ion transfer are simultaneously obtained inside the three-dimension network of the slurry. The research of SSFC have been mainly focused on investigating slurry electrodes for the lithium-ion chemistries and super capacitors in the past years. However, for a larger scale of usage, developing SSFC with a more economical chemistry is a competitive trend to study. Our results demonstrate this “hybrid” RFB system that includes the beneficial features of solid-state Zn/Ni batteries as eco-friendly and deposit-abundant and provides a pathway for the RFB technologies to adapt to the escalation of power system.

1.1.1 Reference


1.2 Additive manufacturing in fabricating the lithium-ion battery

Optimizing manufacturing technologies is necessary in order to fulfill the growing demands for boosting this electrical-powered world.[1, 2] For the industry of Li-ion batteries, the manufacturing mostly refers to the filming processing of electrodes that coats the current collector with a composite layer, which consists of active materials (AM), binder materials, and carbon additives. Within these raw materials, AM are the carriers of electrochemical reactions, while the rest of materials forms a “microstructure framework” to mechanically support the coating layer and provide the ion/electron transfer pathways for AM. A proper microstructure, or rather a high mechanical stability, is crucial and necessary for batteries to survive during the handling, packaging and using procedures.[3, 4] Particularly when accommodating some new materials, such as core-shell structured cathodes[5-7] and silicon/graphite anodes[8-12], a well-established microstructure is essential to strongly host AM during the repeated lithiation/delithiation procedures. Due to their unique material characteristics, electrodes based on these materials would suffer a lot of volume change during cycling (up to 400%).[13] A few in-situ and in-operando experiments
have been conducted to monitor and highlight this challengeable circumstance for batteries.\cite{14-17} During the dynamically service life of batteries, some microstructure conditions in this way restrict advanced materials from reflecting their optimum properties.

For the slurry casting manufacturing (slot-die coating), the usage of solvents (mostly as N-Methyl-2-Pyrolidone (NMP) and water) has been the bottleneck to further control the microstructure of electrodes.\cite{18, 19} Within the past decades, this dominant manufacturing method has been studied in depth to produce Li-ion batteries at an industrial-grade high efficiency.\cite{20-23} However, the mixing and recycling procedures for solvents add some uncertainty to the quality of electrodes during manufacturing.\cite{24, 25} A model has been raised to show how AM particles and binder/carbon particles behave diversely during the drying procedure.\cite{26} Light and nano-sized binder and carbon particles are driven by the heat/mass flux to move toward the heating/evaporation interface, while AM particles separately sediment to the current collectors.\cite{26-28} This brings in the dilemma for manufacturers to make a difficult choice: by keeping a high production efficiency, the high drying rate always sacrifices part of the “serviceable” binder/carbon materials. These binder/carbon materials accumulate at the top/bottom interfaces of the coating and finally be wasted.\cite{24, 25, 29} Due to this inhomogeneous distribution of materials, excess binders are always requested to protect the electrodes from defects caused by the insufficient bonding strength.\cite{20, 30} In contrast, our dry spraying manufacturing avoids this issue as a solvent-free method.\cite{31} All materials are fully dry mixed and deposited onto the current collector via an electrostatic sprayer, and simultaneously calendared to products with required parameters. There takes no waiting time for stirring and drying, and therefore limits the materials redistribution during these procedures. As expected, dry sprayed electrodes have
shown better microstructure conditions and physical properties in our previous works (adhesion/cohesion strength, structure integrity, materials homogeneity, etc.). In addition, it has been demonstrated to be widely viable for state-of-art materials (LiCoO$_2$ (LCO), LiNiCoMnO$_2$ (NCM), LiMn$_2$O$_4$ (LMO), nano-LMO, graphite, carbon additives, binders, etc.), and some advanced formulations (ultra-low binder (less than 1 wt%), thick coatings (300µm), etc.). Most importantly, this method is originally designed as a scalable system to manufacture electrodes/components for batteries at a low-cost basis. Within this method, the transition from conceptualization to commercialization would be accomplished readily for any progresses in coming. Along with the investigations on microstructure control, the dry spraying method is also expected to facilitate the development of high-end designs with specific microstructure preference, such as the hierarchically sandwich structure$^{[1, 36, 37]}$ and the self-stand microstructures$^{[38, 39]}$.

Here we start to discuss the feasibility of dry spraying on the microstructure control through improving the adhesion strength for the widely used graphite anodes. As a common concern for graphite anodes, the adhesion strength between the current collectors and coating layers has been thoroughly studied in the conventional manufacturing.$^{[40-42]}$ This problem mainly comes from the chemical instability of copper in the atmosphere that makes impacts to the surface roughness and surface energy, and in turns affect the wettability of the current collector surface.$^{[43, 44]}$ In the industry, prior-casting treatments for the current collectors are quite indispensable, such as adding corrosive-additives into the slurry recipe and treating the copper foil treatments with lasers.$^{[45, 46]}$ Otherwise, electrodes may face a severe de-lamination and batteries would get a rapid quality degradation.$^{[47]}$ Consequently, improving the adhesion strength for graphite anodes would
be a good example to discuss the application of dry spraying method on modifying the microstructure and manufacturing advanced designs for batteries. The dry sprayed anodes treated with the adhesion enhancer (procedures as shown in Fig. 1) remarkably outperformed untreated anodes electrochemically and mechanically. The bonding strength and the morphology conditions of the dry sprayed graphite anodes with various loading amounts of the interlayer are revealed through the Scan Electron Microscopy (SEM) and bonding tests. The performance comparison between dry sprayed anodes and slurry cast anodes is also provided in this report.

We have demonstrated the prototype to fabricate electrodes for lithium-ion batteries by the electrostatic spraying guns (Figure 5a) to deposit particles (Figure 5b). Hot rollers calendar the electrode with desired thickness and density (Figure 5c, 5d). Dry sprayed electrodes were made at a large area (Figure 5e).

**Figure 5** Dry Painted Battery Concept. a) Manufacturing system for electrodes created by dry particle painting process. b) 3D representation of a dry painted
electrode before thermal activation. c) 3D representation of a dry painted electrode after hot rolling and thermal activation. d) Hot roller configuration. e) Dry painted electrodes on Al foils.

Cost analysis (as shown in Table 1) showed that the dry method can potentially save a 15% off from the original budget due to the saving on drying systems and related procedures. This analysis was done based on the model as Argonne battery performance and cost (BatPaC) model (Nelson et al, 2011). Here we showed the result of comparison between the slurry casting method and our dry methods (Two designs were selected from 7 models).

Table 1 Cost analysis of conventional slurry process with our proposed dry process*

<table>
<thead>
<tr>
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<th>Design 1</th>
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<th>Design 4</th>
<th></th>
<th>Design 4</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Direct Labor, hours/year</td>
<td>Capital equipment, Millions</td>
<td>Plant area, Square meters</td>
<td>Direct Labor, hours/year</td>
<td>Capital equipment, Millions</td>
<td>Plant area, Square meters</td>
</tr>
<tr>
<td>Conventional process</td>
<td>511,871</td>
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<td>595,918</td>
<td>139.10</td>
<td>15,958</td>
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<tr>
<td>Dry process</td>
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<td>94.28</td>
<td>10,918</td>
<td>499,600</td>
<td>112.61</td>
<td>13,326</td>
</tr>
<tr>
<td>Saving percentage</td>
<td>21.6%</td>
<td>14.2%</td>
<td>13.1%</td>
<td>16.2%</td>
<td>19.0%</td>
<td>16.5%</td>
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</tbody>
</table>

The number of battery packs manufactured per year is assumed to be 100,000

1.2.1 Reference


1.3 Objective of this work

Emerging techniques on manufacture engineering and materials science, eliminate the barriers on processing electrodes with superior design. Existing systems can be rebuilt as hybrid ones with proper raw materials selection. In addition, the processing procedure can be precisely planned to fulfill the customers’ requirements on different properties of
electrodes. Here we choose the flow battery system and the dominant li-ion batteries technologies to research on.

In Phase I: we are trying to develop the first fully flow-able Zinc Nickel Flow Battery (ZNFB) and study its reaction mechanism, whose performance is supposed to be suitable for various scales of application. Based on the semi-solid fuel cell (SSFC) technology concept, we incorporate the beneficial features of conventional aqueous Zn/Ni chemistry (essentially sustainable, eco-friendly and deposit-abundant) into the fuel cell structure to effectuate a “hybrid” flow battery system. With the nano-sized carbon network, the balance between electron transfer and ion transfer are obtained in three-dimensions space. Basic electrochemical tests have demonstrated the feasibility of the ZNFB technology. Fundamental characteristics of suspension electrodes were studied and analyzed to improve the electrochemical properties of the ZNFB system.

Three versions of prototype have been developed to improve the system’s capability. The design of ZNFB prototype should take the slurry form of electrodes into consideration as well, which can provide better reaction conditions for the whole system.

In Phase II: we are studying on fabricating lithium-ion battery electrodes using a new, completely dry powder spraying process. No solvents are applied, which are essential in the conventional slurry-casting manufacture. Thermal activation time has also been tremendously reduced due to a lowered time and resource requirement when the evaporation process is no long needed and replaced by a hot rolling process. It has been found that inducing the mechanical bonding of the thermoplastic polymer to the remaining active electrode particles only takes a few seconds for the thermal activation step.
Furthermore, skipping the traditional drying process allows large-scale Li-ion battery production to be more economically viable in markets. Electrochemical results also show that our tested dry-painted electrodes outperform conventional slurry processed electrodes, which are due to their unique binder distribution based on our analysis. Bonding tests of the dry-deposited particles onto the current collector show that the bonding strength of them are greater than the ones of slurry-cast electrodes, 127.14 kPa as compared to 84.29 kPa. In addition, more electrodes design and optimization possibility on this new fabrication method are conducted and tested, and the fundamental researches on its specific electrode microstructure during manufacture and cycling are studied and recognized.

The dry printed cathode electrodes (NCM) outperform the regular slurry cast ones in many aspects. From our current research, the printed electrode has more than 80% capacity retained in 500 cycles, which surpass the slurry cast electrode for comparison. In addition, dry printing technology can achieve the design of thickness up to 200μm to enable the design of thick electrode with high energy density. For the microstructure of electrodes, PVDF works like glue to attach the particles together between the active materials. The hot rolling procedure can strengthen the bonding and improve the combination in the printed electrodes by promoting the distribution of PVDF. Along with better electrochemical and physical properties, dry printing method could reduce 20% of the cost during the production of electrodes and has the potential for further design.

More electrodes design would be attractive to demonstrate the technology’s capability, such as anodes for Li-ion batteries and advanced designs of electrode microstructure. Also, basic mechanism studies about the dry-powder spraying procedure are necessary to understand the design strategy and developing trend of this technology.
CHAPTER 2. PRELIMINARY STUDY OF HIGH ENERGY DENSITY ZN/NI FLOW BATTERIES

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The escalation of power system promotes the development of energy storage technologies (ESTs). Among all of ESTs, battery technologies develop quickly and diversely because of its huge application market. Aqueous redox flow batteries (RFBs) are very attractive to customers in the energy grid system, and their noticeable technological innovations in past decades are driving them to gradually replace the conventional ESTs under certain circumstance. Here, the first fully-flow-able zinc–nickel flow battery (ZNFB) is preliminary reported in this paper, and its superior performance is supposed to be suitable for both large-scale storage need and carry-on powertrain in cars. Through using semi-solid fuel cell (SSFC) technology, we incorporate the beneficial features of Zn/Ni chemistry (essentially sustainable, eco-friendly and deposit-abundant) into RFB structure to make a “hybrid” flow battery system, which can take the advantage of both. The relationship between carbon loading and suspension conductivity is determined. Electrochemical
properties of ZNFB as static test, cycling test, and fully flowing test are studied to demonstrate our design.

2.1 Introduction

The conventional slurry casting method dominates the electrodes’ manufacture of lithium ion batteries, which requires a sequence of long-time and complicated procedures. There exists a main concern of the slurry cast manufacturing that the use of an organic solvent (N-methyl-2-pyrrolidone ) is indispensable, which is toxic and high cost but is necessary to fluidize the material mixture into the slurry. To overcome this limitation, additive manufacture was applied here in our dry printing technology to produce electrodes of the lithium-ion batteries. The additive manufacture technology has been proved to be attractive and competitive in many industries for its unique capability on material loading and layout control. With this dry printing technology, we can address a direct drying printing of electrodes onto the current

Thick fog and haze occurring in China remind the public how PM 2.5 particles, as the solid products of combustion activities (motor vehicles, heavy industries, etc.), can seriously affect our daily life, other than the widely-concerned gaseous ones which lead to the global warming with horrible consequence. These climatic issues lead to the attention on reducing the utilization of fossil fuels\cite{1, 2}, and searching for alternative renewable energy resources\cite{3}.

In this new round of clean energy revolution, the electricity grid system takes a critical role as the main energy transmitter and distributor. However, owing to its deficiency as no time-domain in operation (near real-time circulation)\cite{4}, the grid system
shows a poor compatibility with power generation, especially in where renewable energy accounts for a decent portion. Without a supplemental management of electricity, producers and customers along the distribution stream have to consume the electricity immediately once they generate or receive, otherwise the system is under unstable state, which has been widely acknowledged\textsuperscript{[5]}. For this reason, most of the wind/solar power plants only collect electricity during daytime when there is a sufficient demand,\textsuperscript{[6, 7]} Not only has this characteristic wasted a lot of collected energy, but also caused the maintenance of the energy grid system to be quite complicated. Therefore, a variety of ESTs, which nowadays have become necessary participants of the smart grid mode\textsuperscript{[8]}, were enrolled into the energy grid system to control the power input and output.

Methods such as compress air energy storage (CAES) and hydroelectric (owns 99% of the worldwide storage capacity) are chosen to take the responsibilities,\textsuperscript{[9-13]} However, because there exist a lot of construction restrictions of location and space, these physically methods are usually suitable to large-scale capacity demand. Due to their low cost, easy maintenance, and flexibility, battery technologies have the potential to contribute to the electricity system in the following aspects: maintaining reliability and economy of the power system, responding emergency of facilities, and electrifying the individual transportation. Other than the well-known usage in electronics, batteries have been developed for grid storage and transportation industry, respectively.

Batteries for grid storage are normally installed in substations, power plants and civilian facilities. Significant research advancements made on redox flow battery (RFB) (e.g. vanadium redox flow battery) and sodium-ion battery\textsuperscript{[4, 14, 15]}, have led to the success of their product implementation to help utilizing surplus energy. Furthermore, for
renewable energy that is sustainable but intermittent, batteries show a better adaptability than traditional ESTs, especially for those wide-accessible small-scale ones. Considering that natural renewable resource has been recognized as the developing trend of energy grid\cite{16}, battery technologies, will continually be more and more competitive among their competitors in the near future.

Batteries for the electrical-driven transportation (ET) industry (e.g. electrical vehicles (EVs), subways and high-speed rails) have become an enormous market because of its vigorous growth in the past decades. In order to better serve their ET customers, a sequence of optimizations of existing techniques (e.g. lithium ion battery), and more newly designed ones (e.g. recently published work on ultrafast rechargeable aluminum battery) were raised, which are focused on safety, capacity and rapid charge\cite{17, 18}. The launches of Toyota Mirai and Hyundai ix35 FCEV have become a landmark in the history of flow-batteries\cite{19}, because it successfully demonstrates the feasibility of flow batteries in ET market. Compared with fuel cells, RFBs’ shortcomings, such as relatively low energy density (≈ 40 Wh L− 1), low ion concentrations (typically 1–2M), are obstacles to hinder their development.\cite{20} Recently, Professor Chiang and his team at MIT proposed a semi-solid flow cell (SSFC) concept and a rechargeable lithium flow battery system\cite{21-23}, in which “slurry-like” electrodes can store and release energy through ion/electron transfer between solid particles and dilute nano-scale conductors. Since the energy density is proportional to the concentration of the energy components, this kind of flow batteries possess a much higher volumetric capacity (theoretically 5-20 times) than the conventional ones, which are always limited by their active materials’ solubility in solution\cite{21}. After the development of Li-ion system, several chemistries have been studied to apply this
mechanism, such as the Li-polysulfide and the newly published Na-ion systems.\textsuperscript{[24, 25]} And also, its applications on aqueous system have been fundamentally analyzed by Zheng et al.\textsuperscript{[26]} Therefore, this remarkable breakthrough enhances flow batteries’ advantages on existing energy grid market and potentiating their applications in ET industry.

In this paper, the first “fully-flow” Zn/Ni flow battery (ZNFB) using SSFC technique is proposed and studied. Zn/Ni chemistry is appealing for its high cost-efficiency and favorable high energy density.\textsuperscript{[27]} Several research achievements have been published on the single flow Zn/Ni battery, which is designed for energy grid market. Zhang et al. developed a membrane-free single flow Zn/Nickel battery to lower the battery structural cost.\textsuperscript{[28]} Turney et al. fabricated a similar flow-assisted Zn/Ni battery system at a commercialized scale.\textsuperscript{[29]} Because of the liquidity of slurries, Zinc dendrite redistribution issue in Zinc/Nickel battery is suppressed, which increases the cycle life. Meanwhile, several traditional hazardous additives are abandoned, such as Pb and KF.\textsuperscript{[27, 30]} All these beneficial features can be maintained in ZNFB design, and its improved energy density promotes its development on the transportation market. Figure 6a exhibits the prototype of ZNFB. It is comprised of two conductive suspensions stored in tanks. High surface-area meshed current collectors are inserted into channels to accelerate the electron transfer. Rubber pads are chosen to seal the battery, and a stack battery configuration is used. Separators impregnated with electrolyte and the electrolyte content in suspension-electrodes, together, allow ion transport between the electrodes while preventing electronic current from discharging the cell. Manufactured ZnO (anode) slurry (Figure 6b) and Ni(OH)\textsubscript{2} (cathode) slurry (Figure 6c) are also shown here, respectively. The homogeneous mixture integrated the functions of electrolyte, current collector and active materials.
Figure 6 a) ZNFB prototype. b) Manufactured ZnO (anode) slurry sample. c) Manufactured Ni(OH)2 (cathode) slurry sample. d) Flow cell

2.2 Experimental

2.2.1 ZNFB slurry processing

The energy materials were CoOOH - coated Ni(OH)2 powder (Jinshan, particle size 10 µm) as cathode, and ZnO powder (Grillo, particle size 100 nm) as anode, respectively. Nickel powder was mixed into Ni(OH)2 to further improve the electronic conductivity of Ni(OH)2, at the weight ratio of 1:2 (Ni: Ni(OH)2). Ketjenblack ECP600JD from Azko Nobel Polymer Chemicals LLC (Chicago, Illinois, USA) was added to physically support active material (specific surface area = 800-1200 m2 g⁻¹). Sodium dodecyl sulfate (SDS) was added as the dispersion additive of carbon in aqueous electrolyte, which is also necessary for initial mixing. Electrolyte used here was 6M KOH solution. All solid materials for each slurry were weighed and sealed into a 20 ml glass
vial, originally dispersed on roller machine for 1h, and then mixed to suspension with homogenizer by adding electrolyte.

2.2.2 Conductivity measurement

Conductivity measurement of the ZNFB slurry was performed in a lab-manufactured suspension conductivity tester. A cylindrical cavity (the diameter of 0.8 in. and the depth of 0.05 in.) was machined inside a polytetrafluoroethylene cylindrical bar, and two copper sheets were inlayed on the top surface and the bottom surface, separately, to enable current transfer. Same volume of samples was loaded into the tester and electrochemical data were collected with a Biologic potentiostat/galvanostat using EC-Lab at room temperature. An electrochemical impedance spectroscopy (EIS) was conducted with alternating voltage amplitude of 10 mV over a frequency range of 10-5-10^2 Hz after a 10 minutes open circuit voltage (OCV) to determine the total conductivity. Chronoamperometry was used to estimate the ion transference number. In a normalized chronoamperometric curve of tested suspension, current rapidly decreases with time and asymptotically tends to achieve a constant value, which is predominantly ascribed to the ionic diffusion. And according to the transference number and total conductivity, electronic and ionic conductivity were calculated and obtained.

2.2.3 Static test system and flow test system

Swagelok cells were used to demonstrate the static electrochemical performance of Ni(OH)2 and ZnO slurries. 101 copper alloy (anode) and 200 nickel alloy (cathode) from VWR international LLC (Radnor, Pennsylvania) were machined to an appropriate shape as the current collectors. A circular groove (the diameter of 0.28 in. and the depth of 0.05
in.) was machined on the center of each current collector rod’s surface to store the slurries. To investigate and optimize the performance of each sides of ZNFB, slurries of each electrode were tested with corresponding conventional casted electrodes. Membranes were Celgard 3501 Polypropylene membrane (Celgard LLC, Charlotte, North Carolina, USA).

Flow test system is shown in Figure 6d. Current collectors are made of 101 copper alloy (anode) and 200 nickel alloy (cathode). Separators and sealing layers were assembled between the machined copper and Nickel current collectors. Latches were installed for easy assembling. The same kind of membrane layout were used here. Suspensions were pumped to flow through single channel on each side and to react with the opposite side. Electrochemical testing was performed using a Biological potentiostat VMP 3. Intermittent flow experiments were conducted using manually syringes. Continuous flow experiments were conducted with a Masterflex peristaltic pump (Masterflex, Vernon Hills, Illinois, USA).

2.3 Results and discussion

2.3.1 Electrochemical characteristics of ZNFB suspensions

To better know the relationship between carbon loading and conductivity, samples of 24.10 wt% Ni(OH)2 - coated with CoOOH (<5 wt%), 0.50 wt%-4.50 wt% ketjenblack, 3.61 wt% SDS and KOH solution gel matrix were processed, fabricated, tested, calculated and plotted to curves as shown in Figure 7. The ionic conductivity is lowered (from $1.75 \times 10^{-1}$ S cm$^{-1}$ to $1.33 \times 10^{-1}$ S cm$^{-1}$) as adding more carbon particles and the electronic conductivity is improved (from $2.46 \times 10^{-3}$ S cm$^{-1}$ to $3.08 \times 10^{-2}$ S cm$^{-1}$) because of a better physical contact between energy materials and the carbon network. Total
conductivity is lowered (from $1.77 \times 10^{-1}$ S cm$^{-1}$ to $1.64 \times 10^{-1}$ S cm$^{-1}$) because the increase of electronic conductivity is not as quick as the decrease of ionic conductivity. A condensed suspension shows higher electronic conductivity under the static condition, and what’s more important, it has a less volumetric change between charging and discharging, which is very important for maintaining the physical contact between particles inside the suspension, and between the anode and cathode slurry. However, the subsequent high viscosity and deterioration of distribution during suspension manufacturing limit the carbon loading amount. Based on follow-up electrochemical test results, samples at the carbon content around 4.00 wt% (total conductivity is around $1.64 \times 10^{-1}$ S cm$^{-1}$) begin to show a better electrochemical performance (higher charging/discharging efficiency), which is consistent with the increasing trend of electronic conductivity. So electronic conductivity is still recognized as the constraint step comparing to the ionic conductivity, since the latter one is still maintained at a relatively high level in the suspension. The optimization of conductive additives need to be researched and is in progressing.
2.3.2 ZNFB static performance

Our successful demonstration of both electrodes is shown in Figure 8. Here, cathode slurry (Figure 8a) which is 31.25 wt% Ni(OH)2-Ni mixture (10.42 wt% Ni, 20.83 wt% Ni(OH)2) in a 3.82 wt% ketjenblack-KOH solution gel matrix, was tested with a conventional ZnO electrode through a constant current-constant voltage (CC-CV) charge/discharge procedure between 1.00 V and 1.90 V, at the charging/discharging rate of 1C. There is a rest time for 15 minutes between charge and discharge procedures. The CV procedure is applied here in order to reduce the water electrolysis. Aqueous alkaline batteries always suffer the issue as electrolyte consumption, thus the charging procedure changes to maintain the voltage at 1.9 V at the end of charging, which is useful for preventing the battery from drying itself at an excessive potential. The static tests show (rest voltage 1.75 V) a typical Ni(OH)2 slurry charge-discharge efficiency of 75%. Anode slurry (Figure 8b) which is 23.26 wt% ZnO in a 4.55 wt% ketjenblack-KOH solution gel
matrix, was tested with conventional Ni(OH)2 electrode through a single step galvanic static charge/discharge procedure between 1.00 V and 1.90 V, at the charging/discharging rate of C/2. There is a rest time for 15 minutes between charge and discharge procedures as well. It resulted in a cycle charge/discharge efficiency of 85%. State of charge are determined by measuring the columbic efficiency compared with its theoretical setting.

Figure 8 a) Static half-cell performance test of Ni(OH)2 (cathode) slurry. b) Static half-cell performance test of ZnO (anode) slurry

2.3.3 ZNFB half-cell cycling tests

Cycle life tests for ZNFB slurries were also carried on the static tester to investigate their stability during cycles. The first 10 charge/discharge cycles of the ZNFB cathode and anode, were separately presented in Figure 9 (Time-Current, Time-Voltage, Cycle index-
Coulombic Efficiency/Specific Discharge Capacity). The cathode slurry (Ni(OH)2) (Figure 9a) was charged at the rate of 1C through CC/CV procedure to 1.90 V and hold at this voltage for 15 minute, and then discharged at the rate of 1C to its cutoff voltage (1.00 V). A capacity drop of the cathode slurry was observed during cycles, which should be caused by water electrolysis. Figure 9b shows the anode slurry (ZnO), was charged at C/2 through CC/CV procedure to 1.90 V and hold at this voltage for 15 minute, and then discharged at the same rate to its cutoff voltage (1.00 V). Compared with the cathode suspension, anode suspension performs more stable and efficiently. Further test results also proved that the higher efficiency is achievable for Zn/ZnO (anode) slurry, and the possibility of improving the specific capacity from 153 mAh g\(^{-1}\) to 185 mAh g\(^{-1}\) (anode active material). Because the sedimentation of energy materials is more easily to happen in the cathode slurry when testing, we accelerated the cycling procedure of cathode slurry by setting the rate as 1C to enhance its performance during cycling.

Electronic conductivity is a critical factor for the different charge/discharge efficiency of cathode slurry and anode slurry. The Ni(OH)2 power is made of \(\beta\)-phase, which is a semiconductor ceramic. In order to improve the electronic conductivity, Cobalt was coated on the surface of the Ni(OH)2 powder, and it also helps to maintain the powder structure of Ni(OH)2 during cycling. Also, Ni powder are added to improve the electronic conductivity of the base suspension network. But after all, the intrinsic electronic conductivity of Ni(OH)2 powders is not improved, and this feature can only be improved by changing crystal structure of Ni(OH)2 or doping. In the opposite, ZnO reduces to Zn during charging process, and it is unlikely that all the produced Zn powder are oxidized in the discharging procedure, so the remaining Zn powders tremendously improves the
electronic conductivity of the slurry. As shown in Figure 9b, the cumbic efficiency improves from 30% to 80% after the first cycle, which is related to the contribution of newly produced Zn powder. Another possible reason is that the physical parameters’ difference between our raw materials. As mentioned above, the particle size of Ni(OH)2 power (10 µm) is about 10 times of the size of ZnO powder (100nm), so the cathode suspension is easier to separate into layers than the anode one. During cycling procedure, the sedimentation of Ni(OH)2 happens and water-layer forms, which inhibits the ion and electron transfer on reaction surfaces and therefore leads to a worse water electrolysis issue. Thus, when NiOOH is reduced to Ni(OH)2 during the discharging procedure, water is probably not adequate for counter reaction and then cause the capacity fading during cycles. Both ZNFB suspension electrodes have the sedimentation issue, but the problem on the cathode side shows more apparently due to the chemical and physical property difference.
2.3.4 Full flow test performance

Figure 10 presents five typical charge/discharge cycles for a full ZNFB flow test that loads the same slurry as mentioned above, and these results are a successful demonstration of our ZNFB. Cathode and anode slurry were pumped into their respective channels and cycled at a galvanostatic C/5 charge/discharge rate through CC/CV procedure. ZNFB’s capacity was limited here by the cathode because of its lower capacity loading (49% theoretical capacity of anode), and so the anode was incompletely
charged/discharged. The columbic efficiency was around 60-70%, which can provide the theoretical energy density as 128 Wh L$^{-1}$ (75 Wh kg$^{-1}$).

Since half-cell performance in our experiments shows up to 90% charge-discharge efficiency after adjusting raw material composition (ZnO/Zn slurry), higher columbic efficiency under full cell test should also be possible to be achieved by the charging procedure modification (adding a pre-formation step) or optimizing raw material (energy material selection or conductive additive). And as the constraint step of the battery system, the efficiency of cathode slurry determines the room for improvement. When using the same anode slurry as mentioned above, a semi-solid ZNFB with 18.87 – 37.74 wt% active materials loading of cathode slurry would deliver the theoretical energy densities (1.75 V average discharge voltage) from 126 Wh L$^{-1}$ (70 Wh kg$^{-1}$) to 191 Wh L$^{-1}$ (111 Wh kg$^{-1}$), and a higher energy material weight fraction should be possible with more low density but highly effective raw materials. Thus, ZNFB maintains a high standard of electrochemical performance, which is much higher than conventional RFBs and even reaches the same level of some solid-state batteries but contains no flammable contents at a lowered cost.

In the flow test of ZNFB, the capacity drop is not as bad as in static test. Despite side reaction still happens to the ZNFB system, the extra ZNFB suspensions stored in tanks can mitigate the effect of water loss. However, as a long existing issue of most of aqueous batteries, water electrolysis was specifically aggravated in ZNFB because it did not contain any extra electrolyte. Hardly can these characteristics be ameliorated by pre-adding more electrolyte, because more electrolyte also results in a lowered electronic conductivity. This comes from the technical nature of SSFCs that the ionic conductivity and electronic
conductivity are coupled instead of separated when the electrolyte and energy material go into the battery as a whole part. Hence in SSFC, the effectiveness of additives is more essential than component concentration to determine the electrochemical performance.

Once an electrode of our system begins to lose water, a drying process will happen to the whole system until a fully dehydration state of one side and the subsequent failure of battery. However, all other components of the battery are still intact and functional. In this respect, we have preliminary attempted to recover suspension capacity by adding water, and the results shows that these “refurbished” suspension can still maintain basically the same electrochemical properties as newly manufactured ones.

There is still a lot of room to improve our ZNFB from 65% before further modifying additives and electrolyte ingredients, because cycling columbic efficiency of our commercial raw material powder can reach to 85%-90% when manufactured into casted electrodes. Our first stage of research focused on proving a novel aqueous ZNFB based on a market-obtainable raw material, so lab-fabricated Ni(OH)2 components were not chosen at this time. Nevertheless, these details ought to be made efforts in future work because the vicious circle mentioned above will keep happening if cathode suspension cannot reach its best condition at the very beginning of cycling.
Figure 10 Five typical charge/discharge cycles for a full ZNFB flow test

2.4 Conclusion

Faced with the new era of ET and electric driven appliances, the traditional electrical grid system seems not to prepare itself good enough to accommodate the growing demand of power. Better batteries are needed to address the issue. In this research, we have successfully demonstrated a functional ZNFB and its electrochemical properties was determined. Except for the same structural characteristics as the redox flow batteries, ZNFB maintains the advantageous attributes of solid-state rechargeable Ni/Zn batteries on energy density and unit cost. High energy density electrical performance is obtained while saving the weight of conventional grid network in this battery.

2.5 Acknowledgements
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2.6 References


CHAPTER 3. SCALABLE DRY PRINTING MANUFACTURING TO ENABLE LONG LIFE AND HIGH ENERGY LITHIUM-ION BATTERIES

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Slurry casting method dominates the electrode manufacture of lithium-ion batteries. The entire procedure is similar to the newspaper printing that includes pre-mixing of cast materials into solvents homogeneously, and continuously transferring and drying the slurry mixture onto the current collector. As a market approaching US $80 billion by 2024, the optimization of manufacture process is crucial and attractive. However, the organic solvent remains irreplaceable in the wet method for making slurries, even though it is capital-intensive and toxic. Here we demonstrate an advanced powder printing technique that is completely solvent-free and dry. Through removing the solvent and related procedures, this method is anticipated to statistically save 20% of the cost at a remarkably shortened production cycle (from hours to minutes). The dry printed electrodes outperform commercial slurry cast ones in 650 cycles (80% capacity retention in 500 cycles), and thick electrodes are successfully fabricated to increase the energy density. Furthermore, microscopy techniques are utilized to characterize the difference of electrode microstructure between dry and wet methods, and distinguish dry printing’s advantages on controlling the microstructure. In summary, this study proves a practical fabrication method for lithium-ion electrodes with lowered cost and advanced performance, and allows more advanced electrode designs potentially.
Figure 11 This work was selected as the cover picture for the journal of Advanced Materials Technologies
3.1 Introduction

Lithium-ion batteries (LIBs) have established a leading role for powering electronics and the electrification of vehicles in the past decades. In order to meet the requirements of customers, the manufacture of LIBs has been finely optimized to balance cost, performance, and safety.\textsuperscript{[1]} Commercial LIBs electrodes are mainly produced through a slurry casting technique: mixing powder components into a solvent to make a slurry, pasting the slurry mixture on the metal substrate, evaporating and recycling the solvents, and then calendaring the electrode layer after drying (roll-mill pressing) to finalize product parameters. The organic solvent, mostly as the N-Methyl-2-pyrrolidone (NMP), is utilized extensively in preparing electrode slurries, especially for cathode electrodes. The NMP solvent functions as the carrier of the electrode components, and fluidize this mixture of raw materials to enable a fast gluing of electrode material onto the current collector. However, due to the internal weakness of NMP material as high cost and toxicity, the academia has dedicated a lot of work to look for alternative manufacture methods, such as using economical solvents and direct depositing techniques. These findings in the area of manufacturing have brought the sight for cheaper production of lithium-ion batteries, with higher battery capacity and cycle-ability.\textsuperscript{[2,3,4,5]} As a market growing for billions of US dollars every year, any improvements of the manufacturing procedure would have repercussions far beyond the frontiers of the industry of lithium-ion batteries. Industries including electronics, electricity autos and the electricity grids are directly involved into effects as well. A lowered price of energy storage unit will continue to make important contributions to these industries that belong to the supply chain, and result in the new product restitution and promotion.
Meanwhile, the progress achieved in material science requires the renewal of manufacture method as well, while more and more promising material candidates are taken into consideration. Prior to the effects of manufacturing procedure on the product parameters of the battery, the achievable target of performance had been determined by the quality of electrode materials (active materials (AM), conductive additives (CA) and binders).[6,7,8,9] Therefore, new electrode materials are developing towards superior physical and electrochemical properties. Nano-size AM materials were studied for its advantageous properties on high rates and lowered laminate percolation threshold.[10,11] Layered cathode AMs, as Li[Ni$_{1-x}$Co$_x$]O$_2$ (M = Al (NCA) or M = Mn (NCM)), have been identified as practical candidates with high energy density and reliability to meet industry requirements. Considering the inherent chemical instability of NCM and NCA, which represents the ongoing commercialization of cathode materials, compositionally graded cathode structure was successfully combined in forming AM particle aggregates with a favorable configuration.[12,13,14,15] In addition, the microstructure of the electrode composite layer catches more attention than ever. Low-tortuosity materials were studied and applied in batteries for their unique structure with high areal energy density.[16] The appearance of the magnetic field in electrodes helped to create directional tunnel structure, which accesses a quick charge transport and thus a several-fold higher area capacity.[17,18]

Overall, it is thereby critical to find an affordable method to allow these advanced materials to be utilized in batteries.

In this trend, we have previously proposed a method of solvent-free electrode fabrication for lithium ion battery.[19] The dry printed LiCoO$_2$ and NCM cathode electrodes have shown better electrochemical performance than the slurry casting ones, which
demonstrate the feasibility of this technology. Compared with the traditional slurry casting method, this technique was analyzed to save up to a 20% percentage of the investment (16%-22% on labors, 14%-19% of the capital equipment, and 13%-17% of plant area) based on the Argonne battery performance and cost (BatPaC) model. Besides accomplishing the initial ambition on lowering the fabrication cost, the microstructure of electrodes was found to be controllable under this reformative dry printing manufacture method. This surprising phenomenon stimulates the technology of dry printing fabrication to participate in the study of advanced electrode microstructures.

In the study of layer structured AMs, the physical degradation of the AM particle during cycling (micro-cracks happening among primary particles, and electrically isolated grains existing within secondary particles) has been recognized to partly induce the capacity drop of battery.\cite{20,21,22} A fraction of AM grains would gradually lose the contact with the conductive matrix of the electrode, and stop participating the cell reactions.\cite{23,24,25} Therefore, it is an effective strategy to construct a preferable microstructure of electrode that adapts to the inherent deficiencies of AMs, and therefore minimizing their adverse influence on battery capability. Likewise, a good control of electrode morphology would allow electrode morphology properties as a low tortuosity, an appropriate porosity, and a maximum surface uniformity.

Here, a regular dry printed electrode was cycled for 650 cycles in a coin cell with a graphite anode. In addition, thick electrodes with high areal energy density were fabricated to prove the capability of dry printing technology on fabricating sophisticated electrodes. These electrochemical performances are reported here and analyzed with simulation results. Transmission X-ray Microscopy (TXM) and Scanning Electron Microscopy (SEM) were
chosen to examine the components distribution and to reveal the morphology conditions of the dry printed electrodes.

3.2 Experimental

3.2.1 Electrodes Preparation

All the dry printed cathode electrodes were prepared with 90 wt% NCM (Umicore), 5 wt% Super C65 Carbon Black (Timcal), and 5 wt% PVDF (MTI). They were pre-mixed with zirconia beads in a BeadBug Microtube Homogenizer (Benchmark Scientific) for 60 minutes at 2800 RPM. For thin ones, the pre-mixed powders were added to fluidized bed spraying chamber. The fluidized bed chamber was fed into the spraying system with the electrostatic voltage set to 25 kV while the carrier gas inlet pressure was set to 20 psi. Distance from the deposition head to the grounded aluminum current collector was kept constant at 1.5 in. while the coating time was kept constant at 10 seconds. Surface morphology of the deposited material was investigated using a Helios NanoLab DualBeam operating with an emission current of 11 pA and 5 kV accelerating voltage. The details in spraying setup configuration, thickness control and material composition on spraying behaviors can be found in our previous paper.\textsuperscript{[19]} For thick ones, the pre-mixed powders were filled into the molds to load on the substrate manually, which were designed to test the manufacture of the thick electrode with dry printing techniques. The mold diameter was set based on the required sample size. After the hot-rolling procedure, the porosity of all thin dry printed electrodes was maintained at the range from 29\% to 30\%. Similarly, the porosity of all thick dry printed electrodes was maintained at the range from 20\% to 25\%. 
The slurry casting thick electrode was fabricated in the lab with the same material composition. The cathode slurry was stirred manually for approximately 1.5 hours and then cast on aluminum foil (thickness: 20 µm) with the Automatic Thick Film Coater (MSK-AFA-III). The doctor blade height was used to control the thickness. The coated electrodes were dried in the film coaster at 90 °C for 6 hours and in the vacuumed oven at 80 °C for 8 hours. The mass loading of this thick slurry cast cathode electrode was designed as 63 mg cm\(^{-2}\) at the thicknesses of 200 µm (exclusive of current collector foil). The porosity was set as 30% after calendaring.

The reference slurry cast cathode electrodes were manufactured with 84 wt% NCM, 8 wt% Super P Li Carbon Black, and 8 wt% binder (Kureha). The porosity is set as 44% after calendaring. The reference slurry cast anode electrodes were manufactured with 91.8 wt% graphite, 2 wt% C45 Carbon Black, and 6 wt% binder (Kureha). The porosity is set as 38% after calendaring.

3.2.2 Electrochemical Measurements

Dry sprayed electrodes were electrochemically tested against graphite anode (as reference and counter electrode). Molded thick electrodes were tested against Li foil as reference and counter electrode. For coin cells, cathode and anode electrodes were punched into disks of 12 mm diameter and dried at 60 °C under vacuum overnight. All tests are built in 2032-coin cells. Li foils are from MTI and one piece of Celgard 2500 microporous separator was placed between electrodes. The electrolyte is designed for NCM electrode (15.2 wt% LiPF\(_6\), 25.4 wt% ethylene Carbonate, 59.4 wt% ethyl methyl carbonate) from TOMIYAMA. All the cells were tested with an Arbin BT2043 tester. For the rate
performance, cells were charged to 4.3V and discharged to 2.8V at various rates such as
0.05C, 1C, 0.2C, 0.5C, 1C, 2C, and 3C. The same current rates were set for thin sprayed
electrode at charging and discharging. The constant current charging rate is set at C/20 for
thick electrodes, and the current rates at discharging were the same as the sprayed
electrodes. For cycling performance, cells were charged to 4.3V (NCM) and discharged to
2.8V (NCM) at 0.5 C for thin electrodes and 0.2 C for thick electrodes.

3.2.3 Porosity Measurement

Porosity of the sprayed (or cast) electrode was determined by taking into account of the theoretical density of the mix (active material, carbon black, and binder) according to the following equation. Porosity = \[ T - S (\frac{W_1}{D_1} + \frac{W_2}{D_2} + \frac{W_3}{D_3}) \]/T, where T is the thickness of the electrode laminate (without Al foil current collector), S is the weight of the laminate per area, W_1, W_2, and W_3 are the weight percentage of active material, PVDF binder, and C65 within the electrode laminate, while D_1, D_2, and D_3 are the true density for Li[Li_{1/3}Co_{1/3}Mn_{1/3}]O_2, PVDF, and C65, respectively. The theoretical densities for Li[Li_{1/3}Co_{1/3}Mn_{1/3}]O_2 active material, PVDF and C65 are 4.68, 1.78, and 2.25 g cm^{-3}, respectively. All the porosities were calculated by assuming that the weight fractions and density of each material were not changed by the fabrication process.

3.2.4 Morphology characterization

The cross-section and surface morphology were observed by scanning electron microscopy (SEM) (JEOL JSM-7000F electron microscope). EDS mapping was applied. The TXM experiments were performed at 8BM beamline, advanced photon source (APS) through a transition program of National Synchrotron Light Source II (NSLS II). The
nanotomography datasets were collected with 8.336 keV, using 721 projections over an angular range of 180° with a field of view of 40 × 40 μm² (with a 2 k × 2 k CCD (charge-coupled device) camera binning 2 × 2 camera pixels into one output pixel). Each image was collected with 10 s exposure time. Two samples with different thicknesses (50 μm and 100 μm) were used in this work.

3.2.5 Modeling

The galvanostatic discharge simulation employs the standard one-dimensional porous electrode model.[29] The model parameters used in the simulation are listed in Table 2. The Bruggeman relation $\tau = \varepsilon^{-1/2}$, where $\tau$ and $\varepsilon$ are tortuosity and porosity respectively, is used to estimate the effective diffusivity of electrolyte in electrode and separator. The electrode particles are assumed to electronically well wired and so that the electrostatic potential is uniform in solid across the electrode thickness. Solid diffusion in electrode particles is solved using a parabolic approximation.[30] The equilibrium potential of NCM is taken from Reference.[31]

Table 2 List of parameters for galvanostatic discharge simulation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambipolar diffusivity in electrolyte</td>
<td>3.24×10⁻¹⁰ m² s⁻¹</td>
</tr>
<tr>
<td>Li-ion transference number in electrolyte</td>
<td>0.286 [32]</td>
</tr>
<tr>
<td>Ionic conductivity in electrolyte</td>
<td>0.952 S m⁻¹ [32]</td>
</tr>
<tr>
<td>Initial electrolyte concentration</td>
<td>1.2 mol L⁻¹</td>
</tr>
</tbody>
</table>
Kinetic rate constant for electrode surface flux \(3 \times 10^{-11} \text{ mol [m}^2\text{s(mol m}^{-3}\text{)]}^{3.5}\) 

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li diffusivity in NCM</td>
<td>(10^{-14} \text{ m}^2\text{s}^{-1}) [31]</td>
</tr>
<tr>
<td>Electrode porosity</td>
<td>20%</td>
</tr>
<tr>
<td>Separator thickness</td>
<td>25 (\mu\text{m})</td>
</tr>
<tr>
<td>Separator porosity</td>
<td>55%</td>
</tr>
<tr>
<td>NCM particle size</td>
<td>9 (\mu\text{m})</td>
</tr>
<tr>
<td>Initial Li concentration in NCM</td>
<td>10503 \text{ mol m}^{-3})</td>
</tr>
<tr>
<td>Maximum Li concentration in NCM</td>
<td>23339 \text{ mol m}^{-3})</td>
</tr>
</tbody>
</table>

3.3 Results and discussion

3.3.1 Dry-printing electrode fabrication

In Figure 12, here we show the design scheme of our dry-printing electrode fabrication. In this technique (in Figure 12a), a three-dimensional (3D) printing strategy enables us to manufacture the electrodes within two steps: 1) Spraying the material mixture (active material, conductive additive (C65), binder (PVDF)) onto the substrate; 2) Hot-rolling the loaded material to finalize the product bonding, thickness, and porosity through thermally activating the dispersed binder material. An electrostatic spraying system aligned above the substrate is used to deposit the dry electrode mixture onto the current collector. In this deposition method, the electrode mixture particles are fed to the electrostatic spraying head. As the electrode particle flow through the spraying head, they will become charged due to high voltage. The current collector is electrically grounded so that the charged battery electrode mixture will be attracted and subsequently deposit onto the
current collector surface. After the current collector is coated, the deposited electrode mixture needs to be pressed to its final thickness and heated such that the binder is melted. Two hot-rollers are settled in parallel at the necessary gap thickness and heated to the thermal activation temperature at 180 °C (the melting point of PVDF is 177 °C). As shown in Figure 12b, the current collector loaded with the battery electrode mixture is fed between the rollers to be heated and pressed to the final thickness. More details could be found in the experimental section and in our previous paper.\textsuperscript{[19]} Other than avoiding the usage of solvent and corresponding steps, this technology retains most of the original procedures, which potentiate the modification based on the existing equipment. In Figure 12c, here we show the updates of the printing system to print dry thick electrodes continuously. A continuous molding method was selected to replace the spray guns to deposit materials at higher loading rate. Moreover, since dry mixtures would not flow over the substrate bed easily like liquid, the molded texture can leave extra space for powders to spread when the areal loading is improved. With this texture layout, powders would spread and overlap each other during the following hot rolling procedure. For our current study on thick electrodes, Figure 12d details the steps to prepare dry printed samples. Molds were machined with different dimensions to load mixtures at certain thicknesses. The steps (3) and (4) in 11d show the spreading effect schematically, which illustrates our consideration on this phenomenon.
In our previous study, bonding characteristics of printed electrodes are found to be better (75% higher bonding strength) than the ones of slurry cast electrode at the same composition, especially on the bottom layer attaching to the substrate. For dry printed electrodes, the bonding strength mainly comes from the “green body” effect between particles while the roller goes over the electrode layer and keeps lowering the thickness. Under the pressing process, the electrode powder is compressed into a dense component, similar to a “green” body or “green” component in powder metallurgy. Moreover, the functionality of binder material (PVDF) is enhanced to strengthen the electrode matrix and surface in the dry manufacturing. While evenly dispersed inside and on the surface of electrodes, PVDF performs as “nails” to fasten particles inside the electrode matrix after thermally activated. During the hot-rolling procedure, melt PVDF would wet the surface of AM particles at first, and then separate from the shell of them to build a conductive network beside AM materials while cooling down. After this procedure, the top and bottom

Figure 12 Schematic diagram of “solvent-free” dry printing electrode fabrication
planes of electrodes are mostly reinforced where directly contact to hot-rollers. Unless the double-stage pressing (pasting and calendaring) in the conventional fabrication, the electrode forming is synchronously finished through the hot-rolling procedure.

3.3.2 Regular cathode (NCM) electrodes performance

In Figure 13, we show the electrochemical performance of our regular dry-printed cathode (NCM) electrodes in coin cells, and the performance of commercial electrodes, which provides further evidence of the dry manufacturing. The feasibility of dry printing NCM cathode electrodes have been proposed and compared with lab-fabricated slurry cast electrodes at the same design parameters. Here in this report, we selected the shown commercial “conventional NMC electrode” (well-prepared ones from Argonne National Laboratory, which performs the best among all NCM electrodes that we received) to set up a performance target for our dry printed electrodes. This profile helps us to optimize the quality of dry printed electrodes, which is necessary to scale-up the technique from the lab to the industry. The dry printed electrode cycling at 0.5 C (full cell test with a graphite anode electrode) reaches up to 80% of capacity retention after 500 cycles. Compared with the target performance, the dry printed electrode still shows a competitive capability. Rate performance at different Charging/Discharging (C) rates from 0.1 C to 3 C, is also inserted into the figure. Compared with the target performance, dry printed NCM electrodes performs consistently at different rates of testing. Here we chose the most reliable and simple loading recipe (90 wt% AM, 5 wt% C65, 5 wt% PVDF, 29-30% porosity, 55-56 µm as the final thickness).
In addition to saving the cost on recycling solvents, this technique holds another three noticeable advantages: a quick and simple manufacture procedure (Skipping steps for preparing and recycling the solvent), a well-balanced versatility of electrode material selection (Not limited to a single or a few electrode materials), and a good control of product microstructure on a particle scale (Dry depositing step that enables more strategies to modify the electrode morphology). Particularly due to the last one, the designed material distribution could be “in-situ” obtained in the final product when the deposition becomes under-controlled. Under this circumstance, not only the dispersion efficiency of the pre-mixing procedure can be well reserved in product and contribute to the performance, but also more electrode microstructure layout would be introduced into the manufacture of LIB electrodes possibly. In this way, improvements of cutting-edge materials would be possible to reflect on the performance of battery system to the greatest extent.

Figure 13 Electrode cycling performance of the dry printed electrode (80% after 500 cycles) and the commercial slurry cast electrode at the rate of 0.5 C. Cycling performance is tested on full cells built with graphite anode electrodes. Rate
performance is tested on half cells built with lithium foil. Electrodes and cell parts information can be found in the experimental section.

3.3.3 Regular electrodes microstructure

Microstructure conditions, including the homogeneity of material dispersion and imperfection ratio, greatly affects the electrode performance. However, the control of both is limited in the “drying and calendaring” procedures of the slurry casting manufacture. The homogeneity of the slurry can hardly be fully inherited when the electrodes are gradually undergone the drying procedure, even though huge efforts have been devoted to the slurry preparing step.\textsuperscript{[1]} As a mixture of various solid components, these materials would precipitate from the slurry at diverse kinetic behaviors, which may induce subsidence, segregation, and immoderate agglomeration. Firstly, precipitates tend to grow into large aggregates instead of finely dispersed ones, which could be enabled by the long-time drying procedure. Secondly, precipitates of the slurry may move at the solidification interface and thereby locate “randomly” in the final product. As a result, either some isolated AM particles may lose the contact with the conductive network, or CA\textbackslash binder material would grow up to an unnecessary size, which would add dead material volume and weight to the electrodes. In addition, similar to the metal casting, imperfections would happen to the slurry casting electrodes during solidification. The thermal-dynamic conditions of materials on the slurry top surface enormously differ from materials within the slurry, and so does the bottom layer which attached to the metal substrate. In this circumstance, some “pioneer” precipitates on the outer shell of slurry would suffer from overheat and related expansion effects, while the rest of the slurry still lacks heat during the drying process. Because of their diverse physical properties (contraction coefficient,
heat transfer coefficient etc.), the volume change of the different components also varies widely, which leads to the residue stress. Therefore, imperfections become unpredictable and generated accidentally during drying, which would cause the deterioration of batteries in their service life. Moreover, the calendaring processing is utilized to minimize thickness variance and regional concentration difference, while this step would also add more stress to the structure of electrode when deforming the established particle-particle bonds during drying. These deformations put particles into an unbalanced force field, which potentially grow flaws and cracks. Thus, even though the different components in electrodes are visually well-dispersed, it is quite a different case at the particle level. In summary, these adverse microstructure characteristics are not expected, but the traditional manufacture method of electrodes can hardly avoid them with the procedures as drying and calendaring processes.

Here we prepared dry printed thick electrodes to achieve a more precise control of the microstructure, and to discover more electrode design options with the dry printing technology. Electrodes at a various thickness from 100 µm to 200 µm were fabricated through dry printing. In Figures 14a-14d, the surface morphology of the dry printed electrodes at the thickness of 100µm are shown here at different scales of magnification, which are prepared with molding procedure. Figures 14e and 14f show the regular dry printed electrodes through spraying procedure, which has similar surface morphology as molded ones that contain a directional texture after the hot rolling. As recognized in these figures, the surface is much smoother than the regular slurry cast one, and no autogenetic crack or imperfections were found in all dry printed thick electrodes (see more details in Figure 15). Here we provide the surface morphology of commercial slurry casting
electrodes in Figures 14g and 14h as well. These electrodes are designed for advanced electrochemical properties with a high porosity of 44%. In these slurry-cast samples with high porosity, the formation of microstructure imperfections was better observed. Some AM secondary particles are uncovered on the surface rather than embedded into the conductive matrix, which shows a bumpy texture of the electrode. Small cavities, aggregates of carbon and binder, and slight cracks also happen to these samples (more evidence with cross-section view in Figure 16), which is consistent with the discussion above for the conventional fabrication method. Larger magnification views of dry printed electrode are provided in Figures 14c and 14d, and EDS mapping of elements are shown in Figures 14i. AM particles are well covered, and gaps at nanoscale are left on the surface to enable the ion diffusion. These pores are big enough for Li$^+$ ions to transport, but would simultaneously limit the movement of electrode materials at a larger particle size. In the element mapping images, the NCM particles locate evenly in the surface area, and binder/CA materials are shown to be well dispersed and to form a conductive matrix through the 2D level. The element of F represents the distribution of PVDF, and the element of C represents the distribution of CA as C65. These NCM particles are embedded into the conductive network built by binder/CA. This homogeneity would lead to a profitable steady reaction interface along the electrode, which may explain the lowered over-potential we observed in our previous study and may contribute to the improved cycling performance.$^{[19]}$
Figure 14 SEM surface morphology comparison: thick dry printed electrode (at the scale of a) 500, b) 4000, c) 10000, and d) 40000), regular dry printed electrode (at the scale of e) 500 and f) 4000) and slurry cast electrode after calendaring (at the scale of g) 500 and h) 4000). i) SEM-EDS mapping of printed electrode at the thickness of 100 µm (shows elements of F, C, Mn, Co, Ni, O)
Figure 15 SEM surface morphology of dry printed thin electrode: a) at the scale of 500 magnification; b) at the scale of 4000 magnification; c) at the scale of 40000 magnification;
Figure 16 SEM surface morphology of slurry cast thin commercial electrodes: a) surface view at the scale of 200 magnification; b) surface view at the scale of 500 magnification; c) cross-section view at the scale of 950 magnification; d) cross-section view at the scale of 2000 magnification;

TXM is a full-field non-destructive in situ 3D X-ray nanotomography method that provides unique information that is difficult/impossible to be obtained by other methods.\cite{26} In the study of battery materials, it can be applied to in-situ monitor and quantitatively analyze the 3D microstructural changes of the electrode during cycling, including chemical states and the phase transformations. It successfully correlates the morphological changes with the electrochemical reactions, and has intuitively presented the reaction process of the lithiation-delithiation and sodiation-desodiation at high-quality.\cite{27,28} TXM technology was also utilized in our research to examine the structural layout of AM particles in 3D. Under
the hard X-Ray, only the elements of Co, Mn, and Ni could be obviously observed, which may provide a great opportunity to concentrate on recognizing the distribution of NCM particles. Therefore, all clear-visible particles are the NCM ones, and the vacant room around them includes the rest as the binder, the CA and the pore space. As shown in Figure 17a, there are their views of a 3D model of our dry printed electrode at the thickness of 50 µm, which was collected and built by the TXM technique (See supporting information for this 3D model in the video version). More TXM information of electrodes is provided in Figure 18 of the supporting information. In Figure 17b, a thick electrode sample at the thickness of 100 µm in 2D is present as a mosaic picture through combining a sequence of single images (at the monitor window of 50 µm × 50 µm). Figure 17c shows 8 enlarged views of the cubic room, which were taken while rotating every 45 degrees of the sample. By collecting pictures of the cubic room at continuous rotation angles, a 3D model can be built in this way. In these pictures, spherical secondary NCM particles at the diameter of around 10 µm are evenly dispersed in the space, and some primary NCM particles at the nanoscale are finely stuffed and enveloped in the PVDF-Carbon conductive matrix.
Figure 17 TXM morphology. a) A 3D model of thin dry printed electrode. b) TXM surface morphology of a thick dry printed electrode. c) Views at different angles of the cubic detected room of sample.
Figure 18 TXM of dry printed electrode: a) and b) samples of electrodes. Limited to our preliminary study on TXM, Focused Ion Beam (FIB) technique was not selected to prepare samples, which cause sample particles to peel off the substrate during cutting. c) selected from the square area of sample b, we took 720 pictures of the cubic room while rotating the sample at a constant speed and built a 3D model based on them. The model in video format is attached in the supplemental information file as well. More in-situ monitoring of the reaction of electrodes is accessible for TXM, and is interested to us for later study, which could include chemistry analysis in motion and un-destructive probing of the sample during cycling. More 3D models were built by the TXM in our study, but were not clearly enough to present here due to the thickness of our sample at 100 um, which would have an overlapping pattern of NMC particles in certain directions of view while X-ray detects the sample in the rotation. (Detection window is set as a cubic at the dimensions of 50um x 50 um x 50 um)

3.3.4 Thick electrodes microstructure
An improved areal capacity of electrodes always means a higher percentage of AM using in battery devices, which would result in a decreased manufacture cost with fewer procedures but an outstanding energy storage capability. In the conventional fabrication, a thick electrode design takes more treatments than usual and has a higher possibility of forming internal defects and imperfections. In this case, a fraction of AM may not be accessible for Li$^+$ ion, and a part of CA and binder would not work as they should, which both counteract the benefits from high areal loading. In addition, high tortuosity and large impedance limit the thickness of the conventional electrode to be as low as 100 µm. To overcome these constraints on charge transport, obtaining a low-tortuosity microstructure with proper electron transport pathways would require either a specific selection of materials (AMs and CAs) or a concise morphology modification, which is barely accessible for the traditional fabrication method. However, thick electrodes are feasible with our dry printing technique. Figure 19a-19c show the cross-section images of the three electrodes, which are at the thickness of 200 µm, 150 µm, and 100 µm. The thickness is consistent through the electrode layer at all locations in the sample of 200 µm as shown in Figure 19d. Figure 19e shows an enlarged area of Figure 19d, and there are no obvious cracks as well. In comparison, the thick electrodes (around 200 µm) were slurry cast in our lab, and shrinkage cracks are detected as shown in Figure 20. Corresponding SEM-EDS mapping data reveals a clear view of all components dispersed in the area. More EDS data are available for the material in two white square area in Figure 19e, which locates at the surface and bottom of the thick electrodes (see details in the Figure 21). The boundary between substrate and electrode material layer is clear, and the bonding is strong without separation, which corresponds to the analysis in our previous study. Additional
morphology and detailed EDS mapping data are available in Figure 22- 24 to show the electrode morphology at different thickness, including the SEM morphology and elements mapping. The high flatness of the electrodes surface would provide a well-defined contact area throughout the reaction layer, which would lower the possibility of dendrite formation. In this way, diffusion distance is consistent at the entire reaction interface basically, and similar reaction route is obtained to prevent the problems of material diffusion and contamination.

Figure 19 SEM cross-section morphology showing the precision on controlling the thickness and components homogeneity: at the thickness of a) 200 µm, b) 150 µm, and c) 100 µm, d) molded electrode thickness consistency (the thickness of sample is 200 µm), e) SEM-EDS mapping of the cross-section of the same 200 µm sample. The elements of F, C, O, Co, Ni, Mn are included.
Figure 20 Slurry cast thick electrode at the thickness of 200 um: a) overview of the product; b) enlarged view

Figure 21 Cross-section areas of the thick dry printed electrode at the thickness of 200 um: a) bottom area EDS mapping; b) surface area EDS mapping
Figure 22 SEM morphology and EDS mapping of dry printed thick electrode at the thickness of 100 um: a) Surface EDS mapping; b) cross-section view at the scale of 50, 400, 750 magnification, respectively; c) surface view at the scale of 500, 4000, 40000 magnification, respectively;
Figure 23 SEM morphology and EDS mapping of dry printed thick electrode at the thickness of 150 \( \mu \text{m} \): a) cross-section view at the scale of 50, 400, 750 magnification, and surface view at the scale of 500, 2000, 10000 magnification, respectively; b) EDS mapping of the surface; c) EDS mapping of the cross-section
Figure 24 SEM morphology and EDS mapping of dry printed thick electrode at the thickness of 200 um: a) cross-section view at the scale of 50, 400, 750 magnification, and surface view at the scale of 500, 2000, 10000 magnification, respectively; b) EDS mapping of the surface;

3.3.5 Thick electrodes performance

In Figure 25, we present the electrochemical properties of thick electrodes fabricated by the dry printing method, and thin dry electrodes are added as a reference profile. Porosity is controlled at 20-25%, which is designed and confirmed with the porosity test. Here we show the rate performance for different thickness in Figure 25a. Compared dry printed electrode at the regular thickness, these thick electrodes start to drop
a lot on a higher rate of testing. While the thickness is increased, the performance at a high rate is lowered, which is due to the longer diffusion distance. All the samples match this trend, including the thin dry printed electrodes as a reference. While the sample is thicker, the performance on a high rate drops more. However, at the rate of 0.1 C, the sample of 200 μm (144 mAh g⁻¹) shows a higher specific capacity than the sample of 150 μm (130 mAh g⁻¹). We believe that this may come from the variance of porosities during fabrication. For a thicker electrode with higher porosity, it is possible to perform better at a low rate than a thinner electrode with a lower porosity. For the rest thick electrodes that we tested, this phenomenon was not repeated. The areal capacity comparison between the thin dry printed electrode and thick dry printed electrodes at 0.1 C are also provided in Figure 25b. When the thickness of electrodes is increased, the areal capacity loading is improved from 2.45 mAh cm⁻² to 9.11 mAh cm⁻². This improvement would be beneficial for using lithium-ion batteries at a larger scale of energy storage, such as emergency back-up stations and transformer substations. Cycling performance for thick electrodes is provided in Figure 25c as well. Limited by obtaining a counter graphite electrode with high areal capacity, these cycling performance tests were also based on lithium foil at half-cell configuration. The cycling performance drops quickly compared with regular thin electrodes. In addition, the thicker the electrodes, the faster they decay. Higher porosity and lower tortuosity should benefit the performance on both rate and cycling, because extra diffusion and transfer room would enable a better reaction atmosphere. In this way, we prove the control of electrode product morphology with the dry printing technique and fabricate advanced designs of thick electrodes in this fast and economic dry printing technology of electrodes.
Figure 25 Electrochemical performance of dry-molded thick electrodes with the reference of thin “regular” dry printed electrodes (56 µm thickness): a) rate performance (half-cell built with lithium foil for all the thickness of electrodes), b) areal capacity at the rate of 0.1 C, c) cycling performance at the rate of 0.2 C (half-cell built with lithium foil for all the thick electrodes, and full cell built with graphite anode electrode for the regular thickness electrode).

3.3.6 Modeling

To better understand the rate performance of the fabricated thick electrodes, the galvanostatic discharge process was modeled by the porous electrode theory.[29] Figure
Figure 26a shows the simulated discharge capacity at various Charging/Discharging rates for three thickness values (100 µm, 150 µm, and 200 µm). While the simulation predicts good capacity up to 3 C for electrodes at the thickness of 100 µm and 150 µm, the rate capability of the electrode at the thickness of 200 µm is significantly inferior. To shed light on the rate-limiting steps in the discharge process, Li concentration distributions in the electrolyte and solid particles along the electrode thickness direction were plotted in Figure 26b and 15c, respectively, for the electrode that is at the thickness of 200 µm and discharged at 3C. They show that ion transport in both electrolyte and solid particle limits the high rate capacity, while the former has a more significant effect. On the electrode level, electrolyte depletion near the current collector occurs shortly after discharge starts. Due to the increased electrode thickness, Li ions cannot be transported efficiently from Li anode to the current collector side of the cathode, where the Li concentration in liquid remains close to zero during discharge. As a result, electrode particles in this region are hardly lithiated until the end of discharge (t = 613 s), Figure 26b. Reducing the tortuosity of the thick electrode, e.g. through the creation of low-tortuosity channels in the electrode,[17] is necessary for alleviating this issue. Appreciable polarization is also seen in solid particles starting at the early stage of discharge, which is illustrated by the difference between the average and surface Li concentrations in the NCM particles as shown in Figure 26b. This should be mainly attributed to the large size (~9 µm) of NCM secondary particles, which are assumed to have no internal porosity. Creating interconnected micro-porous channels inside the secondary particles may thus be an effective approach to improve the rate performance.
Figure 26  a) Rate performance of thick electrodes from the porous electrode simulation. b) Simulated Li concentration profiles in electrolyte at the beginning of discharge (time = 120s) and the end of discharge (time = 613s) in an electrode discharged at 3C at the thickness of 200 µm, and Li-ion concentration in electrolyte along the thickness direction. c) Average (cs) and surface (csf) Li concentration in secondary particles along the thickness direction, normalized to maximum Li concentration in NCM.

Compared with the simulation, the electrodes experimentally display more rapid capacity decay with increasing rate for all three-electrode thickness (Figure 25a). Possible reasons for the discrepancy include: the electrode tortuosity is significantly larger than the value estimated in the model based on the Bruggeman relation; Li diffusion in solid is impeded by undetected defects (e.g. cracks) in the dry printed electrodes; there exist other rate-limiting steps in the discharge process than considered in the model, (e.g. electronic conduction in the solid). In addition, the preliminary low-porosity setting of dry printed thick electrode should be taken into consideration as well. The lowered porosity would contribute to a smaller specific surface area and thereby fewer reaction interface than improved porosity. These physical conditions of electrodes may limit the reaction happening in deeper sites along the thickness direction. NCM particles that locate close to the electrode surface may react at a higher rate and form a layer of the reaction product, which would impede the reaction of materials that locates further from the surface. Moreover, the usage of lithium foil may also be a factor. Due to the higher areal capacity
design of dry printed thick electrodes (4 times more than thin electrode), the degradation of lithium foil during testing should also be even worse. While consuming more lithium metal than regular thin electrodes during testing, the formation of lithium dendrite should be more likely to happen to the thick electrodes than regular electrodes during lithium plating procedure. In order to allow enough diffusion time, all cells that tested rate performance of thick electrodes were charged at C/20 consistently. Therefore, due to the rate testing sequence from a low rate to a high rate, performance at a higher rate was tested after the lithium foil suffered longer reaction time, and this setting routine may contribute a little to the larger difference in high rate between the modeling and the experimental data as well. Clarification of these possible causes will provide further insights on the optimization of the dry-printing manufacturing technology. For further optimization of thick electrodes, the porosity, the tortuosity, and the binder/CA agents should be modified, which could be studied later.

3.4 Conclusion

With the dry printing technique, we successfully fabricated long cycle life (>650 cycles) electrodes at a regular thickness (56 µm), and demonstrated high-energy thick electrodes (up to 200 µm). The quick and simplified procedure helps to maintain the initial loading structure and the material dispersion during pre-mixing, which enable the possibility to control the morphology of product electrodes starting by the mixing step. The demonstration of thick electrode brings the sight of microstructure control in a practicable way. The dry printing technology is possible to allow more potential electrode designs, which cannot be achieved by the slurry casting technique.
3.5 Acknowledgements

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3.6 References


CHAPTER 4. UNDERSTANDING INTERFACIAL-ENERGY-DRIVEN DRY POWDER MIXING FOR SOLVENT-FREE ADDITIVE MANUFACTURING OF LI-ION BATTERY ELECTRODES

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Lithium-ion battery electrodes are manufactured using a new additive manufacturing process based on dry powders. By using dry powder-based processing, the
solvent and its associated drying processes in conventional battery process can be removed, allowing for large-scale Li-ion battery production to be more economically viable in markets such as automotive energy storage systems. Uniform mixing distribution of the additive materials throughout the active material is the driving factor for manufacturing dry powder-based Li-ion batteries. Therefore, this article focuses on developing a physical model based on interfacial energies to understand the mixing characteristics of the dry mixed particulate materials. The mixing studies show that functional electrodes can be manufactured using dry processing with binder and conductive additive materials as low as 1 wt% due to the uniformly distributed particles. Electrochemical performance of the dry manufactured electrodes with reduced conductive and binder additive is promising as the cells retained 77% capacity after 100 cycles. While not representative of the best possible electrochemical performance of Li-ion batteries, the achieved electrochemical performance of the reduced conductive and binder additive electrodes with LiCoO$_2$ as the active material confirms the well distributed nature of the additive particles throughout the electrode matrix.

4.1 Introduction

Li-ion batteries are critical in enabling proliferation of electric vehicles and various portable electronics in the near future. While common in portable devices, the use of Li-ion batteries in larger platforms such as electric vehicles has not been as practical due to manufacturing and material costs.$^{[1]}$ Li-ion batteries are made of four basic components: two electrodes (anode and cathode), separator, and electrolyte. Commercial Li-ion electrodes are manufactured by coating a metallic substrate (current collector) with a slurry. An electrode slurry is made of active material particles, conductive particle additives
(CPA), binder particle additives (BPA), and a solvent. Slurry preparation is an essential part of the manufacturing process as it directly influences the morphology of the electrodes, and subsequently, the battery performance.\textsuperscript{[2,3]} The preparation of the slurry is strongly dependent on the mixing conditions. Previous mixing studies can include as many as four mixing steps and can take up to 48 h to complete.\textsuperscript{[4]} The slurry mixing process can also change due to the type of solvent used in the slurry. Slurry types are typically classified into two types: aqueous based and organic solvent based.\textsuperscript{[4-8]}

N-Methyl-2-pyrrolidone (NMP) is the most commonly used organic solvent and is mixed with polyvinylidene fluoride (PVDF) to create a homogenous binder suspension while CPA, typically carbon black, are added to the slurry to improve electrical conductivity. Care must be taken when using NMP as it is flammable and toxic, necessitating the use of recovery systems to reduce the environmental hazards.\textsuperscript{[7-11]} The use of water as the solvent can eliminate these disadvantages with the advantage of being less expensive than organic solvents.\textsuperscript{[6,11]} Carboxymethyl cellulose is used in place of PVDF when an aqueous system is incorporated and also represents a less expensive option as opposed to PVDF.\textsuperscript{[5, 7, 10, 12]} However, aqueous-based slurries require additional care due to strong hydrogen bonding causing the particles to agglomerate.\textsuperscript{[11]} High surface tension of the slurry can also cause issues with the wettability of the slurry on to the current collector, but this can be counteracted by adding a cosolvent to reduce the surface tension.\textsuperscript{[11]} High surface tension of aqueous slurries can also lead to electrode cracking problems upon drying.\textsuperscript{[13, 14]}

Electrodes made by either type of slurries must eventually be dry and porous to enable electrolyte uptake. Aqueous-based slurries are more stringent on the removal of
moisture, as compared to organic solvent-based slurries, where the water amount must be below 10–20 ppm.\textsuperscript{[15]} This restriction on moisture content caused the industry to prioritize organic solvent-based slurries. In both slurry types, a high temperature oven is needed to dry out the electrodes, further increasing manufacturing costs due to the time and energy needed to fully dry. Drying time can take up to 24 h with the temperature ranging from 80–120 °C depending on the slurry type.\textsuperscript{[16, 17]} Higher solids loading can be a way of reducing drying time, but this can lead to difficulties in coating the current collector due to higher viscosities.\textsuperscript{[8]}

Eliminating the solvent completely represents an ideal scenario as doing so would remove any recovery equipment and remove the high energy drying process. Previous studies using pulsed laser and sputtering deposition have shown that dry particle deposition can produce working batteries. However, they are not suitable for commercial applications due to prolonged manufacturing time.\textsuperscript{[19-23]} Our previous work has shown that dry electrodes manufactured using a new dry electrostatic spraying technique (Figure 27) is a promising new manufacturing method.\textsuperscript{[24]}
Figure 27 Additive manufacturing system for electrodes created by dry powder process.
From a manufacturing standpoint, our solvent-free dry spray manufacturing process represents a promising alternative for reducing the costs of Li-ion battery production by \( \approx 15\% \). Here, the effect of particle interfacial energy on the morphology of electrodes fabricated with the new additive manufacturing process for lithium ion battery electrodes is presented. The use of dry powders in this new method makes the electrode morphology dependent on mixing uniformity. The main objective of this article is to understand the dry mixing characteristics of the battery materials. An interfacial energy-based model was used to reveal submicrometer level mixing is possible even with minimum amount of BPA and CPA. To this conclusion, it is shown that BPA and CPA are well dispersed throughout the active material which allows for a reduction in BPA and CPA to 1 wt% while maintaining mechanical and electrochemical performance comparable to slurry casted electrodes. The mechanical strength of the fabricated cathodes with reduced BPA material displayed higher strength (93.8 kPa) than slurry-cast cathodes (83.4 kPa) while also delivering strong electrochemical performance. For this interfacial-driven-mixing study, LiCoO\(_2\) (LCO) was used as the active material due to its well-known electrochemical properties. For the dry printed electrodes at lowered concentrations of additive components, the electrochemical results show good rate performance from 134 mAh g\(^{-1}\) with a current rate of 0.1 C (98.1% of the theoretical capacity) to 75 mAh g\(^{-1}\) with a current rate of 3 C (54.7% of the theoretical capacity), and a well-reserved capacity retention during cycling (77% after 100 cycles).

4.2 Experimental

4.2.1 Additive Manufacturing Process
Figure 27 shows an electrostatic spraying system to deposit completely dry electrode particles to the current collector. It consisted of a powder mixing and feeding unit and an electrostatic spraying gun. A spraying gun was used to charge the fluidized dry particles which were then drawn to the ground current collector and deposited. A hot roller was used in place of the traditional slot die or doctor blade to control thickness and porosity by pressing the deposited electrode powders. Thermal activation was also achieved during the hot rolling step.

4.2.2 Electrochemical Measurements

Dry cathode materials, LCO (MTI), Super C65 carbon black (Timcal), and PVDF (MTI), were mixed with zirconia beads in a BeadBug Microtube Homogenizer (Benchmark Scientific) at 2800 RPM. For heated LCO the powder was washed with acetone, ethanol, and isopropyl alcohol. The washed LCO powder was then rinsed with water and heated to 500 °C for 1 h. Surface treatment of C65 as specified by Park et al. was completed by immersing the C65 powder in a 0.1 N NaOH solution and then rinsing with deionized water and dried. Surface morphology of the mixed powders were investigated using a Hitachi S-4700 field-emission scanning electron microscope operating with an emission current of 10 µA and 10 kV accelerating voltage.

4.2.3 Mechanical Bonding Measurements

Mechanical bonding tests were performed on hot rolled samples to quantify the binder performance. A hot roller was used for thermal activation of the binder, and to increase the density of the deposited electrode powders. The top and bottom rollers were to 180 °C. A Mark-10 Series 4 force gauge was paired with a Mark-10 ES10 manual hand
wheel test stand. To perform the test, the electrode sample was mounted onto the test stand base with the center of the coated region directly below the force gauge. A 0.5 in. diameter flat head (Mark-10) with double sided tape (7 mm by 12 mm) attached to the flat bottom surface was connected to the force gauge to obtain a flat pressing surface. The force gauge was lowered until the taped surface touched the sample and then further compressed to 50 N. After compression, the force gauge was decompressed at a rate of 1 rotation over 20 s until the tape attached to the flat head was brought into tension and decoupled from the coated area. The maximum tensile force was recorded and converted to the maximum strength by incorporating the known contact area of the tape.

4.2.4 Surface Energies Measurement

The sessile drop technique was used as the characterization method for surface energy. An OCA15EC/B Contact Angle Measuring Device by DataPhysics was used to capture the contact angles and subsequently calculate polar, dispersive, and total surface energies of the battery electrode materials. The sessile drop technique is typically performed on a flat bulk solid material; therefore, packing each electrode powder as densely as possible is required. This will allow the densely packed particles to be analyzed as a single solid material. If the powders are not packed well the probing liquid will readily soak through the pores between the particles. LCO, PVDF, and Super C65 carbon black (C65) were the three materials tested and each required their own set of packing requirements. LCO was characterized with an LCO sputtering target from Kurt J. Lesker Company due to the difficulty of pressing the LCO powder to the porosity needed to obtain closed pores. The target provides a highly pure (99.7%) and dense material to perform the surface energy characterization. In the cases for PVDF and C65 powders, samples needed
to be laboratory made by compressing the powders into dense green bodies. This method was proven to be successful in a previous study for measuring sessile drop contact angles on powders.\textsuperscript{[37]} The green components were fabricated by loading the powders into a pressing die and compressed with a pressure of 263 MPa. A Carver Bench Top Press was used for the pressing process. PVDF samples were successfully made with this procedure while graphite (MTI) needed to be used in place of C65 for the surface energy calculations of carbon.

4.2.5 Electrochemical Measurements

Dry sprayed electrodes were electrochemically tested against graphite anode for cycling test and against Li foil for rate performance test (as reference and counter electrode). For coin cells, cathode and anode electrodes were punched into disks of 12 mm diameter and dried at 60 °C under vacuum overnight before assembling. All electrodes were built in 2032-coin cells and were tested with an Arbin BT2043 tester. Li foils were from MTI and two pieces of Celgard 2500 microporous separator were placed between electrodes. The electrolyte was at the composition of 15.2 wt% LiPF6, 25.4 wt% ethylene carbonate, and 59.4 wt% ethyl methyl carbonate (from TOMIYAMA). For rate performance, cells were charged to 4.2 V and discharged to 2.5 V at various rates such as 0.05, 0.1, 0.2, 0.5, 1, 2, and 3 C. For cycling performance, cells were charged to 4.2 V and discharged to 2.5 V at 0.5 C. Constant current charging and discharging were used for all tests.

4.3 Results and discussion

4.3.1 Mechanical Bonding Measurements
As-received LCO and PVDF were mixed together as the active and binder materials at 99 and 1 wt%, respectively, to observe the mixing behavior of the binder throughout the active material. Uniform BPA distribution is needed for ensuring strong mechanical properties, thus limiting binder particle agglomeration is essential when attempting to more efficiently use the binder content in the cathode mixture. A scanning electron microscope (SEM) image (Figure 28a) shows PVDF particles decorating the surface of LCO with minimal occurrences of PVDF binder agglomerates. The same powder was deposited onto an aluminum current collector and heated to 250 °C to observe the melting behavior of PVDF on LCO. It is essential for PVDF to wet the surface of LCO upon melting to increase the viability of producing cathodes without the assistance of a solvent to coat the active materials with liquefied binder as is the case with conventional slurry-cast processing. An SEM image (Figure 28b) shows PVDF wetted the surface of LCO upon melting, showing that PVDF and LCO are compatible materials. Super C65 carbon (C65) was added to LCO and PVDF at 98 wt% LCO, 1 wt% PVDF, and 1 wt% C65 to observe the change in morphology after C65 is added. Exposed PVDF in the presence of C65 along with C65 chains is needed for enhancing mechanical strength through melted PVDF contact points and enhancing cathode conductivity through connected C65. Evidence of both can be seen in Figure 28c which leads to the next step of thermally activating the PVDF to observe binder contacts points.
Figure 28 a) PVDF assembly on LCO surface. b) Melted PVDF wetting the surface of LCO. c) PVDF and C65 distributed amongst each other after mixing with LCO. d) Melted PVDF creating contacts between LCO surfaces with C65 assembled on the PVDF surface. (Scale bars in (a)–(d) represent 500 nm.) e) Mechanical pull-off test results.

A current collector was coated by dry spraying the cathode powder and then hot rolled. Bonding tests were performed on the thermally activated LCO/PVDF samples with low strength being observed (5.82 kPa). Previous results indicate a hot rolling and pressing step is needed to thermally activate the binder and compact the cathode powder into a high strength layer.[24] An SEM image (Figure 28d) was taken after the cathode underwent hot rolling and shows exposed PVDF melted and created contact points between LCO particles, evidence of exposed C65 were also present. Bonding tests were performed on the cathode samples to quantify the mechanical strength and compare with previous studies. Previously, the mechanical strength of cathodes manufactured using dry spray technique (148.8 kPa) with 5 wt% PVDF and 5 wt% C65 were shown to eclipse the mechanical strength of slurry-cast cathodes (84.3 kPa) with similar composition.[24] Cathodes fabricated with 1 wt% PVDF and 1 wt% C65 display mechanical strength of 93.8 kPa. While the dry sprayed 1 wt% additive cathodes show a noticeable decrease in mechanical strength when compared to dry sprayed 5 wt% additive cathodes, it is important to note that it displays higher strength than cathodes manufactured with the conventional slurry-casting method (Figure 28e).

4.3.2 Surface Energy Measurements

Surface energy measurements using the sessile drop technique were performed on the three materials to better understand the interfacial interactions causing the binder and
conductive particle distribution. A dense LCO sputtering target (Kurt J. Lesker Company) was used for LCO characterization to eliminate the possibility of deposited droplets soaking through the powder material. Three probing liquids were used for characterizing LCO, which include diiodomethane, dimethyl sulfoxide (DMSO), and thiodiglycol (TDG). Table 3 shows the polar and dispersive surface energy components for all probing fluids used for surface energy characterization. The results show that the droplets form contact angles of 44.6° for diiodomethane (Figure 29a), 62.0° for DMSO (Figure 29b), and 74.8° for TDG (Figure 29c). Each of the contact angles was entered into the software to determine the polar, dispersive, and total surface energy components for LCO. The Owens, Wendt, Rabel, and Kaelble (OWRK) method for calculating surface free energy was used for characterization. Surface energy due to polar interactions was 1.35 mN m\(^{-1}\) while the surface energy due to dispersive interactions was 37.0 mN m\(^{-1}\). The low polar component was unexpected considering previous surface energy results for lithium based active material show significantly larger polar energy. Low polar energy can readily be observed by the contact angle measurements as TDG and DMSO have similar dispersive energy (34.7–39.2 mN m\(^{-1}\)) but differing polar energies (8.68 mN m\(^{-1}\) for DMSO, and 14.8 mN m\(^{-1}\) for TDG). Since the dispersive energy is similar for the two liquids any change in contact angle should be related to the changing polar components. TDG with the higher polar component displayed the larger contact angle.
Figure 29 LCO Surface Energy Characterization. Droplets formed by (a) diiodomethane, (b) DMSO, and (c) TDG on LCO to determine the contact angles needed for surface energy characterization for LCO. d) Surface energy plot for each of the probing liquids using the WORK method to estimate the surface free energy components of LCO.

Table 3 Surface tension properties of probing liquids used in contact angle measurements

<table>
<thead>
<tr>
<th>Liquid</th>
<th>$\sigma_1$ [mN m$^{-1}$]</th>
<th>$\sigma^P$ [mN m$^{-1}$]</th>
<th>$\sigma^P$ [mN m$^{-1}$]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thiodiglycol</td>
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<td>39.2</td>
<td>14.8</td>
<td>25</td>
</tr>
<tr>
<td>Dimethyl sulfoxide</td>
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<td>34.86</td>
<td>8.68</td>
<td>26</td>
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<tr>
<td>Liquid</td>
<td>$\sigma_l$ [mN m$^{-1}$]</td>
<td>$\sigma_l^D$ [mN m$^{-1}$]</td>
<td>$\sigma_l^P$ [mN m$^{-1}$]</td>
<td>Reference</td>
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<td>----------------</td>
<td>--------------------------</td>
<td>----------------------------</td>
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<td>-----------</td>
</tr>
<tr>
<td>Diiodomethane</td>
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<td>50.8</td>
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<td>27</td>
</tr>
<tr>
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<td>28</td>
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<td>Formamide</td>
<td>58.2</td>
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<td>28</td>
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<tr>
<td>Water</td>
<td>72.8</td>
<td>21.8</td>
<td>51</td>
<td>27</td>
</tr>
</tbody>
</table>

The low surface energy of LCO, particularly the polar component, is expected to be due to the moisture and carbon contents on the LCO surface. This phenomenon was studied by Kim et al. where it was found that moisture and carbon content accumulate on the surface when exposed to air. In their study, washing and annealing the LCO surface was found to decrease the surface contents. Therefore, the LCO target was heated to 500 °C to create an annealed LCO surface for further surface energy measurements. The same probing liquids were tested with TDG and DMSO droplets completely wetting the surface while the diiodomethane measured 33.1° (Figure 30a). Since diiodomethane exhibits zero polar component, it was possible to calculate the dispersive surface energy component of the annealed LCO by using the Young (Equation 1) and Owens and Wendt (Equation 2) equations for surface energy.\[30, 31\]
where $\sigma_{sl}$, $\sigma_s$, $\sigma_l$, and $\theta$ represent the solid–liquid interfacial energy, solid surface energy, liquid surface energy, and contact angle, respectively. D and P are used to denote the use of dispersive and polar surface energy components. Annealed LCO dispersive energy was calculated as 42.5 mN m$^{-1}$ using this approach.

To estimate polar component of LCO, water was used as a probing liquid due to its large polar component of surface energy (50.8 mN m$^{-1}$) and contact angle measurement found the droplets completely wetting the annealed LCO surface (Figure 30b). By comparison, a water droplet contact angle of $70.7^\circ$ was observed on as-received LCO (Figure 30). It is possible to estimate the minimum polar surface energy component by using the known water surface energy, solid dispersive surface energy, and using a value of $0^\circ$ as the contact angle in Equations 1 and 2. It is found that for water to completely wet
LCO, the polar surface energy of LCO would at least need to be 35.0 mN m$^{-1}$ using Equation 3

$$\sigma_p = \frac{\sqrt{\sigma_d \sigma_p - \sigma_1^2}}{\sigma_1}$$  \hspace{1cm} (3)

A PVDF measurement surface was made in the laboratory by pressing as-received PVDF powder into a 12.5 mm diameter disc-shaped green body. Three fluids were used to characterize the PVDF: ethylene glycol (EG), formamide, and TDG. The EG droplet formed a contact angle of 57.12$^\circ$ (Figure 31a) while formamide and TDG droplets formed contact angles of 64.40$^\circ$ (Figure 31b) and 59.97$^\circ$ (Figure 31c), respectively. Like LCO, the contact angles for each of the probing liquids were entered into the surface energy software and the polar, dispersive, and total surface energy components for PVDF were calculated. The OWRK method was used for the calculation and returned a polar surface energy component of 6.18 mN m$^{-1}$ and dispersive surface energy component of 24.33 mN m$^{-1}$. Previous results for PVDF surface energy show similar component surface energies; therefore, the obtained surface energy components were used for future analysis involving PVDF.$^{[32, 33]}$
Figure 31 PVDF Surface Energy Characterization. Droplets formed by a) EG, b) formamide, and c) TDG on PVDF to determine the contact angles needed for surface energy characterization for PVDF. d) Surface energy plot for each of the probing liquids used to estimate the surface free energy components of PVDF.

Surface energy measurements using the sessile drop technique proved to be the most challenging for C65. Initial C65 results were performed on pressed samples with the same method as PVDF. For C65, the small particle size leads to many pores throughout the packed material which lead to the probing liquid being quickly absorbed once dropped onto the surface of the packed material. As a result, conductive graphite powder (MTI Corp.) was used due to its planar structure allowing it to achieve more closed structure. A graphite green body was pressed similarly to the PVDF green body. EG, formamide, and TDG were used as the probing liquids to characterize graphite. The EG droplet formed a contact angle of 60.06° (Figure 32a) while formamide and TDG droplets formed contact
angles of 79.82° (Figure 32b) and 75.05° (Figure 32c), respectively. The OWRK method shows a polar component of 0.54 mN m\(^{-1}\) and dispersive component of 56.27 mN m\(^{-1}\). This is in agreement with a previous study using a similar surface energy characterization technique for graphite powders.\(^{[34]}\) For comparison, surface energy measurements from previous studies on carbon black and graphite were collected and summarized in Table 4.\(^{[34-39]}\)

![Graphite Surface Energy Characterization](image)

Figure 32 Graphite Surface Energy Characterization. Droplets formed by a) EG, b) formamide, and c) TDG on graphite to determine the contact angles needed for surface energy characterization for graphite. d) Surface energy plot for each of the probing liquids used to estimate the surface free energy components of graphite.

<p>| Table 4 Surface energy measurement comparisons for graphite and carbon blacks |</p>
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<tr>
<th>Material</th>
<th>$\sigma_s$ [mN m$^{-1}$]</th>
<th>$\sigma_s^p$ [mN m$^{-1}$]</th>
<th>$\sigma_s^p$ [mN m$^{-1}$]</th>
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<td>11.71</td>
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<td>0.60</td>
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</tr>
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<td>Carbon black</td>
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<td>14.80</td>
<td>35</td>
</tr>
<tr>
<td>Carbon black (oven-dried)</td>
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<td>18.43</td>
<td>2.12</td>
<td>35</td>
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<td>64.2</td>
<td>31.1</td>
<td>33.1</td>
<td>38</td>
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<tr>
<td>BP2000</td>
<td>96.2</td>
<td>96.2</td>
<td>0</td>
<td>39</td>
</tr>
</tbody>
</table>

Due to the minimal polar component of graphite, it is expected that graphite would show a hydrophobic surface. This behavior was confirmed when a water droplet on the graphite surface formed with a contact angle of 98.5° (Figure 33a). While previous liquids soaked through C65, it is speculated the as-received C65 will have similar surface energy
as graphite. To verify the hydrophobic nature of C65 a water droplet was tested on surface of packed C65 particles. The water droplet failed to deposit onto the C65 surface, signifying a hydrophobic surface (Figure 33b). To study the carbon polar component in mixing, surface treatments can be applied to increase the polar surface energy which leads to a possible change in mixing characteristics. C65 was modified by the acid/base treatment as specified by Park et al. to observe any possible polar surface energy increase.\textsuperscript{[37]} A water droplet was used to compare the C65 before and after surface treatment. While a water droplet failed to interact with the untreated C65, a water droplet on treated C65 readily detached and absorbed into the lightly pressed powder (Figure 33c), signifying a change from hydrophobicity (contact angle >90°) to hydrophilicity (contact angle <90°). By using a contact angle of 90° and the known water surface energy components, an estimation of the treatment effect on the carbon polar component can be made using Equation 4. When inserting a range of dispersive energy components (15–60 mN m\(^{-1}\)) the minimum polar energy needed to become hydrophilic ranges from 6.58–0.001 mN m\(^{-1}\)

\[
\sigma_s^p = \frac{(2\sqrt{\sigma_s^d \sigma_s^p} - \sigma_t)^2}{4\sigma_t^p}
\]  

(4)

Figure 33 a) Water droplet on the hydrophobic graphite surface. b) Water droplet showing the hydrophobicity of as-received C65. c) Water droplet soaking through treated C65, showing a change to hydrophilicity.
4.3.3 Theoretical Model for Mixing Particles with Large Size Difference and Model Validation

Consider particle \( i \) and particle \( j \) in contact (Figure 34a), a planar interface between two particles will be created (Figure 34b). The interfacial (contact) area, \( a_0 \), can be found by using radius of the contact area based on Johnson-Kendall-Roberts (JKR) theory.\(^{[40]}\)

![Figure 34 PVDF particle assembly on (a) as-received LCO and (b) annealed LCO. (Scale bar represents 5 μm)](image)

\[
a_0 = \left( \frac{9\pi w_{ij} R^2}{2E} \right)^{\frac{1}{3}} \quad (5)
\]

where \( R \) and \( E \) are the effective particle radius and elastic moduli of the two particles in contact, and \( w_{ij} \) is the adhesion work. \( R \) and \( E \) are defined by

\[
\frac{1}{R} = \frac{1}{R_i} + \frac{1}{R_j} \quad (6)
\]

\[
\frac{1}{E} = \frac{1-v_i^2}{E_i} + \frac{1-v_j^2}{E_j} \quad (7)
\]
where $v$ is the Poisson ratio. The work of adhesion $w_{ij}$ between two particles can be calculated by Fowkes equation.\(^{[41]}\)

\[
w_{ij} = 2\left(\gamma_i^d \gamma_j^d\right)^{0.5} + 2\left(\gamma_i^p \gamma_j^p\right)^{0.5}
\]  

(8)

where $\gamma_i^d$ and $\gamma_j^d$ are the dispersive surface energies of material $i$ and $j$ while $\gamma_i^p$ and $\gamma_j^p$ are the polar surface energies of material $i$ and $j$. The contact area is then defined as $A_{ij} = \pi a_0^2$.

Figure 35 a) Diagram showing particles $i$ and $j$ touching with the interface and contact area of the particles after collision (b). c) Formation of a $j$-particle agglomerate with an isolated $i$-particle. d) Formation of a $j$-particle monolayer on the surface of an $i$-particle.

It can be shown that the total surface energy of two particles in contact can be written as

\[
E_{ij} = A_i \gamma_i + A_j \gamma_j - A_{ij} w_{ij}
\]  

(9)

where $A_i$ and $A_j$ are the surface area of particle $i$ and $j$, respectively, and the last term accounts for the area in contact. Equation 9 can be extended to a system with multiple particles. Consider a system with one particle $i$ and $N_p$ particles $j$, the total surface
energies $E$ can be written for two situations described as aggregate formation and intermixed (Figure 35c, d). For aggregated situation

$$E_{\text{aggregate}} = A_i y_i + N_p A_j y_j - N_p \frac{CN_{3D}}{2} A_j y_j$$  \hspace{1cm} (10)

It is assumed that the small particles $j$ is uniform in size and their agglomerate is a 3D assembly and the number of contacts within the assembly is $N_p \frac{CN_{3D}}{2}$, where $CN_{3D}$ is coordination number in 3D assembly.\textsuperscript{[42]} For intermixed situation

$$E_{\text{intermixed}} = A_i y_i + N_p A_j y_j - N_p \frac{CN_{2D}}{2} A_j y_j - N_p A_j y_j$$  \hspace{1cm} (11)

In this case, $j$ particles form a monolayer, which is considered as a 2D assembly, on the particle $i$ surface. The number of contact points among particles $j$ is $N_p \frac{CN_{2D}}{2}$, where $CN_{2D}$ is the 2D coordination number. The mixing outcome can be evaluated by simply calculating

$$\Delta E = E_{\text{aggregate}} - E_{\text{intermixed}}$$

$$= \left\{ A_j y_j + A_j y_j \left( \frac{CN_{2D} - CN_{3D}}{2} \right) \right\} N_p$$  \hspace{1cm} (12)

with a positive $\Delta E$ value indicating intermixing and negative value indicating aggregate formation. Using $CN_{3D} = 12$ and $CN_{2D} = 6$, $\Delta E/N_p$ can be simplified as\textsuperscript{[43]}

$$\frac{\Delta E}{N_p} = A_j y_j - 3A_j y_j$$  \hspace{1cm} (13)
This model is used for materials with large differences in particle size as is the case when LCO (5–10 µm) is mixed with PVDF (∼250 nm) or C65 (∼50 nm). The $\Delta E/N_p$ is first calculated for LCO ($i$) and PVDF ($j$) particles. Measured surface energy components of PVDF (dispersive: 24.33 mN m$^{-1}$, polar: 6.18 mN m$^{-1}$) are used with LCO allowed to vary. The contour plot of $\Delta E/N_p$ is shown in Figure 36a where a combination of low polar (0–20 mN m$^{-1}$) and low dispersive (0–5 mN m$^{-1}$) surface energy components (blue region, aggregate) for LCO will correlate to negligible PVDF assembly on the LCO surface. This behavior was also verified by an independent Discrete Element Simulation study.[44] A transition area (blue–yellow) was observed where the PVDF agglomerate was attached to LCO but the work of adhesion between LCO and PVDF was not strong enough to overcome the work of cohesion between PVDF particles to fully break apart the PVDF particle agglomerate. The yellow region (intermixed) is associated with PVDF monolayer assembly. The surface energy components of as-received LCO and annealed LCO (indicated by red) are found to be in yellow region. Experimental mixing results of as-received LCO with PVDF (Figure 28a) and annealed LCO with PVDF (Figure 34) show the distribution of PVDF throughout the LCO particles are in agreement with the predicted mixing behavior.
Figure 36  a) LCO-PVDF modeling showing the preferred PVDF assembly with varying LCO surface energy values (red arrow next to annealed LCO signifies that the measured polar surface energy component is a minimum value) (blue area denotes aggregation).  

b) LCO-C65 modeling results showing preferred mixing of C65 with LCO dispersive and polar surface energy set to 40 and 100 mN m−1, respectively (yellow denotes C65 coverage on LCO). Red dots in (a) and (b) denote as measured values, yellow dots denote value from literature. c) LCO-C65 modeling showing preferred mixing of C65 with LCO dispersive and polar surface energy set to 40 and 2 mN m−1, respectively (yellow denotes C65 coverage on LCO). Histogram comparison for C65 coverage on LCO for as-received LCO mixed with as-received C65 d), annealed LCO with as-received C65 e), and annealed LCO with treated C65 f).

The $\Delta E/N_p$ is computed for LCO (i) and C65 (j) and a contour plot was developed with the dispersive and polar LCO surface energy set to 40 and 100 mN m$^{-1}$, respectively,
for the case representing LCO with a large polar component (e.t. annealed LCO). Figure 36b shows a large range of polar (0–100 mN m⁻¹) and dispersive (0–70 mN m⁻¹) values of C65 will cause assembly on the LCO surface. In the LCO and C65 study, the transition from intermixed (assembly) region to aggregate region shows a C65 agglomerate attached to LCO. The work of adhesion between C65 and LCO is large enough such that the C65 agglomerate will attach to the surface of LCO. In this case, the work of cohesion of the C65 prevents the C65 agglomerate from breaking apart. A second LCO-C65 contour plot (Figure 36c) was developed to observe the LCO-C65 mixing characteristics when the LCO polar surface energy was lowered to 2 mN m⁻¹. This configuration represents the surface energy case for the measured as-received LCO. In this configuration, the area representing C65 assembly on LCO is greatly reduced to lower-left corner with polar and dispersive energy combinations between 0–15 and 0–40 mN m⁻¹, respectively. As can be seen from modeling, polar component of the LCO has major impact in carbon distribution.

An experimental comparison was made with three different LCO and C65 powders to observe any changes in C65 distribution, the mixing combinations were as-received LCO with as-received C65, annealed LCO with as-received C65, and annealed LCO with treated C65. First, it is found minimal untreated C65 particle coverage was observed on as-received LCO. By increasing the polar surface energy component of LCO (annealed LCO), untreated C65 was found to more readily assemble on the LCO surface. This behavior was confirmed with electron-dispersive X-ray quantification studies performed on the surface of individual LCO particles. Histograms (Figure 36d–f) show that the as-received LCO particles contained lower amounts of C65 than the annealed LCO particles. This agrees with the modeling results where C65 showed minimal assembly on the low polar surface
energy surface of as-received LCO (Figure 36e). Furthermore, experimental mixing results for untreated versus treated C65 mixed with annealed LCO were shown to display similar C65 coverage on the LCO surface. This can be explained by the treated and untreated C65 surface energy values lying in the same region denoting assembly on a high polar LCO surface (Figure 36b) despite higher polar components in treated C65.

4.3.4 Theoretical Model for Mixing Particles with Similar Sizes and Model Validation

A separate model was developed where two materials, \( i \) and \( j \), are similar in size. This model also has two surface energy situations where the two materials are intermixed amongst each other and where the two materials exhibit minimal mixing forming an aggregate (same type of particles tend to agglomerate with minimal intermixing of different particle types) (Figure 37). The aggregate situation shows strong bonding amongst similar particles, preventing different particle types to break apart and intermix. In this model, there will be \( N_p \) number of \( j \) particles and \( nN_p \) number of \( i \) particles. For aggregate situation

\[
E_{\text{aggregate}} = N_p \sigma_i \gamma_i - N_p \frac{CN_{13}}{2} \sigma_i \gamma_i + nN_p \sigma_j \gamma_j - nN_p \frac{CN_{13}}{2} \sigma_j \gamma_j
\]  

(14)
A. 

**Aggregate**

Particle Agglomerate

B. 

**Intermixed**

Intermixed Particle Agglomerate

C. 

**Aggregation**

Dispersive (mN/m) vs. Polar (mN/m) plot

- Carbon Black
- Graphite
- Intermixed
In the aggregate situation, it is assumed that $I$ particles form a 3D assembly in contact with a $j$ particle 3D assembly (Figure 37a). In the intermixed situation, it is assumed an $i$ particle is surrounded and intermixed amongst $j$ particles in a 3D assembly (Figure 37b). For intermixed situation

$$E_{\text{intermixed}} = N_p A_i \gamma_i + n N_p A_i \gamma_j - (n N_p - N_p) \frac{CN_{3D}}{2} A_j \gamma_j - N_p \frac{CN_{1D}}{2} A_j w_j$$

The mixing outcome for this model was evaluated by

$$\Delta E = E_{\text{aggregate}} - E_{\text{intermixed}}$$

$$= (A_j w_j - A_i \gamma_i - A_j \gamma_j) N_p \frac{CN_{3D}}{2}$$

with a positive $\Delta E$ value indicating intermixing, and negative value indicating an aggregate is formed.

This model for similar sized particle was applied to predict the mixing of PVDF and C65 due to their comparable sizes. PVDF ($i$) surface energy was kept constant at the measured surface energy values previously discussed and C65 ($j$) was allowed to vary. A contour plot (Figure 28c) shows a combination of polar surface energy values from 0 to 20 mN m$^{-1}$ and dispersive surface energy values from 10 to 45 mN m$^{-1}$ will result in intermixed PVDF/C65 particles. Measured carbon black surface energy values in literature
are located near or within the intermixing area which is in agreement with the intermixed nature found in SEM images (Figure 28c) when C65 and PVDF are mixed together. The contour plot shows the graphite surface energy values are located just outside of the intermixed zone. The graphite used for surface energy measurements was mixed with PVDF and it was found that PVDF will decorate the graphite surface (Figure 38). The behavior of graphite and PVDF is expected to be due to the measured graphite surface energy being in a transitional area where PVDF and carbon materials will begin to display lesser mixing uniformity.

Figure 38 PVDF particles attaching to the surface of graphite. (Scale bar represents 5 μm)

4.3.5 Electrochemical Characterization
There exist specific concentration requirements for BPA and CPA in the industry of Li-ion batteries to enable all active material to be functionalized properly. Limited to the mixing characteristics of the conventional slurry casting method, aggregates of BPA and CPA are unnecessarily formed during the manufacturing procedure and thereby these “dead materials” would increase the concentration requirements of them. However, more efficient usage of the additives can be possible by making use of the information gained in the previous mixing studies to obtain uniform BPA and CPA distribution throughout the active material. PVDF particles were found to be uniformly distributed among LCO regardless of the surface condition (as-received vs annealed), and strength tests show a reduction to 1 wt% yields sufficient bonding. There was a change in C65 distribution depending on the surface condition of LCO with the annealed surface displaying an increase in C65 uniformity. It was shown surface treatment of C65 influenced the surface energy; however, the effect on mixing uniformity among LCO was minimal.

Therefore, electrochemical tests were performed with annealed LCO, as-received PVDF and as-received C65. The reduction in CPA was performed to show that the fabricated cathodes still exhibit reasonable electrochemical performance due to the CPA particles being uniformly distributed amongst the active material and BPA. Figure 39a shows the rate performance of the dry printed cathode electrodes with lowered additives loading (98 wt% LCO, 1 wt% PVDF, and 1 wt% C65) over the voltage range 4.2–2.5 V versus Li/Li⁺. The cell achieved a specific discharge capacity of 134 mAh g⁻¹ at 0.1 C, which is 98% of theoretical capacity. At the rates of 0.2, 0.5, 1, 2, and 3 C, these rate performances were lowered to 132, 127, 120, 100, and 75 mAh g⁻¹, respectively, which exhibit a consistently stable rate capability of the samples. Up to the current rate of 3C,
these dry printed samples can still supply 55% theoretical capacity of the active material, which provides good evidence of the uniform mixing behavior of this new electrode manufacturing process. Cycling data (Figure 39b) show the cell's capacity steadily decayed from 127.8 to 98.5 mAh g\(^{-1}\) at the current rate of 0.5 C after 100 cycles 77% capacity retention. Electrochemical impedance spectroscopy tests were also performed during cycling (provided in the Supporting Information).
Figure 39 Electrochemical performance of sample with lowered binder/conductive additive loading (98 wt% LCO, 1 wt% PVDF, and 1 wt% C65): a) Rate performance. b) Cycling performance for 100 cycles.

4.4 Conclusion

A largely decreased loading of BPA and CPA means lowered bonding effects and electroconductivity of the electrode during cycling, which both would lead to a decline of the electrochemical performance. Even so, the experimental results show favorable mechanical strength capacity retention during cycling, which support our analysis on the beneficial dispersion homogeneity of our dry printing method through optimal material mixing. LCO was used as the active material in this mixing study but other materials, such as LiNiMnCoO$_2$, LiMn$_2$O$_4$, and LiFePO$_4$, can also be characterized as the presented mixing models can be extended to any range of surface energy values. Based on the mixing results, annealed LCO was used for electrochemical testing as C65 was found to be more uniformly mixed, allowing for a functional battery to be fabricated with CPA concentration as low as 1%. BPA concentration was also reduced due to the uniform dispersion of PVDF throughout LCO, regardless of the surface condition of LCO. In addition, the fabricated samples showed stable physical characteristics while being built into the test coin cells. The surface of samples is strongly bonded, and no particles were observed to detach from the electrode layer matrix. In summary, there appear no major technical barriers by using dry powder in achieving sub micrometer level mixing. It is anticipated that the mechanical and electrochemical performance of dry manufactured electrodes can be comparable to slurry casted ones by optimizing BPA and CPA concentrations due to excellent mixing efficiency, driven by the interfacial energies.
4.5 Supporting Information

4.5.1 Surface Energy Measurement and Discussions

To understand the mixing behavior of the electrode powders the surface energy needed to be measured. The sessile drop contact angle technique was used as the characterization method. In this technique, known probing liquids are deposited on a surface. Based on the contact angle and known surface energy components of the probing liquid an estimation of the unknown solid surface energy can be made. Ideally, this method is used for solid bulk materials where liquid absorption into the solid material is avoided due to closed porosity.

An OCA15EC/B Contact Angle Measuring Device by DataPhysics was used to capture the contact angles and to calculate polar, dispersive, and total surface energies of the battery electrode materials. As previously mentioned, the Sessile Drop Technique is typically performed on a flat bulk solid material; therefore, packing each electrode powder as densely as possible is required. This will allow the densely packed particles to be analyzed as a single, solid material. If the powders are not packed well the probing liquid will readily soak through the pores between the particles. LiCoO2 (LCO), polyvinylidene fluoride (PVDF), Super C65 carbon black (C65), and graphite were analyzed with this method.

LCO was characterized with an LCO sputtering target from Kurt J. Lesker Company. The target provides a highly pure (99.7%) and dense material to perform the surface energy characterization. Diiodomethane, dimethyl sulfoxide (DMSO), and thiodiglycol (TDG) were used for LCO characterization. The results show that the droplets
form contact angles of 44.6° for diiodomethane (Figure 29a), 62.0° for DMSO (Figure 29b), and 74.8° for TDG (Figure 29c).

Each of the contact angles were entered into the software provided by DataPhysics to determine the polar, dispersive, and total surface energy components for LCO. The Owens, Wendt, Rabel, and Kaelble (OWRK) method for calculated surface free energy was used characterize LCO. It was found that the surface energy due to polar interactions was 1.35 mN m⁻¹ while the surface energy due to dispersive interactions was 37.0 mN m⁻¹. A line fitted to the plotted points for each of the probing liquids used in the OWRK method gave an error value of 0.997 and the fitted line represents a very close fit to the plotted points (Figure S1d).

A previous paper measuring the surface energy of a lithium active material (LiFePO4) showed a similar dispersive energy component to LCO but with a significantly higher polar energy component. The LCO target was washed with acetone, ethanol, and isopropyl alcohol and then rinsed with deionized water to eliminate any surface contamination. Afterwards, the LCO target was heated to 500°C to eliminate any moisture left from washing and rinsing. The probing liquids were deposited onto the surface after the target cooled to room temperature. DMSO and TDG completely wetted the surface while diiodomethane was reduced to 33.1°. As mentioned in the main text, diiodomethane could be used to calculate the dispersive energy component of the heated LCO surface (42.5 mN m⁻¹). Water was used to estimate the polar surface energy due to its large polar energy component (51 mN m⁻¹). Water completely wetted the heated LCO surface (Figure S2b) and formed a contact angle of 70.7° on the as-received LCO surface (Figure 30c). The minimum polar component associated with the heated LCO surface was calculated to
be 35.0 mN m⁻¹ by using the known water surface energy components, dispersive energy of the heated LCO, and a contact angle of 0°.

The PVDF sample used for surface energy characterization was made in the laboratory. An as-received PVDF green component with closed porosity was made by pressing the PVDF powder into a 12.5 mm diameter disc-shape using a pressing die. A pressing pressure of 263 MPa was used and the pressing process was completed using a Carver Bench Top Press. Three fluids were used to characterize the PVDF: ethylene glycol (EG), formamide, and TDG. The EG droplet formed a contact angle of 57.12° (Figure 31a) while formamide and TDG droplets formed contact angles of 64.40° (Figure 32b) and 59.97° (Figure 32c), respectively. A polar surface energy component of 6.18 mN m⁻¹ and dispersive surface energy component of 24.3 mN m⁻¹ were found using the OWRK method. A fitted line to the plotted points (Figure 31d) shows a very close fit (error value of 0.999). The calculated surface energy for PVDF is in agreement with previous studies on PVDF surface energy and was used in further testing.¹³,¹⁴

Polar and dispersive surface energy measurements using the Sessile Drop Technique proved to be most difficult for C65. A C65 green component was made similar to that of the PVDF green component, but the small particle size leads to many pores throughout the packed material. The probing liquids was readily soaked into the packed C65 once dropped onto the surface. As a result, conductive graphite powder (MTI Corp.) was used due to its planar structure allowing it to be achieve a closed porosity surface more readily. A graphite green body was pressed and EG, formamide, and TDG were used as the probing liquids for characterization. The EG droplet formed a contact angle of 60.06° (Figure 32a) while formamide and TDG droplets formed contact angles of 79.82° (Figure
32b) and 75.05° (Figure 32c), respectively. Again, the OWRK method was used and a polar component of 0.54 mN m\(^{-1}\) and dispersive component of 56.27 mN m\(^{-1}\) were found. A fitted line to the plotted probing liquid points again show a very good fit (Figure 32d).

While graphite and C65 are both carbon materials, more studies were conducted on C65 since the surface energy measurements for graphite may not be representative of C65. Surface energy measurements of carbon black, as well as graphite, from previous studies were gathered as can be seen in Table 4.\(^{[5-10]}\) It was found that the graphite surface energy measurement in previous studies also show low dispersive energy.\(^{[5]}\) This can readily be observed by the hydrophobic (contact angle of 98.5°) nature of the graphite when depositing a water droplet on the surface (Figure 33a). Previous studies also show that an increased polar component can be achieved by performing an acid/base treatment on the carbon black. Surface treatment was performed on C65 by following the procedure specified by Park et al.\(^{[8]}\) Water droplets were tested on as-received C65 and treated C65 to observe any differences made by the surface treatment. The as-received C65 displayed a hydrophobic nature as can be seen in Figure 33b where the water droplet failed to detach from the probing syringe and deposit on the surface. However, a water droplet deposited on the treated C65 surface readily detached from the probing syringe and soaked through.

4.5.2 Binder Distribution on As-Received LCO and Annealed LCO

Changes in LCO surface energy were observed when the LCO was washed and heated. A minimal increase in dispersive energy was observed while the polar energy increased from 1.35 mN m\(^{-1}\) to >35.0 mN m\(^{-1}\). PVDF was mixed with both types of LCO since PVDF distribution is essential for created a strongly bonded electrode. SEM
micrographs in Figure 34 show similar PVDF behavior where the PVDF particles decorate the surface of LCO. This behavior matches modeling results where surface energy components for both types of LCO are contained in the contour plot area signifying PVDF assembly on the LCO surface.

4.5.3 Graphite/PVDF Mixing Result

Graphite and PVDF were mixed with zirconia beads in a BeadBug Microtube Homogenizer (Benchmark Scientific) at 2800 RPM to understand the mixing behavior of particles when the surface energies are next to the zone transitioning from particle separation and particle intermixing. Figure 38 shows that PVDF particles are attached on the surface of graphite particles.

4.5.4 EIS Measurement

Impedance in Figure 40 is a collective response of kinetic processes with different time regimes. Electrochemical Impedance Spectroscopy tests were performed with a galvanostat/potentiostat/impedance analyzer (Bio-logic VMP3), and was carried out from 0.05 Hz to 200 KHz using a 10 mV AC signal. The Nyquist plots of the printed LCO/Graphite cell at fully discharged state are shown in Figure 38. The printed electrodes were designed and fabricated with the lowered concentration of binder/CA material. The Nyquist plots of the dry printed LCO/Graphite electrode showed an increased chemical reaction impedance during the cycle test, and the impedance was becoming larger while
testing for more cycles. This phenomenon can be attributed to the cracks and shape deformation which occurred during the intercalation/deintercalation of Li+ process.

Figure 40 EIS measurements of the cell during at the fully discharged state after the 10th cycle, the 60th cycle and the 100th cycle.

4.5.5 References


4.6 Acknowledgements

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4.7 References


CHAPTER 5. RECOMMENDATIONS FOR FUTURE WORK

In this work, we have successfully demonstrated a functional ZNFB and its electrochemical properties was determined. Except for the same structural characteristics as the redox flow batteries, ZNFB maintains the advantageous attributes of solid-state rechargeable Ni/Zn batteries on energy density and unit cost. High energy density electrical performance is obtained while saving the weight of conventional grid network in this battery.

- We recognize that more researches are necessary on the electrode optimization and new system layout design to overcome the interaction effects between the electronic conductivity and the ionic conductivity, which is caused by the unique “semi-solid” electrode design of SSFC technology.

- A new prototype of cell is proposed to get accustomed to the unique characteristics of ZNFB, such as the interactive relationship between ion and electron conductivity. The circulation of slurries should be enhanced in the new system, which would bring the sight of device optimization into the SSFC scheme. With the new cell, the columbic efficiency should be improved for both slurries.

- The balance between viscosity (related to the flow-ability) and electrochemical properties (related to raw material selection) should be taken into consideration while we further understand the SSFC system.
• More collaborations would be appreciated to work on this system, which is a big project to deep study the entire ZNFB including fundamentals of the electrochemistry reactions and physical properties.

Also, with the dry printing technique, we successfully fabricated long cycle life (>650 cycles) electrodes at a regular thickness (56 µm) and demonstrated high-energy thick electrodes (up to 200 µm). The quick and simplified procedure helps to maintain the initial loading structure and the material dispersion during pre-mixing, which enable the possibility to control the morphology of product electrodes starting by the mixing step.

• The demonstration of thick electrode brings the sight of microstructure control in a practicable way.

• The dry printing technology is possible to allow more potential electrode designs, which cannot be achieved by the slurry casting technique.

• More structure could be tested with advanced design, and more material could be proposed to use with the dry printing technique.

• Silicon/Graphite, All Solid State Batteries, Purely Powder-Based Manufacturing of the Entire Batteries. A lot of advanced designs should be taken into consideration for the future study.
CHAPTER 6. RELEVANT PUBLICATIONS AND PRESENTATIONS


• MRS Fall Meetings and Exhibit (talks and posters, 2014-2018)

• 229th Electrochemical Society Meeting (talk and poster, 2016)

• National Science Foundations Conference (talk and poster, 2018)