New Aqueous Binders for Lithium-ion Batteries

Final CRADA Report

**Chemical Sciences and Engineering Division
and
Energy Systems Division**

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EXECUTIVE SUMMARY

This final report summarizes the research effort of the CRADA between PPG Industries and Argonne National Laboratory (CRADA # C1400501 and Amendment 1 - ACK 85C11, Rev. 1), and completes the requirements of Task #5 in the CRADA.

The results from Argonne represent a combined effort between the MERF and CAMP Facility (Materials Engineering Research Facility and the Cell Analysis, Modeling and Prototyping Facility). The key points of this report can be briefly summarized as:

1. The multicomponent aqueous binder for NCM cathodes developed by PPG shows promising results when used on the CAMP Facility's pilot-scale coater.
2. NCM523 cathode electrodes exposed to water exhibit a voltage anomaly in the first two formation cycles that appears to have little effect on the material capacity, but needs to be explored further.
3. The experimental LFP electrode produced by PPG does cycle electrochemically, but with reduced capacity and an uncharacteristic voltage profile.
4. There is no obvious correlation between the pH and zeta-potential of materials that are commonly used in the lithium-ion battery.
5. Lithium ions are more readily dissolved out of NCM523 by water than the transition metals (by two orders of magnitude), and suggests that the plating bath may need to be spiked with a lithium salt.
6.   The approach of creating sub-micron size NCM523 particles via ball milling results in a cathode material with poor electrochemical performance.

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Task 1: Standard Cathode

High energy density is the main criteria in nearly all portable applications, and especially so for electric vehicles (EVs). While lithium cobalt oxide is the cathode material of choice in portable electronics like laptops and smart phones, the raw material cost of cobalt makes this option too expensive for EVs. Rather than use only cobalt as the transition metal in cathode materials, other transition metals such as nickel and manganese are added to reduce the raw material cost with little loss in electrochemical performance. These materials are referred to as NCM type cathodes, and in this effort the emphasis will be placed initially on NCM523. The voltage profile of an NCM523 electrode versus lithium metal (half-cell) is shown in Figure 1 for the first four cycles at a C/10 current rate. For a voltage window of 3.0 to 4.3 V, a reversible capacity of 170 mAh/g can be obtained with a typical first cycle efficiency of 88 %.
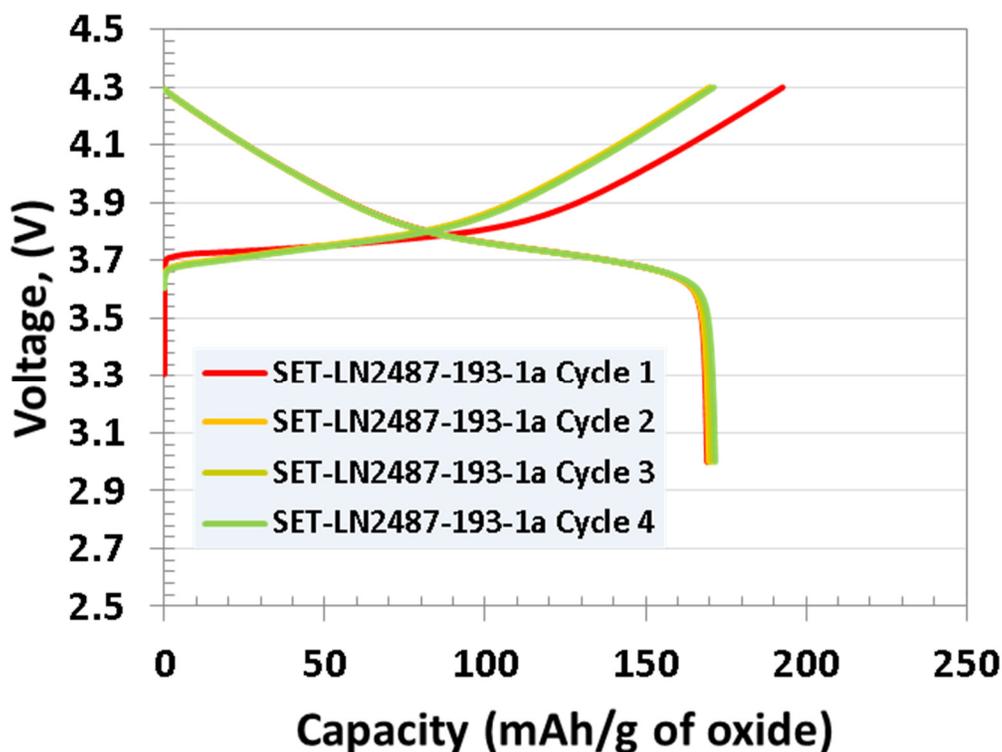
Figure 1: First four voltage profiles for NCM523 cathode using conventional PVDF binder versus Li with 1.2 M LiPF$_6$ in EC:EMC (3:7 by wt.) electrolyte at a C/10 current rate and 30°C

Lithium iron phosphate (LFP) is another material that is used in EVs (primarily in China), but it has an energy density lower than NCM cathodes. LFP has a relatively flat voltage plateau near 3.45 V and a reversible capacity of 160 mAh/g. The lower average voltage of LFP compared to that of NCM is the main reason for LFP's lower energy density. Another alternative cathode system under consideration is NCA, which is the cathode used in the Tesla EV. NCA has an

average voltage and specific capacity comparable to NCM. However, NCA is sensitive to moisture and will lose significant lithium content if it is soaked in water. This problem might be mitigated with a protective coating on the NCA particle.

PPG's Aqueous Binder and NMC Cathodes on Argonne Pilot-Scale Coater:

Efforts were also directed to developing aqueous e-coating for NCM-based cathodes. The first step in this process is developing an aqueous binder system that will then form the foundation for later e-coating development. PPG created an experimental multi-component water-based binder system tailored for NCM particles. The feasibility of this new binder system was tested by Argonne's CAMP Facility on their pilot-scale coater using commercial un-modified NCM523 powder. This new binder system was readily adapted to continuous roll-to-roll coating by Argonne.

An initial NCM523 electrode using the experimental binder was made on the CAMP Facility's pilot scale coater for scoping purposes. This initial electrode adhered well to the aluminum foil, but its capacity loading was low. The electrochemical performance of this electrode was evaluated in half-cells (versus lithium metal) in a voltage window of 3.0 to 4.1 V. This lower upper voltage cutoff (4.1 V) was used initially because of uncertainty of the oxidative stability. A capacity of nearly 140 mAh/g was achieved, which is typical for NCM523 in this voltage window.

This NCM523 electrode was further evaluated for rate performance capability (C/24 to 2C) and then life cycle tested at a C/3 current rate. The results of these tests are summarized in Figure 2. A slow rate capacity was achieved with these electrodes, which is lower than the conventionally-made NCM523 electrode capacity in this voltage window. The capacity retention of these electrodes during cycling at the C/3 rate is very good as can be seen from the figure below. Overall, these results demonstrate that this new class of aqueous binders can serve as the starting point for e-coating of NCM cathodes.
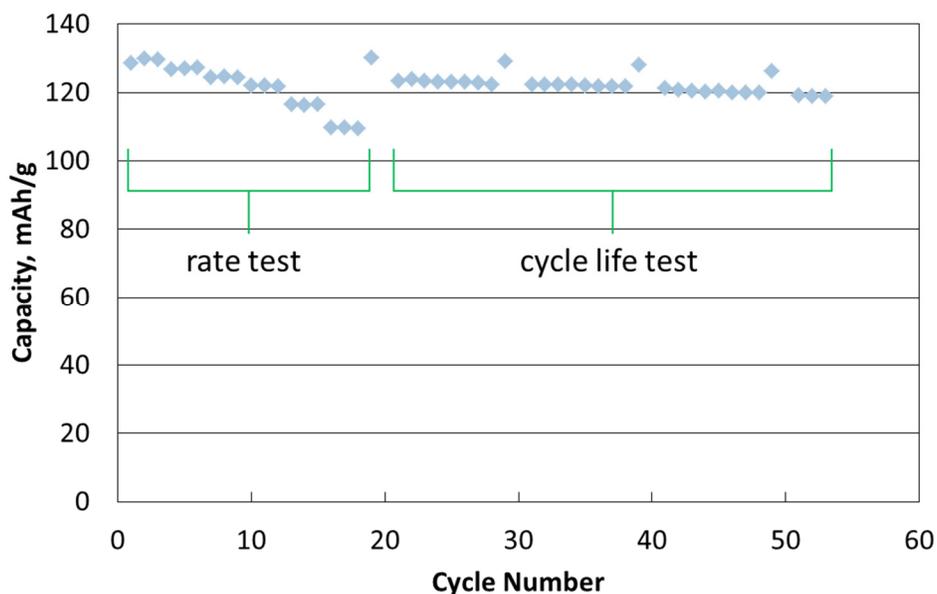
Figure 2: Discharge capacity for rate performance and cycle life tests for NCM523 cathode (1.3 mAh/cm²)using the experimental multi-component water-based binder versus Li with 1.2 M LiPF$_6$ in EC:EMC (3:7 by wt.) electrolyte, 3.0 – 4.1 V (C/3 current rate for cycle life), and 30°C

Based on these promising results, a thicker electrode was made with a capacity loading of 2 mAh/cm², which matches the anodes used in the CAMP Facility's Electrode Library. (There was evidence that higher capacity loadings were possible.) Shown in Figure 3 are two photos of the resulting cathode electrode. This electrode was very flexible as demonstrated by the 3 mm roll-pin test shown in the right photo.
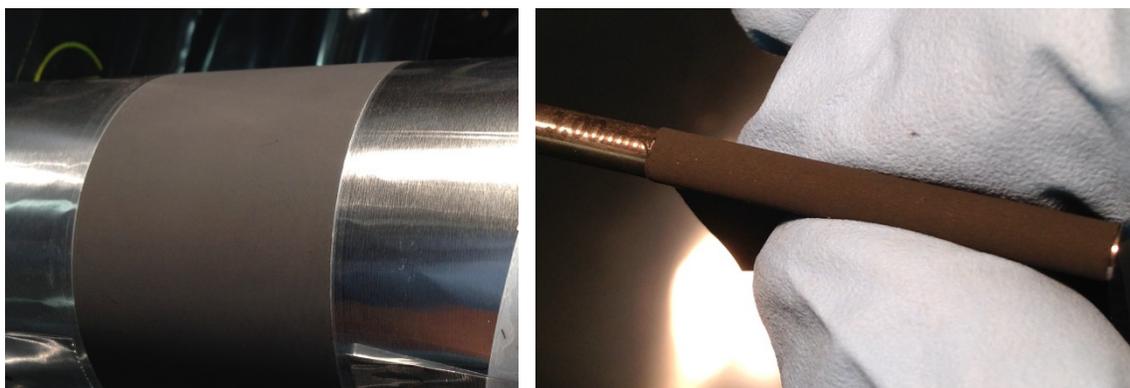
Figure 3: Photo of NCM523 electrode (2.0 mAh/cm²) using the expiremental multi-component water-based binder on aluminum foil and CAMP Facility's pilot scale coater (left). Photo of same electrode passing the 3 mm roll-pin test (right)

The electrochemical performance of this electrode (2.0 mAh/cm²) was evaluated in half-cells in a voltage window of 3.0 to 4.1 V. Shown in Figure 4 is the voltage profiles of the first three formation cycles at a C/10 current rate. A capacity of nearly 140 mAh/g was achieved, which is typical for NCM523 in this voltage window. However, the initial voltage profile was altered for

both the charge and discharge. Possible causes of this change could be water damage of the NCM523 particle or residual water retained in the electrode. These scenarios are discussed later.
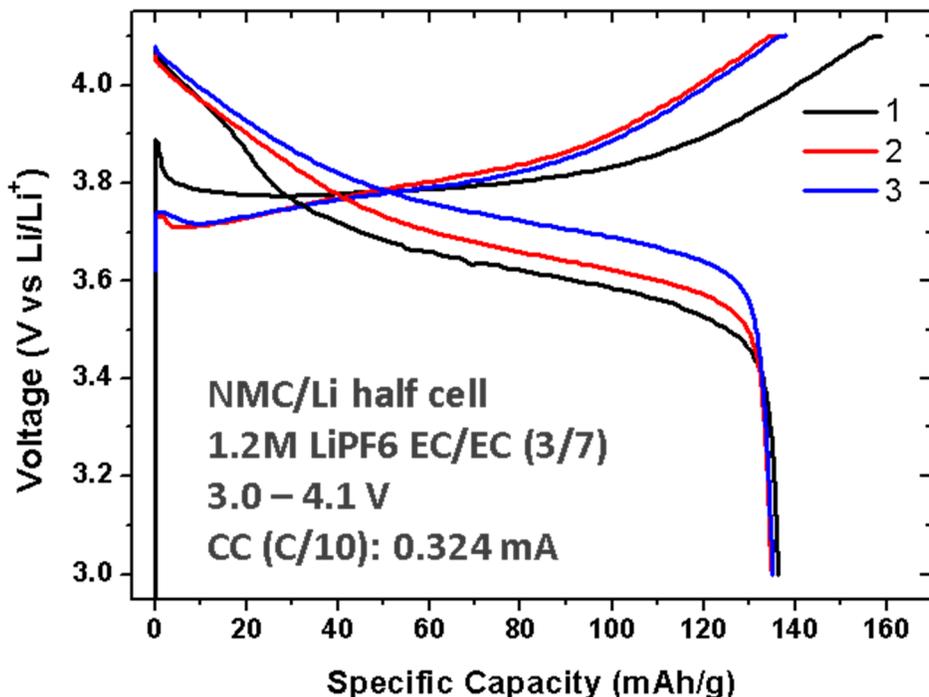
Figure 4: First three voltage profiles for NCM523 cathode (2.0 mAh/cm^2) using the experimental multi-component water-based binder versus Li with 1.2 M LiPF$_6$ in EC:EMC (3:7 by wt.) electrolyte at a C/10 current rate, 3.0 – 4.1 V, and 30°C

The oxidative stability of the experimental aqueous binder was tested by making fresh half cells and cycling them between 3.0 and 4.3 V. The formation voltage profile is shown in Figure 5, which also exhibited similar voltage anomalies as seen in Figure 4. This NCM523 electrode (2.0 mAh/cm²) was further evaluated for rate performance capability (C/10 to 2C) and then life cycle tested at a C/3 current rate. The results of the rate test are summarized in Figure 6 and Figure 7. A slow rate capacity of 170 mAh/g was achieved with these electrodes, which is similar to conventional NCM523 using PVDF-NMP binders. However, at faster rates such as 2C rate, the capacity is lower than the conventionally-made NCM523 electrode (see Figure 15). This indicates that the electrode using the experimental binder has higher impedance and needs to be optimized for better rate performance. The capacity retention of the experimental binder electrode during cycling at the C/3 rate is relatively good as can be seen from Figure 8. Based on these results, there is little evidence that the experimental multi-component binder is incompatible with the NCM523 cathode or with the conventional electrolyte system. The faster capacity fade rate for the data in Figure 8 compared to the scoping data in Figure 2 might be attributed to the extra lithium that is shuttled back and forth for the thicker cathode electrode, which degrades the lithium metal electrode due to dendrites.
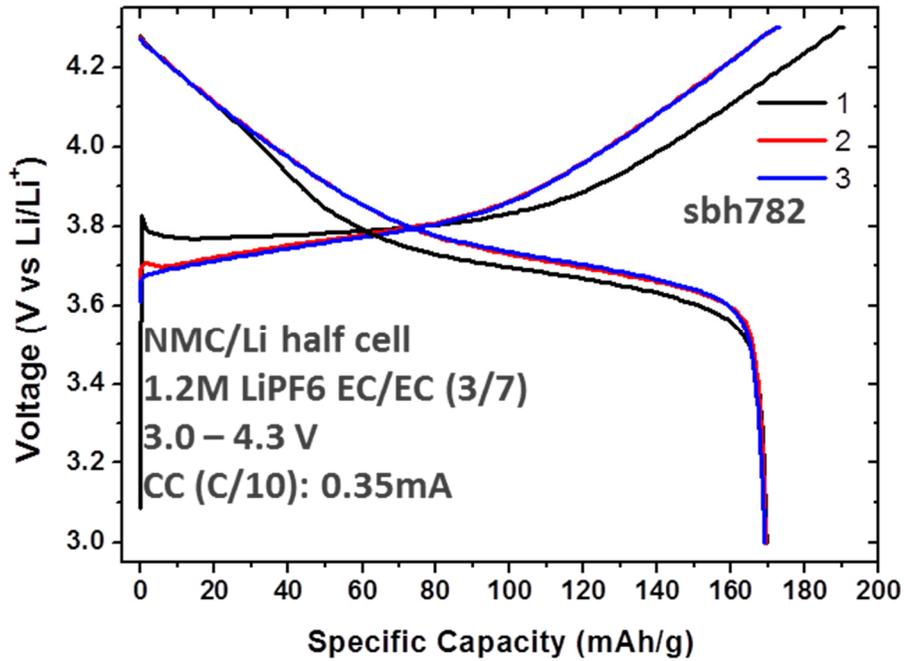
Figure 5: First three voltage profiles for NCM523 cathode (2.0 mAh/cm²) using the experimental multi-component water-based binder versus Li with 1.2 M LiPF6 in EC:EMC (3:7 by wt.) electrolyte at a C/10 current rate and 30°C, with an upper cutoff voltage of 4.3 V.
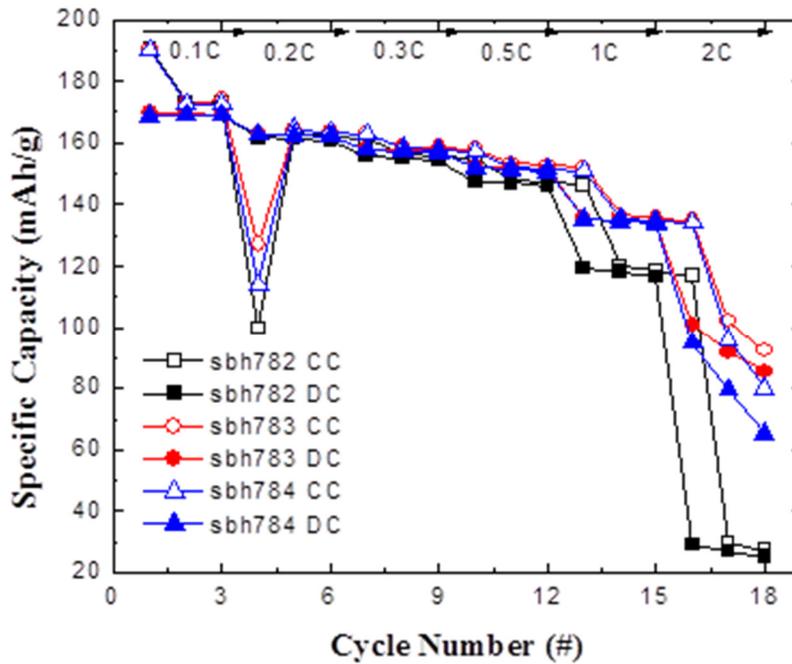
Figure 6: Charge and discharge capacity for rate performance tests for NCM523 cathode (2.0 mAh/cm²)using the experimental multi-component water-based binder versus Li with 1.2 M LiPF$_6$ in EC:EMC (3:7 by wt.) electrolyte, 3.0 – 4.3 V, and 30°C
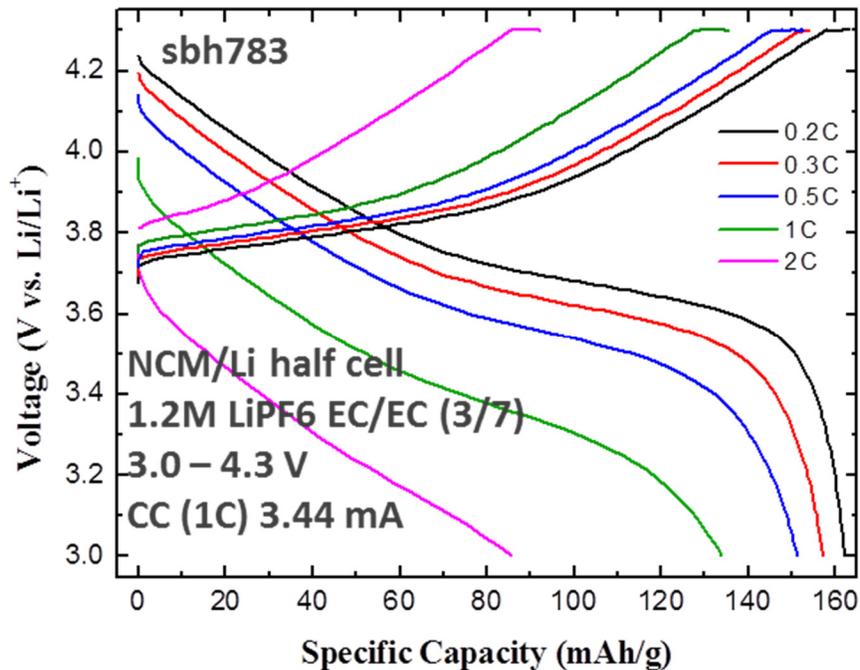
Figure 7: Voltage Profiles from rate performance tests for NCM523 cathode (2.0 mAh/cm^2)using the experimental multi-component water-based binder versus Li with 1.2 M LiPF$_6$ in EC:EMC (3:7 by wt.) electrolyte, 3.0 – 4.3 V, and 30°C
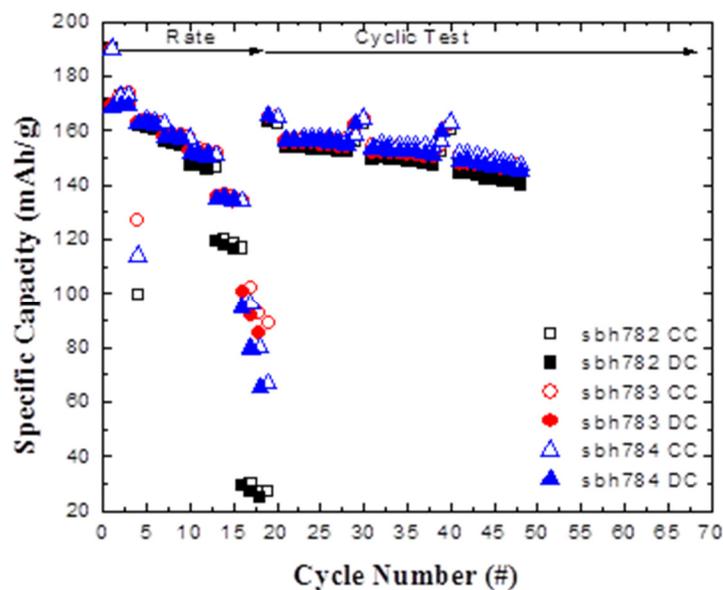
Figure 8: Charge and discharge capacity for rate performance and cycle life tests for NCM523 cathode (2.0 mAh/cm^2)using the experimental multi-component water-based binder versus Li with 1.2 M LiPF$_6$ in EC:EMC (3:7 by wt.) electrolyte, 3.0 – 4.3 V (C/3 current rate for cycle life), and 30°C

Water-soaked NCM523 Powder using Conventional PVDF Binder in NMP:

Cathode electrodes are typically made with PVDF-based binders in NMP carrier solvent. While switching to water-based cathode binders is the desire, concern exists that water may negatively affect certain cathode active materials. To test the effect of water on NCM523, a sample of this cathode powder was soaked in water for two days, filtered, and then vacuum baked. The dry cathode powder was then used with a NMP-PVDF binder and coated on Argonne CAMP Facility's pilot-scale coater. Half cells were made and tested with the resulting electrode – the results of which are shown in Figures 9, 10, and 11. While the capacity was relatively unaffected by the water soak, the initial voltage profiles during formation showed an anomaly at the start of the first charge. This anomaly may be associated with residual moisture bound in the particles, but there is some evidence from on-going work at Argonne that the initial voltage overshoot at the beginning of the first charge is due to Li_2CO_3 that formed during the water exposure. This suggests that the water exposure time should be kept to a minimum.
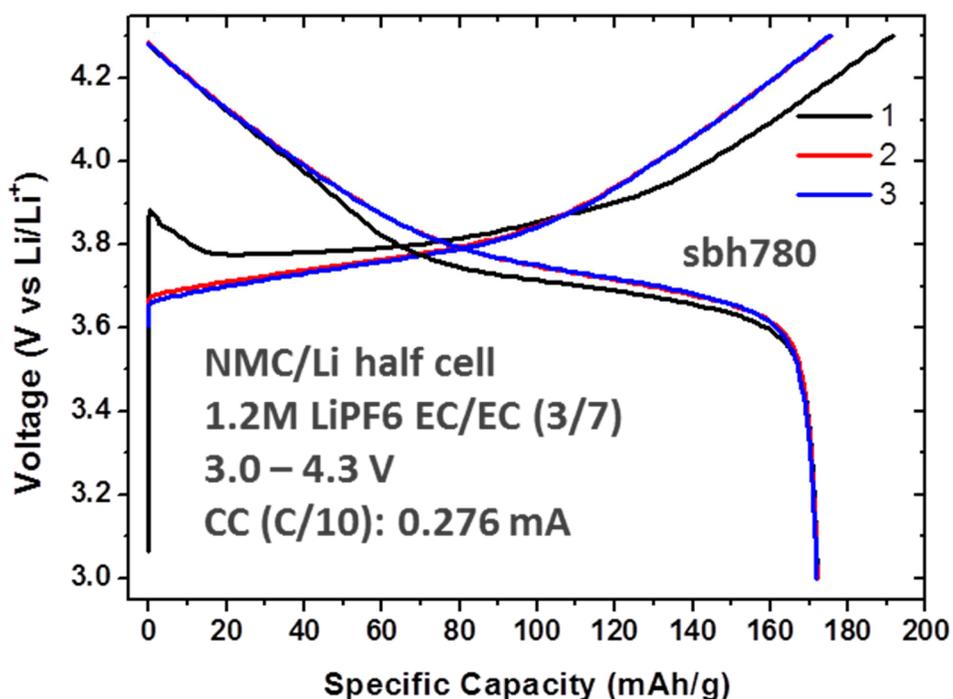
Figure 9: First three voltage profiles for NCM523 cathode powder soaked in water for 48 hours and then dried and coated onto aluminum foil using convential PVDF binder in NMP, versus Li with 1.2 M LiPF6 in EC:EMC (3:7 by wt.) electrolyte at a C/10 current rate and 30°C, with an upper cutoff voltage of 4.3 V.
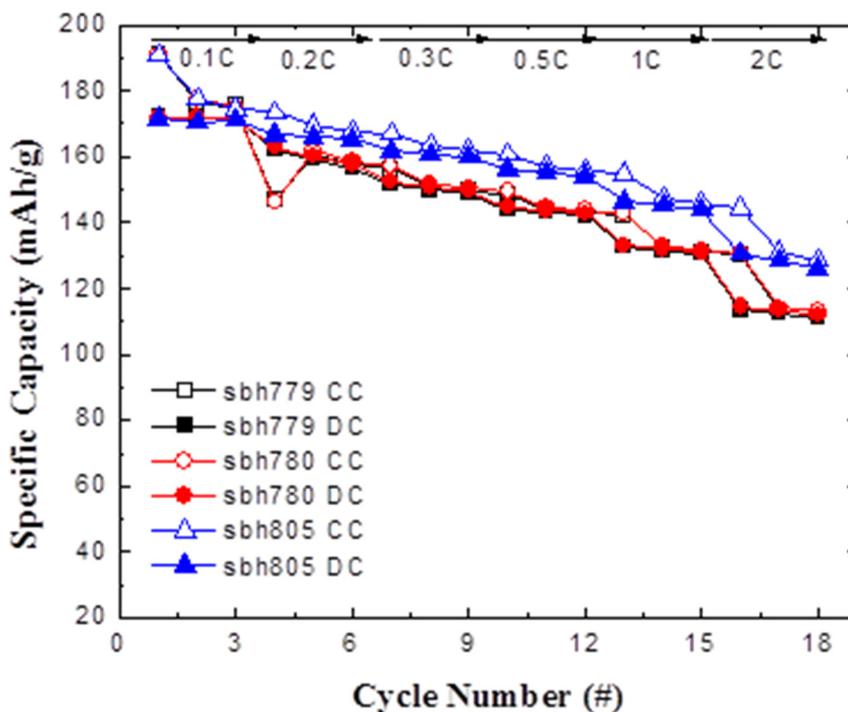
Figure 10: Charge and discharge capacity for rate performance tests for water soaked NCM523 powder and coated onto aluminum foil using convential PVDF binder in NMP, versus Li with 1.2 M LiPF$_6$ in EC:EMC (3:7 by wt.) electrolyte, 3.0 – 4.3 V, and 30°C
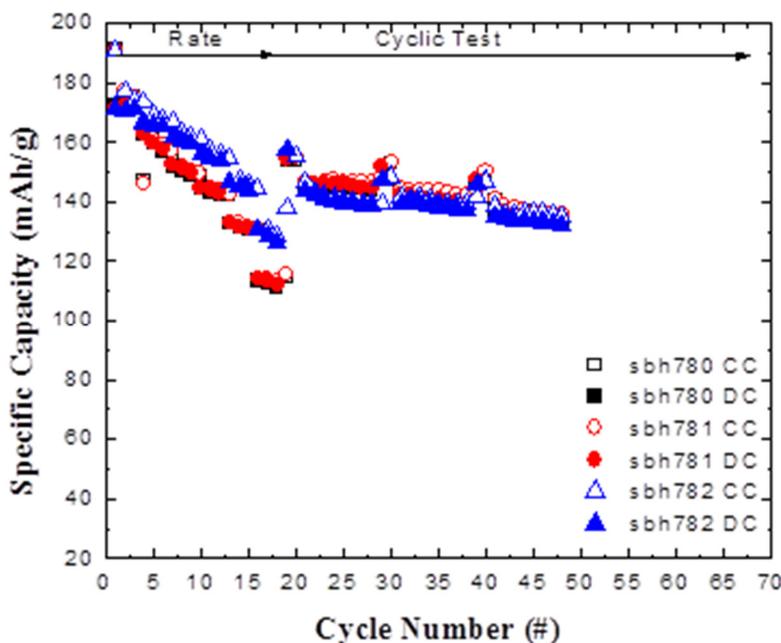
Figure 11: Charge and discharge capacity for rate performance and cycle life tests for water soaked NCM523 powder and coated onto aluminum foil using convential PVDF binder in NMP, versus Li with 1.2 M LiPF$_6$ in EC:EMC (3:7 by wt.) electrolyte, 3.0 – 4.3 V (C/3 current rate for cycle life), and 30°C

Water-soaked NCM523 Powder using PPG's Aqueous Binder:

The effect of water exposure on NCM523 was further explored using PPG's experimental multi-component aqueous binder. Similar to before, a sample of this cathode powder was soaked in water for two days, filtered, and then vacuum baked. The dry cathode powder was then used with the experimental aqueous binder and coated on Argonne CAMP Facility's pilot-scale coater. Half cells were made and tested with the resulting electrode – the results of which are shown in Figures 12 and 13. As was seen in the previous water exposed NCM523, the capacity was relatively unaffected by the water soak, but the initial voltage profiles during formation showed an anomaly at the start of the first charge. This further suggests that the water exposure time should be kept to a minimum, or the cathode particle or plating bath need to be adjusted to minimize this effect.
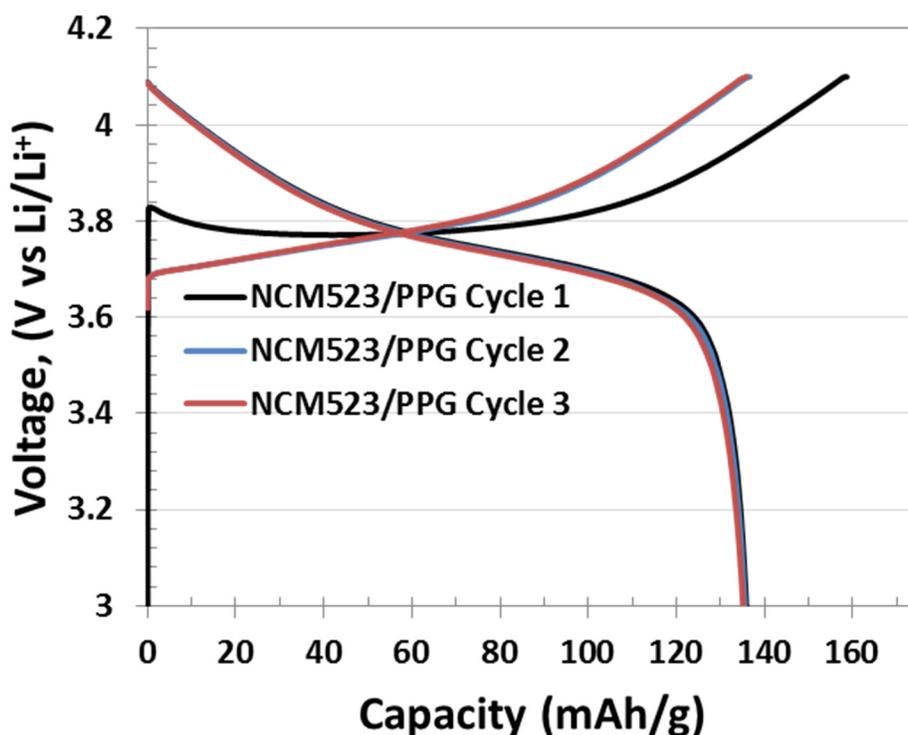
Figure 12: First three voltage profiles for NCM523 cathode powder soaked in water for 48 hours and then dried and coated onto aluminum foil using the experimental multi-component aqueous binder, versus Li with 1.2 M LiPF$_6$ in EC:EMC (3:7 by wt.) electrolyte at a C/10 current rate and 30°C, with an upper cutoff voltage of only 4.1 V (compare to Figure 4)
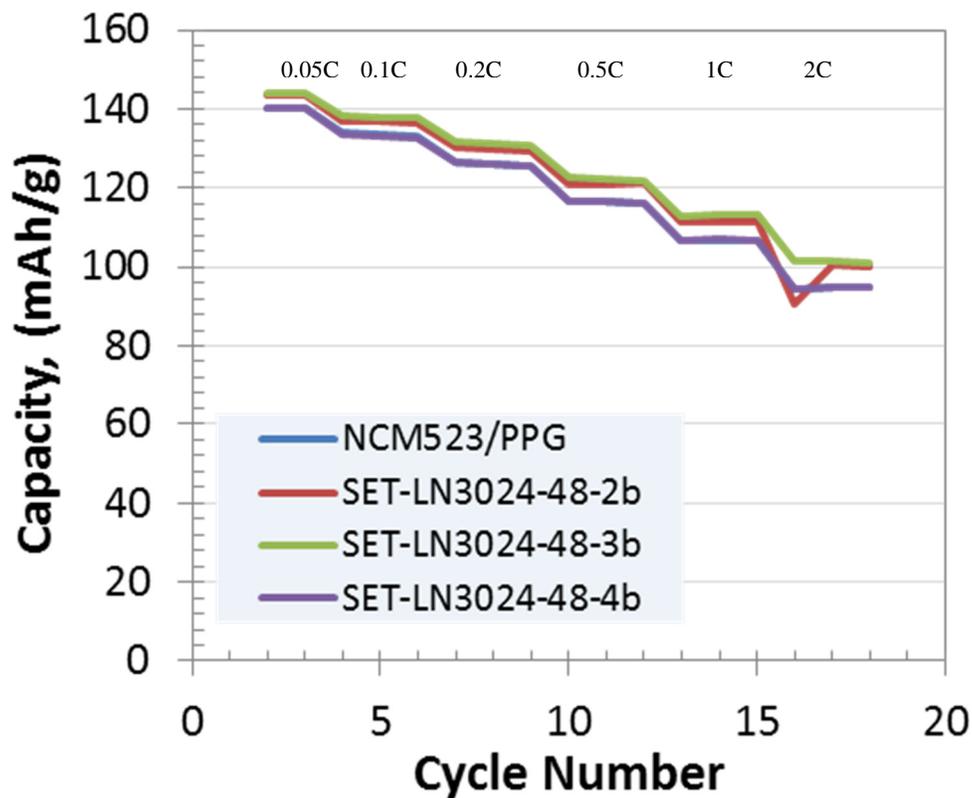
Figure 13: Discharge capacity for rate performance tests for water soaked NCM523 powder and coated onto aluminum foil using the experimental multi-component aqueous binder, versus Li with 1.2 M $LiPF_6$ in EC:EMC (3:7 by wt.) electrolyte, 3.0 – 4.1 V, and 30°C (capacity is lower due to only 4.1 V cutoff)

Baseline NCM523 Powder using Conventional PVDF Binder in NMP:

A conventional NCM523 electrode using PVDF binder in NMP was fabricated using Argonne CAMP Facility's pilot-scale coater. Half cells were made and tested with the resulting electrode – the results of which are shown in Figures 14, 15, and 16.
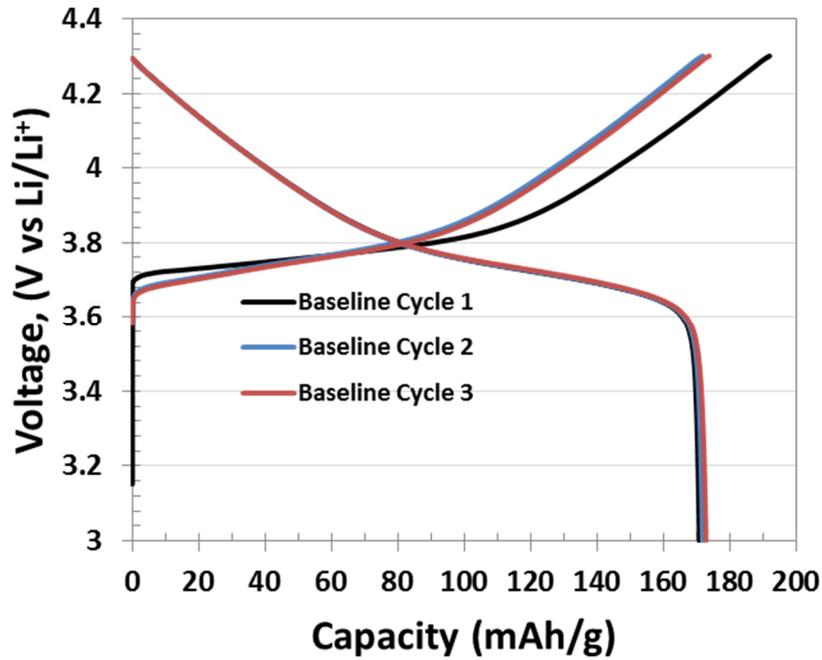
Figure 14: First three voltage profiles for baseline NCM523 cathode powder coated onto aluminum foil using convential PVDF binder in NMP, versus Li with 1.2 M LiPF6 in EC:EMC (3:7 by wt.) electrolyte at a C/10 current rate and 30°C, with an upper cutoff voltage of 4.3 V.
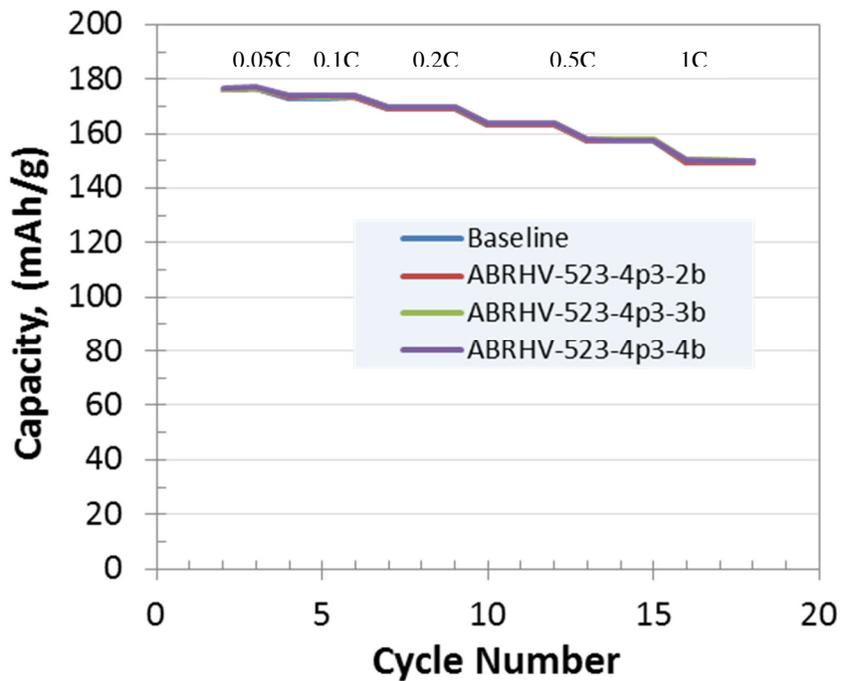
Figure 15: Discharge capacity for rate performance tests for baseline NCM523 cathode powder coated onto aluminum foil using convential PVDF binder in NMP, versus Li with 1.2 M LiPF$_6$ in EC:EMC (3:7 by wt.) electrolyte, 3.0 – 4.3 V, and 30°C
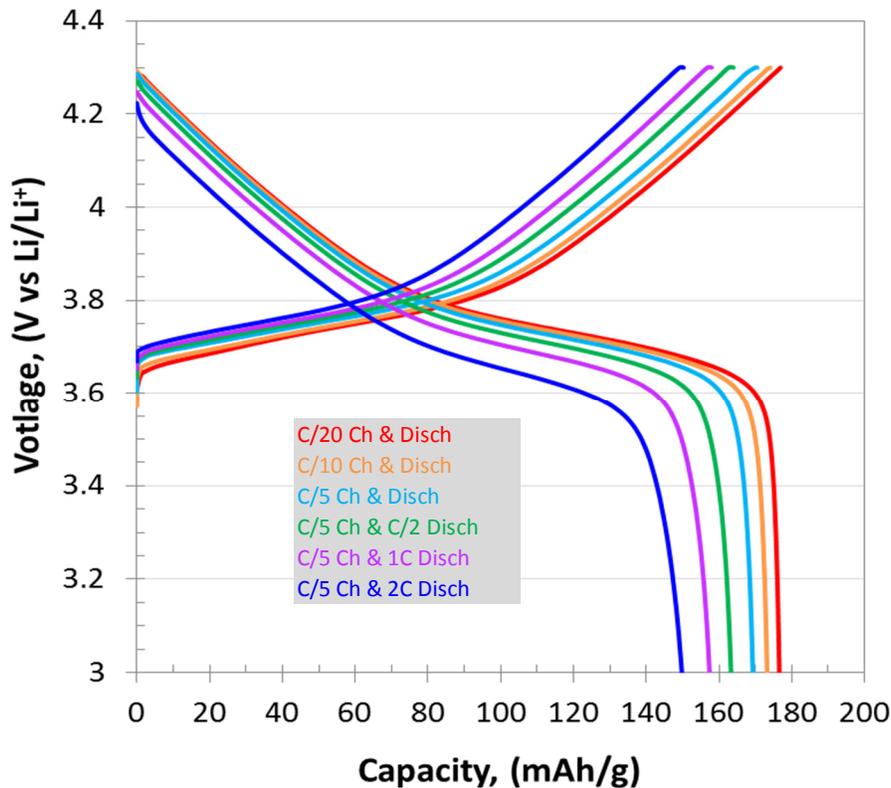
Figure 16: Voltage Profiles from rate performance tests for baseline NCM523 cathode powder coated onto aluminum foil using convential PVDF binder in NMP, versus Li with 1.2 M LiPF$_6$ in EC:EMC (3:7 by wt.) electrolyte, 3.0 – 4.3 V, and 30°C

Task 2: E-coat Cathode

PPG E-Coated LFP Electrodes Tested at Argonne:

Aqueous e-coated electrodes were made by PPG and tested at Argonne under this CRADA effort to establish proof of concept. LFP cathode powders were used because of their sub-micron particle size, which should e-coat more readily than the larger particles (~10 µm) typically obtained for NCM materials. Two of the experimental electrode coupons made by PPG via aqueous electrodeposition onto carbon-coated aluminum foil used the latest experimental aqueous binder. The composition and thickness of these electrodes is shown in the following table.

Sample	LFP/C65/Binder	Thickness
15-AHO-038-A-6	86.5/9/4.5	39 µm
15-AHO-039-A-3	77.5/18/4.5	50 µm

Argonne evaluated the electrochemical performance of these electrodes in half cells with a voltage window of 2.75 to 4.0 V and formation at a C/10 current rate. The voltage profile of these electrodes is shown in Figure 17 for uncalendered (A3, A6) and calendered (A3C, A6C) conditions. As can be seen from the figure, calendering improved the performance, especially for the A6 electrode. However, the voltage profile from these experimental e-coated LFP electrodes are not as flat as typically obtained from conventionally-made LFP electrodes, indicating that more development is still needed.
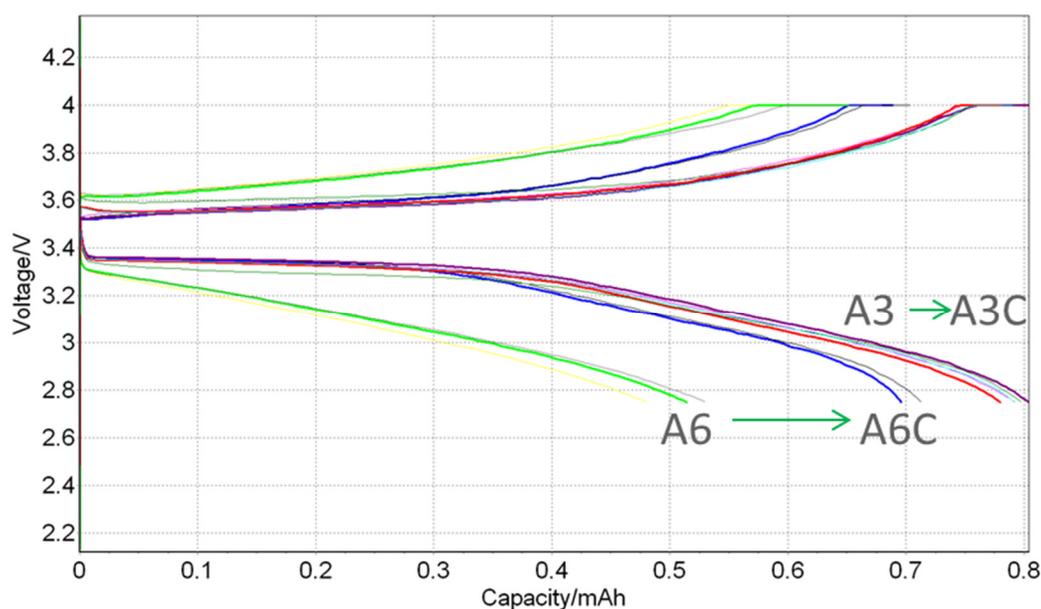
Figure 17: Voltage Profiles for LiFePO$_4$ (LFP) e-coated onto aluminum foil, versus Li with 1.2 M LiPF$_6$ in EC:EMC (3:7 by wt.) electrolyte, 2.75 – 4.0 V

These cells were further evaluated for their rate performance capability (C/24 to 2C) and then life cycle tested at a C/3 current rate. The results of these tests are summarized in Figure 18. A slow rate capacity was achieved with these electrodes, which is lower than the conventionally-made LFP electrode capacity. The capacity retention of these electrodes during cycling at the C/3 rate is very good as can be seen from the figure. Overall, these results demonstrate that e-coating of lithium-ion battery electrodes is possible and should be developed further.
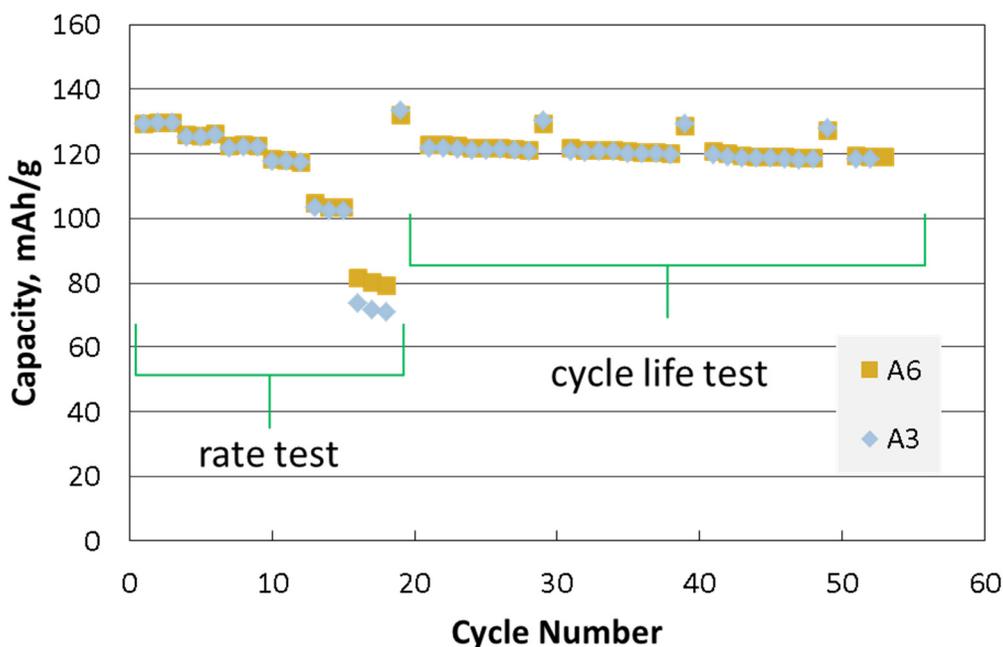
Figure 18: Discharge capacity for rate performance (C/24 to 2C) and cycle life tests (C/3 current rate) for LiFePO$_4$ (LFP) e-coated onto aluminum foil, versus Li with 1.2 M LiPF$_6$ in EC:EMC (3:7 by wt.) electrolyte, 2.75 – 4.0 V

Task 3: Active Material Characterization

pH and Zeta-Potential Measurements:

Key to designing an e-coating binder system is a full understanding of the surface moieties of all particles involved in the electrode. Some of the particle properties to monitor (and modify) include the zeta potential and the pH. A collection of representative materials used in lithium-ion batteries was assembled by Argonne and shared with PPG. Argonne performed the pH measurements (1 part material to 10 parts water), while PPG conducted the zeta-potential measurements. These results are summarized in the tables below for a representative variety of active materials (positive and negative), carbon additives, and binders.

Common Name	Type	Material	Water added at 10:00 am		pH Reading	
			1 hour	6 hour	73 hour	11 days, 3 hr
H2O (ref.)	W	18 MΩ H2O from Millipore (+24 hr degassing) -> used to fill all vials	8.96	8.72	7.86	8.18
$LiMn_2O_4$	C	Toda 4V Spinel, HPM-9051B, Lot#: 9110504	9.38	9.40	9.37	9.20
$LiFePO_4$	C	Lithium Iron Phosphate, Hanwha Chemical SafEnPo, LFP-1000, Lot#:U1207122em	9.51	9.71	9.22	9.75
$LiMn_{1.5}Ni_{0.5}O_4$	C	NEI Corp. 5V Spinel, SP-10	10.77	10.82	10.64	10.10
$LiCoO_2$	C	BTR LCO, 3000-C	10.82	10.81	10.43	9.60
NCM 111	C	Toda, original, NM3100	11.22	11.34	11.39	10.97
HE-5050	C	Toda HE-5050, Lot 5-P767	11.23	11.25	11.22	10.73
NCM 424	C	Toda NCM 424, NM4100L, Lot# 7720802	11.43	11.54	11.61	11.23
NCM 111 w/ Add	C	Toda NCM 111, NM-3102h	11.52	11.69	11.88	11.69
NCM 523	C	Toda NCM 523 (04ST), Lot#:240202	11.74	11.86	11.99	11.94
NCM 622	C	ECOPRO NCM 622, NCM040-10A	12.06	12.18	12.35	12.39
NCA	C	Toda, original, NAT-1050, Lot#: 1230403	12.54	12.58	12.70	12.70
NCA w/ BO	C	Toda NAT-7051, Boron oxide, Lot# 1130614	12.57	12.60	12.66	12.68
PVDF	B	Solef 5130	8.49	8.19	8.16	-
CMC	B	MAC350HC	-	6.70 (jell)	6.60 (still jell)	6.53
PAA	B	Poly acrylic acid, 450,000 Mv	-	2.40	2.45	2.43
SFG-6	A	Timcal Timrex Graphite	5.68	5.85	6.16	6.33
MAG-E	A	Hitachi Chem graphite, Lot#: 130808	8.52	8.30	7.33	7.02
A12	A	Phillips 66, Cpreme A12	8.63	8.27	7.31	7.30
SLC1520P	A	Superior Graphite, Lot#: 022626-376-551	8.81	8.52	7.45	7.62
LTO	A	Lithium Titanate, BE-10, NEI Corp. Li4Ti5O12	11.81	11.83	11.89	11.84
C45	A	Timcal Carbon Black	Cannot Measure	-	-	-

Setup -> 1 gram of powder in 10 gram deionized + degassed H2O in glass vial (however PAA and CMC x3 amounts and in amber nalgene)

18 MΩ H2O from Millipore (+24 hr degassing by flowing nitrogen through water) -> pH = 7.03 immediately following degassing

Material	Zeta Potential (mv)		
	Test 1	Test 2	Avg
NCM 523 (Toda 04ST)	0.46	0.43	0.45
NCM 111 (Toda NM-3102h)	0.54	0.81	0.68
NCM 424 (Toda lot #7720802)	0.47	0.95	0.71
LiMn2O4 (Toda 4V spinel HPM-9051B)	-3.55	-2.14	-2.85
$LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM 622, ECOPRO)	0.95	0.70	0.83
$LiNi_{0.8}Co_{0.15}Al_{0.05}(BO_3)_{0.01}O_2$ (Toda NAT-7051)	2.49	2.89	2.69
$Li_{1.2}Ni_{0.15}Co_{0.1}Mn_{0.55}O_2$ (Toda HE-5050 lot 5-P767)	-6.67	-7.91	-7.29
$LiMn_{1.5}Ni_{0.5}O_4$ (5V spinel, SP-10, NEI Corp.)	14.20	16.06	15.13
Timcal C45	4.01	3.82	3.92
Timcal Timrex SFG6L	-2.02	-3.05	-2.54
CPreme A12 graphite (Conoco Phillips)	0.67	0.95	0.81
Mag-e graphite (Hitachi Chemical)	0.22	0.49	0.36
Graphite (SLC1520P, Superior Graphite)	-0.26	-0.26	-0.26
Lithium Titanate (BE-10 $Li_4Ti_5O_{12}$, NEI)	-49.22	-43.46	-46.34
LFP (LFP-1000, Hanwha Chemical)	-13.44	-22.85	-18.15
LCO (BTR)	0.16	1.50	0.83
PVDF (Solef 5130)	-4.68	-5.23	-4.96
Measurements were made on 1% dispersions in deionized water. The samples were first sonicated for 25 minutes using a Branson Sonifier 450 and then stirred overnight to allow equilibration before measurement.			

pH and ICP Analysis of NCM523:

More extensive studies of pH &ICP were conducted for the baseline NCM523. These measurements were done in two different routes. In the first route; two samples, each containing ~ 1g of active material, mixed with 10 cc and 30 cc of ultrapure water (18MΩ Millipore water, degassed under nitrogen for 24 h; pH =7.16), respectively. After mixing, pH measurements were done in predetermined time intervals for both samples. In the meantime, after each pH measurement, ~2 mL of supernatant was withdrawn from the sample having 3.3% solid ratio.

In the second route; nine identical samples containing ~ 1 g of active materials were mixed with 10 cc of ultrapure water (18MΩ Millipore water, degassed under nitrogen for 22 h, 30 min; pH =6.93).

First group – pH studies

pH measurements were done for two samples having different solids to liquid ratio. The pH of first sample (labeled as virgin) having 10% solids loading was found to increase immediately after mixing with ultrapure water. pH was found to stabilize at 11.96, after 2 weeks (336 hours) of water soaking time was passed (Figure 19). Once it stabilized, ~ 2mL of supernantant was

withdrawn for ICP analysis of Li and TM. Sampling for ICP was continued weekly till the end of 4th week (672nd hour). It seems after 2 weeks, there is no gradual change in the pH, instead it slightly decreases (e.g: pH= 11.88 at 672nd hour). It should be noted that, after withdrawing the liquid, the solid to liquid ratio also changes. There was no filtration conducted while sampling the liquid.

The pH of second sample having 3.3% of solids loading (1g/30cc) increased till 168th hour and then decreased to around 10 at 672th hour. For the ICP analyses, ~ 2mL of the liquid was continously withdrawn at the predetermined times. The continous withdrawing of liquid at the predetermined time intervals changed the solid to liquid ratio of the test sample. By the time the solvent (ultrapure water) amount was decreased, it created saturated conditions. There was no filtration conducted while sampling the liquid.

	Sample description	Time intervals for pH measurement	ICP sampling	Notes
First group	1g/10cc	0-1-2.5-3-4-24-72-168-336-508-672 h	From 336th to 672th hour	After pH stabilized
	1g/30cc	0-1-2.5-3-4-24-72-168-336-508-672 h	@ all predetermined times	Changing solid/liquid ratio
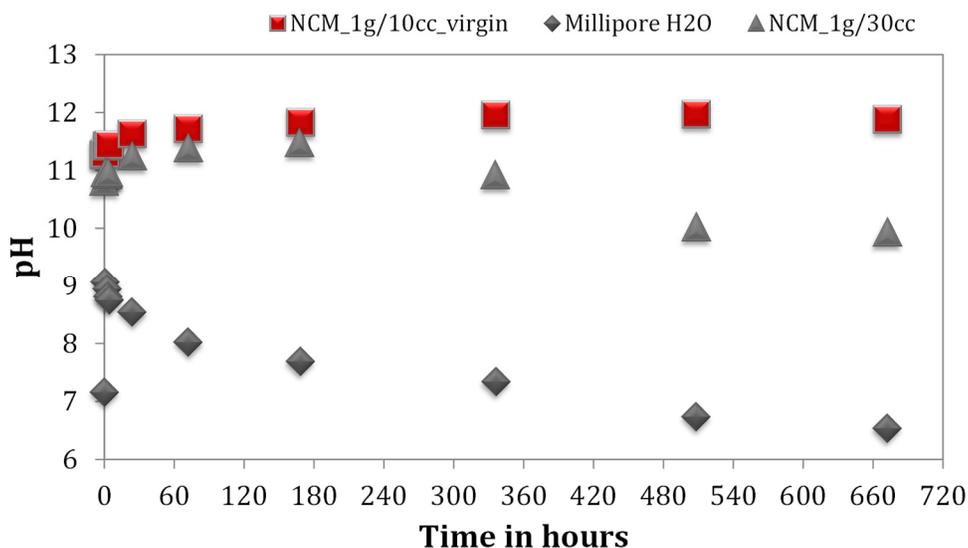
Figure 19: pH trend of water soaked NCM_523 particles as a function of time

First group – ICP analyses

ICP analyses were done to determine the Li, Ni, Co, Mn contents. Figure 20 shows the lithium concentrations for the withdrawn liquids. As noted above, continuous sampling changed the solid

to liquid ratios. As the liquid amount decreased, it was hard to withdraw liquid without getting solids from the settled mixture. Although utmost importance was given while sampling the liquid and there was no solids observed, the liquid was not filtered at any levels. The spike in the lithium dissolution levels might be due to pull from the solid part.
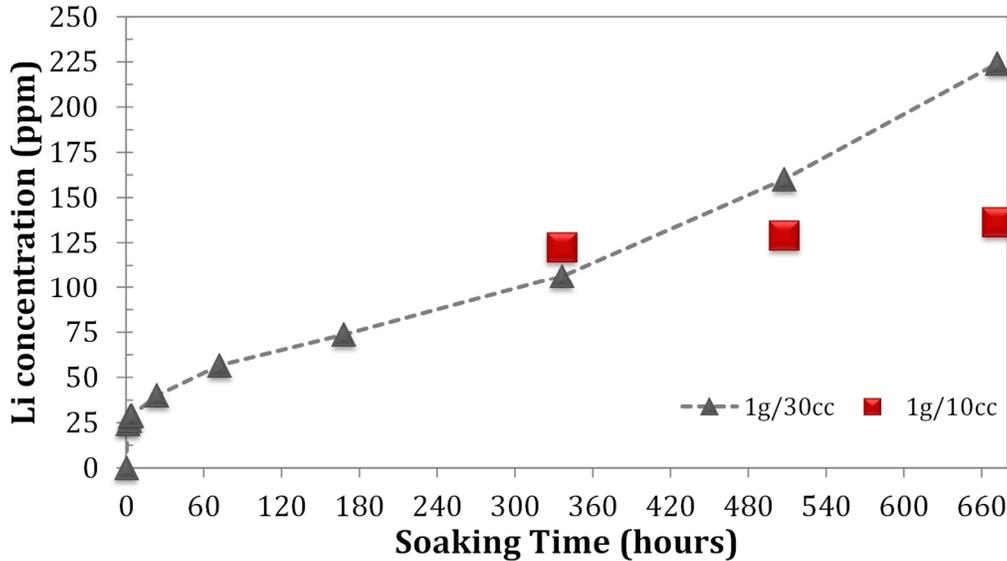
Figure 20: Lithium dissolution in ultrapure water (different solid/liquid ratios)

In parallel with the analysis of lithium content, transition metal (TM) content was also analyzed. It was seen that, no cobalt dissolution took place whereas nickel and manganese were detected in liquid sample for both sample having 3.3 % (Figure 21) and 10 % (Figure 22) solid ratio. Manganese dissolution for the 3.3 % solid loading seems to stabilize after 1 week of water soaking duration passes and keeps about the same concentration till the end of 3rd week. This unusual dissolution behavior might be contributed to a possibility of solid withdrawal while sampling the liquid, although there was no cobalt value detected. Nickel dissolution, on the other hand, spikes in the first three hours (0.91 ppm) in the liquid and seems to decrease gradually after 3rd hour till the end of 3rd week to a value of 0.041 ppm in the liquid.
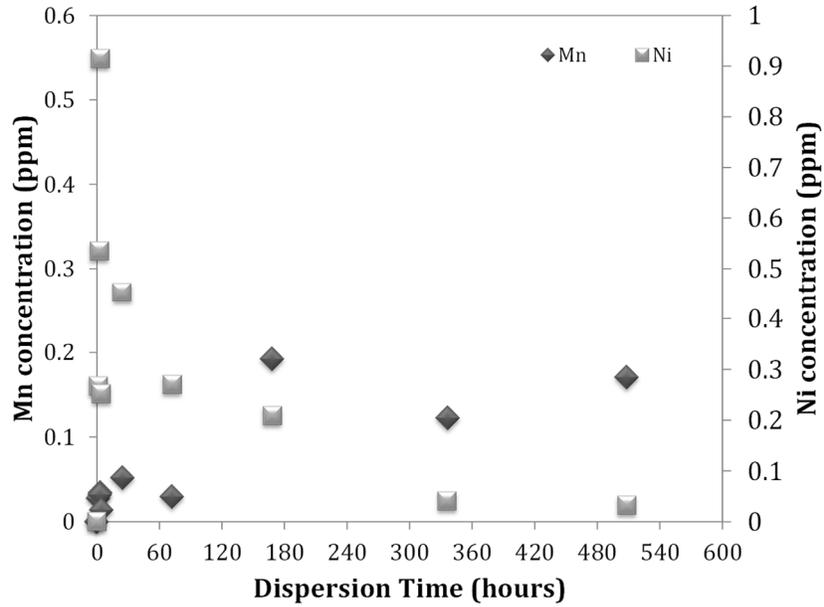
Figure 21: TM dissolution in ultrapure water for the sample with 3.3% solid ratio

After pH stabilizes at the end of second week (Figure 19) for the sample with 10% solid loading, an aliquot from the liquid was withdrawn weekly for ICP analyses. Lithium concentration was already given in Figure 20, indicating a stable plateau after 2nd week of water soaking. Compare to the lower solid loading; this sample also showed similar Mn dissolution values around 0.14 ±0.02 ppm for 2 and 3 weeks of soaking time (Figure 22). Similar behavior for nickel was also observed: at the end of second week the nickel was measured as 0.067ppm and it was decreased to 0.041 ppm on 3rd week.
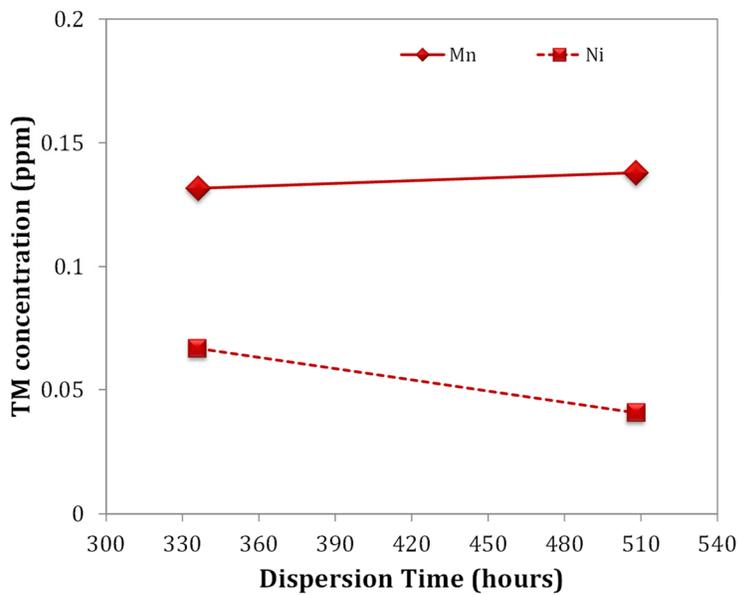
Figure 22: TM dissolution in ultrapure water for the sample with 10% solid ratio

Further, we also analyzed Li and TM concentrations of the dried powders as a counter check point to observe lithium and transition metal contents after soaking in water for a definite time. The resultant average compositions based on ICP analyses are listed in Table 1. As it can be seen, even after 4 weeks of water soaking the lithium content appears to change more obvious than the transition metals in the solid, which also seems to be a slight change. Transition metals, on the other hand, seem to keep intact within the host structure.

Table 1: ICP analysis of water soaked (after 4 weeks)/dried samples vs pristine

Material	Li (ppb)	Mn (ppb)	Ni (ppb)	Co (ppb)	Ave. Composition
Pristine (NCM_523)	16.06	40.06	70.84	28.63	$Li_{0.9553}Mn_{0.3011}Ni_{0.4984}Co_{0.2006}$
NCM in18MΩ H_2O (1g/10cc)_pH	15.54	39.50	70.11	28.19	$Li_{0.9363}Mn_{0.3006}Ni_{0.4994}Co_{0.2000}$
NCM in18MΩ H_2O (1g/30cc)_ICP	15.66	40.06	71.14	28.64	$Li_{0.9293}Mn_{0.3004}Ni_{0.4994}Co_{0.2002}$

(each value is an average of 3 readings)

Morphology

We also investigated the surface morphologies of secondary particles (agglomerates) before and after soaking in water. The comparison is shown below in Figure 23:

| Pristine NCM 523 | Water soaked sample (4 weeks) |
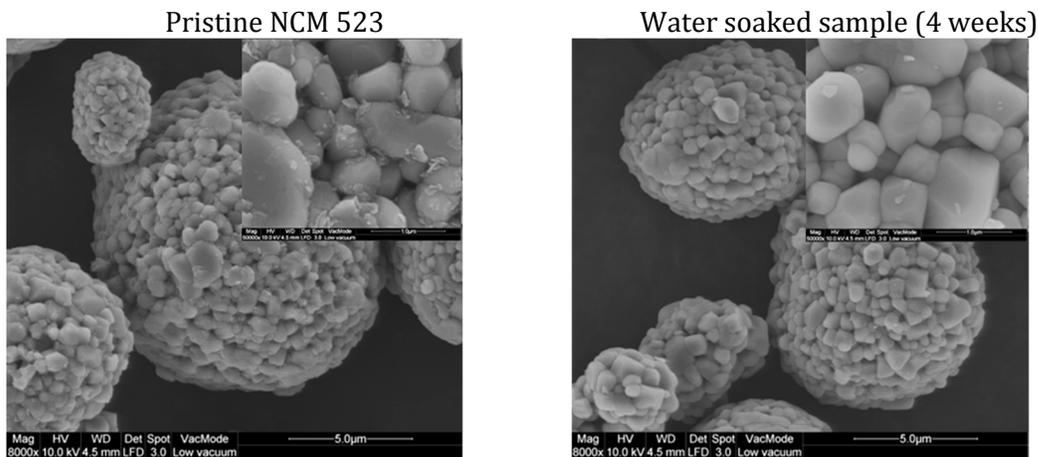
Figure 23: Surface morphologies of pristine vs processed powders

As it is seen, there is no apparent change with the particle size /morphology, although surface of pristine particles have flaky structures distributed throughout the surface; those were cleared of after soaking into water.

Second Group

In order to eliminate ambigiousness of the first test conditions, a second set of pH samples were prepared. 9 identical samples, containing ~1 g of active materials for each, were soaked into 10

cc of ultrapure water. Each sample is intended for exact time of water soaking and at the end of the predetermined time, each sample was filtered: the liquid and the vacuum dried solids were analyzed by ICP for the Li and TM contents. Detailed experimental plan is given in Appendix A.

	Sample description	Time intervals for pH measurement	ICP sampling	Notes
Second group (~1g/10cc)	Virgin-0	0-672 hours	none	
	#1	1 h	@ 1st h	At the end of pH measurements, samples were filtered and liquid was analyzed by ICP. Solids were vacuum dried and ICP analyses were done.
	#2	1–3 h	@ 3rd h	
	#3	1–3–24 h	@ 24th h	
	#4	1–3–24–48 h	@ 48th h	
	#5	1–3–24–48–168 h	@ 168th h	
	#6	1–3–24–48–168–336 h	@ 336th h	
	#7	1–3–24–48–168–336–504 h	@ 504th h	
	#8	1–3–24–48–168–336–504–672 h	@ 672nd h	

pH measurements (Figure 24) of the samples indicated an increase after dispersing the solids into ultrapure water, although this was within ±0.3 range for the first 2 min and could be regarded as similar.
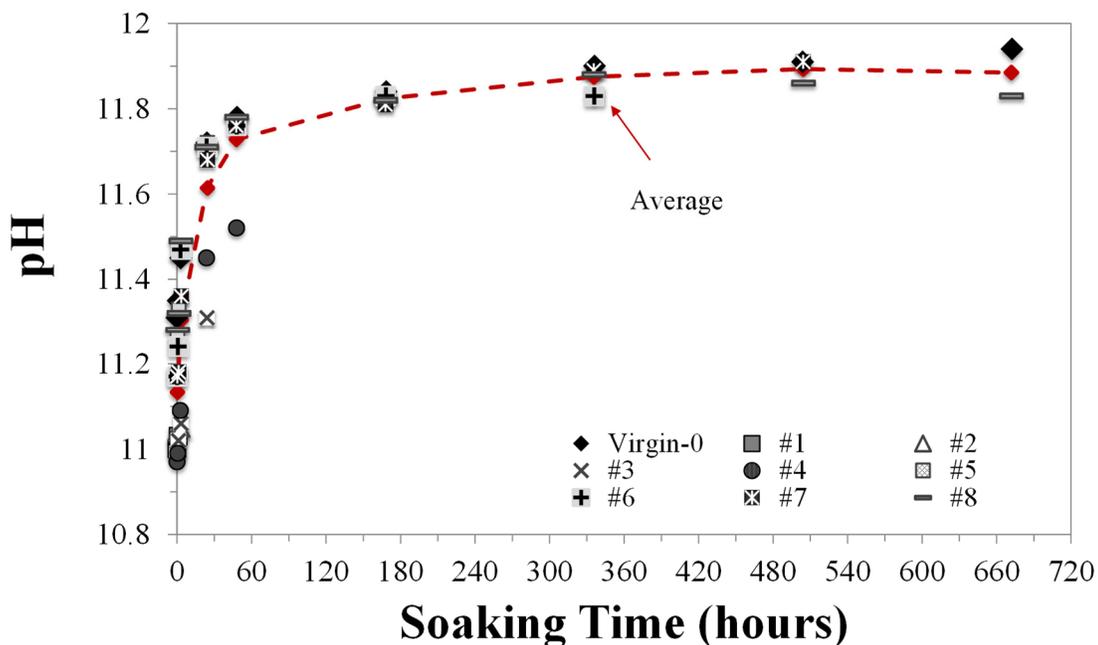
Figure 24: pH trend of water soaked commercial NCM 523 cathode powders

Figure 25 shows the concentration of elements dissolved from the solid in ultrapure water as a function of dispersion time. While lithium dissolution appears more severe (>100 ppm), the

transition metal dissolution is in the range of ~ 0.09 – 0.25 ppm within the first week of dispersion time. Note that, the second group of this study also showed cobalt dissolution that wasn't detected in the first group samples. Lithium dissolution is found to stabilize at the third week which was also in good agreement with the pH trend.
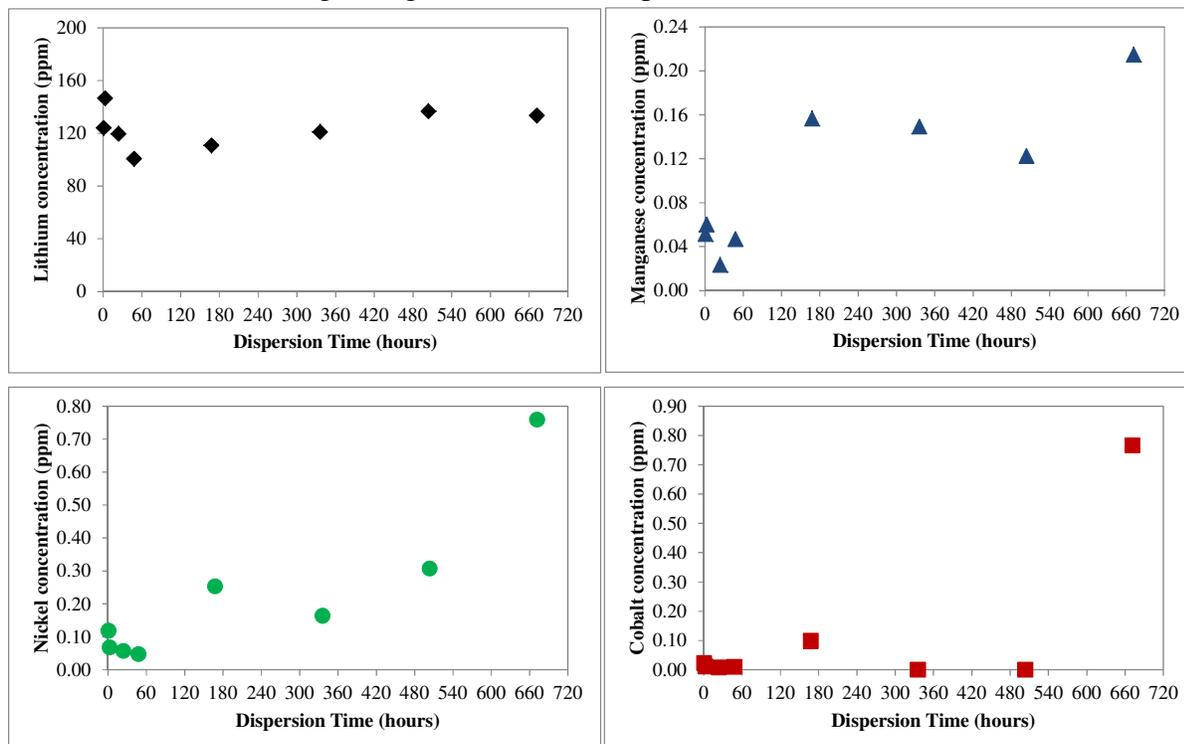
Figure 25: ICP analyses of elements in the solvent as a function of dispersion time

Li and TM concentrations of the dried powders were also analyzed by ICP as a counter check point to observe remaining lithium and transition metal contents. The resultant average compositions based on ICP analyses are listed in Table 2.

Table 2: ICP analysis of water soaked/dried samples vs pristine

Material/ Soaking Time	Ave. Composition
Pristine (new measurement)	$Li_{1.0097}Mn_{0.2966}Ni_{0.4999}Co_{0.2005}$
1 hour	$Li_{1.0015}Mn_{0.2979}Ni_{0.5018}Co_{0.2003}$
3 hours	$Li_{0.9972}Mn_{0.2983}Ni_{0.5017}Co_{0.2001}$
1 day	$Li_{1.0051}Mn_{0.2983}Ni_{0.5016}Co_{0.2001}$
2 days	$Li_{1.0008}Mn_{0.2977}Ni_{0.5016}Co_{0.2006}$
1 week	$Li_{0.9972}Mn_{0.2994}Ni_{0.5002}Co_{0.2004}$
2 weeks	$Li_{0.9640}Mn_{0.3001}Ni_{0.4994}Co_{0.2005}$
3 weeks	$Li_{0.9641}Mn_{0.3004}Ni_{0.4989}Co_{0.2006}$
4 weeks	$Li_{0.9765}Mn_{0.3010}Ni_{0.4982}Co_{0.2008}$

(each value is an average of 3 readings)

Task 4: Particle Size Study

Sub-micron NCM523 Powder via Milling:

Preliminary e-coating experiments with LFP cathode particles showed promising results and the hope exists that e-coating of NCM/NCA-based powders will also be possible. It remains to be seen what the influence of cathode particle size will be in e-coating systems. While LFP cathode particles are typically submicron, most NCM/NCA particles are made via a different synthesis route that yields particles in the 5 to 30 µm size. It was beyond the scope of this CRADA to create a new synthesis route for NCM/NCA cathodes that would yield submicron particles. Instead, a relatively simpler route was taken based on milling.

Detailed task steps:
1.   Generate submicron particles of NCM or NCA either by classification or milling
2.   Analytical measurements of submicron particles and their pristine version
3.   E-chem test before and after processing
4.   Deliver submicron particles (20-50 g from nano milling, ball milling, air classifying) to CAMP for electrode build

Results:
We started this task using commercially available NCM 523 powders. The target was to obtain 300 nm particle size with a sharp particle size distribution for an advanced wet coating system. These powders were processed using three different methods to obtain submicron size of the pristine.

The pristine material and its specs are given below:

Material   : TODA 523-NCM 04ST
Tap density   : 2.56 g/cc
D10/D50/D90 : 6.39/11.01/19.08 µm
Dmean   : 12.03 µm
Morphology   : Spherical ~ quasi-spherical
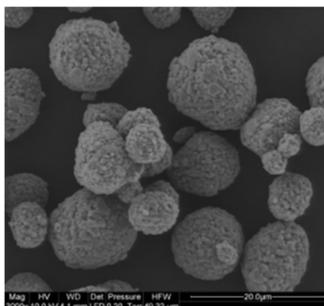
SEM of pristine material

Size reduction and classification
First trials were conducted using colloidal milling principles (in isopropanol, NMP or water) in a Retsch Planetary PM 400 ball-mill. The experimental conditions/variables are given in Table 3. The listed rotation speeds correspond to the central wheel rotation; the ball-mill provides three vial rotations for every one wheel rotation and provides a higher net rate range of 300 – 1200 rpm and higher power input to the system. Rotation speeds are referenced with respect to the wheel rotation (100 to 400 rpm) for clarity. After milling, the vials were allowed to rest and cool down to room temperature. The powder was then filtered in a 12 inch diameter, 180 - 250 µm sieve for 6 -10 minutes in a W.S. Tyler Ro-Tap motorized sieve shaker to isolate the zirconia balls. The powder was collected and used for analysis.

Table 3: Experimental conditions/variables for size reduction of commercial NCM 523 material

Material	Toda 523- NMC
Jar and ball material	ZrO_2 (fixed), 500mL
Ball size	1-2-3-5 mm or mixture of those
Ball to powder weight ratio (BPR)	6.7:1 – 3.5:1 – 4:1
Milling time	2 – 40 hours
Rotation speed	100 – 400 rpm
Experimental constants	Original NMC material, reversal rotation

A general summary of the size reduction/classification study is listed in Table 4 and Appendix C.

Table 4: Size reduction and classification study, particle size analysis

Sample	Milling Cond**	PSA (D10/D50/D90)	Remarks
NCM 523-org.	-	6.39/11.01/19.08µm (Dmean=12.03µm)	• Pristine material
NCM 523 - IPA milled	In IPA (4h milling)	0.05/0.18/0.89µm (Dmean=0.30µm)	• Difficulty in removing all IPA from the dried powder (confirmed with TGA) • Strong aggregation • Electrode slurry got clumped→uneven electrode surface (due to residual IPA inside the pores; binder is not soluble in IPA) • NMP usage increased due to high surface area of the milled powders. Preliminary e-chem data for half-coin cell was done by MERF.
NCM 523 - NMP milled	In NMP (2 h milling)	0.05/0.20/0.94µm (Dmean=0.34µm)	• Processed into pouch cell (data will be provided by CAMP)
NCM 523 - Water milled	In DI water (2 h milling)	0.05/0.22/1.01µm (Dmean=0.39µm)	• Difficulty in removing all water from the dried powder (confirmed with TGA) • Electrode slurry got clumped → uneven electrode surface • Increase NMP percentage in the slurry
Microfluidizer	10 g NMC in 90 g water	0.39/0.91/4.99µm	• Strong aggregation (no effect on PSA) • PSA was done in T20 solution • Recommendation: use of surfactants to eliminate aggregation
Air classifier	-	6.15/10.62/18.56 µm (Dmean=11.63 µm)	• Negligible effect due to lack of submicron particles

*: Best values from each process
**: @400rpm; Ball/Powder Ratio = 4:1

A series of analytical work has been done to evaluate processed powders. Figure 26 shows the morphologies of both pristine and ball milled samples. Although particle size analysis indicate a D90 value of 0.89 µm for the milled sample, SEM images shows substantially higher particle size along with fine powders. This can be correlated with the strong aggregation after drying these powders. As PSA uses ultrasounds, these aggregates are easily segmented into fine particles which results in true size analysis of the said powders. A higher magnification was also included in Figure 26 to show the larger particles are actually comprised of very fine particles. We also conducted BET analysis of the ball milled samples as a check point to confirm the particle size/surface area. The pristine material has a surface area of 0.28m^2/g (value obtained

from the supplier) and this value is significantly increased to a value of ~17 m^2/g which suggests finer particles are obtained. XRD analysis (Figure 27) also confirms the nano character of the powders: the peak width at desired orientation becomes larger. No additional peaks in the ball milled sample confirm that no significant contamination occurred during milling in zirconia medium. In order to confirm that, we also ran ICP analysis for the ball milled sample and saw no zirconia impurities.

Pristine NCM 523   Ball milled sample (in IPA)
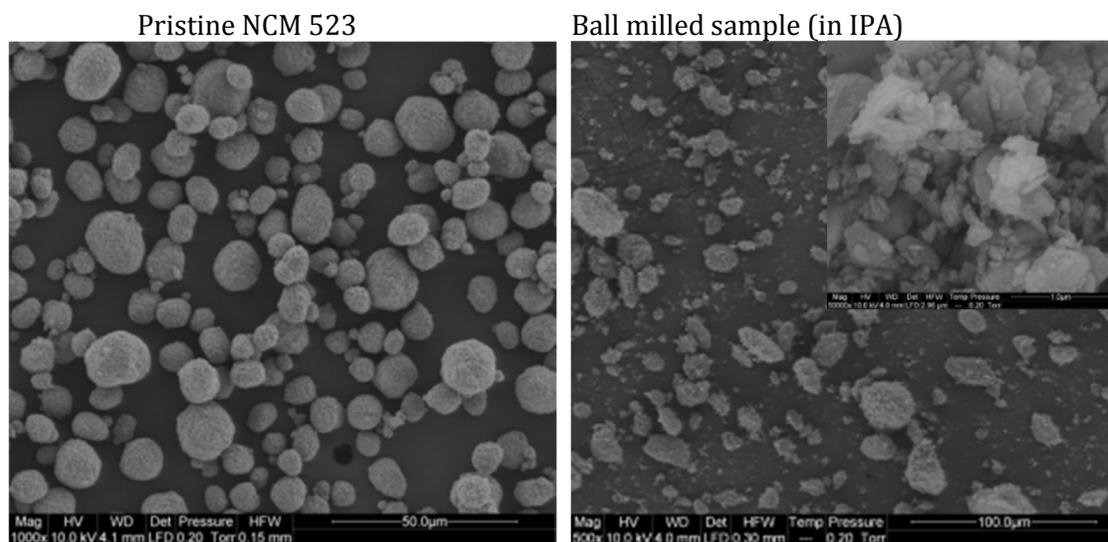
Figure 26: Morphologies of NCM 523; pristine vs ball milled samples
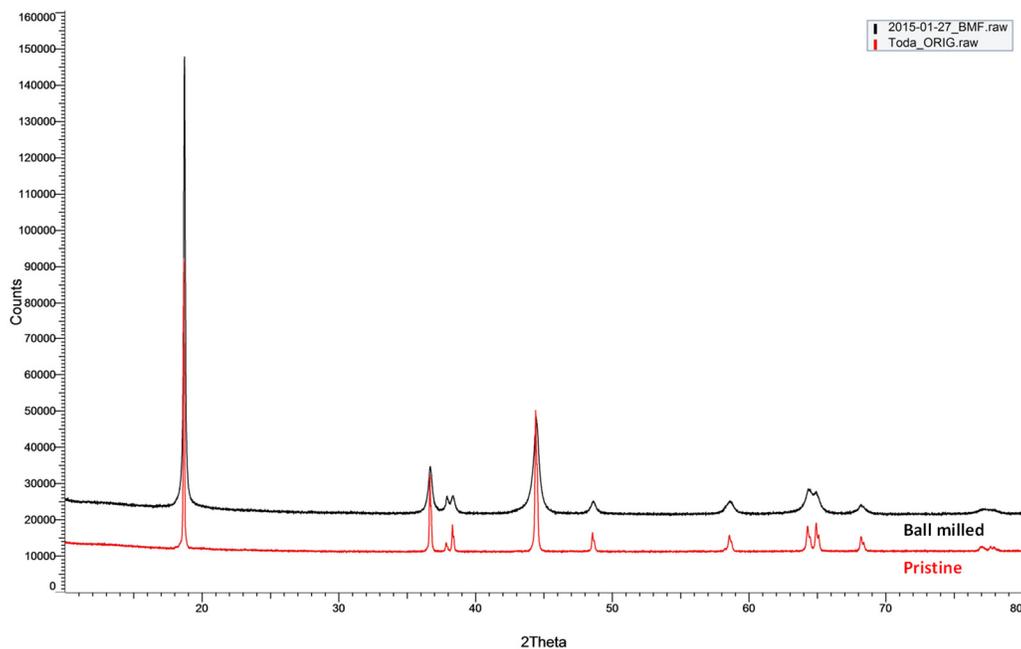
Figure 27: X-ray diffraction patterns; pristine vs ball milled samples

Electrochemical tests of ball milled NCM523:

Commercially available NCM523 powder was initially milled in water or isopropanol to around 300 nm. However, electrodes could not be later made with these powders using PVDF-NMP binders because the milled powders contained too much residual water, which caused gelling problems in the slurries. This problem was solved by switching to NMP as the solvent during milling.

Electrochemical performance of both pristine and ball milled samples were evaluated in a conventionally built (NMP-PVDF binder) half-cells in a voltage window of 3.0 to 4.3 V at C/20 current rate for the first cycle and at C/10 current rate for the rest of the cycles (Figure 28 a&b). Initial discharge capacities (at C/20) of 162 mAh/g and 151 mAh/g were achieved for the pristine and ball milled samples, respectively. Following cycle (e.g. 2nd cycle) at a C/10 current rate delivered 160 mAh/g capacity for the pristine material whereas 142 mAh/g capacity was observed for the ball milled sample. The voltage profile of the half-cells using the NMP-milled NCM523 cathode powder with NMP-PVDF binder is shown in Figure 28c with a comparison to the baseline NCM523. The large amount of damage inflicted on the milled particles negatively impacted their electrochemical performance. However, these milled powders may be useful for development of the e-coating binder system for NCM materials while new synthesis routes are created or modified to make smaller particles.

(a)

(b)

(c)
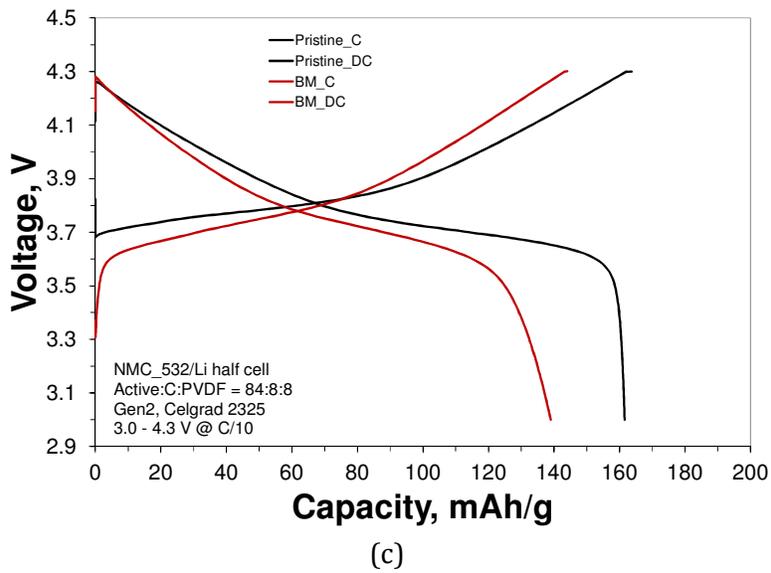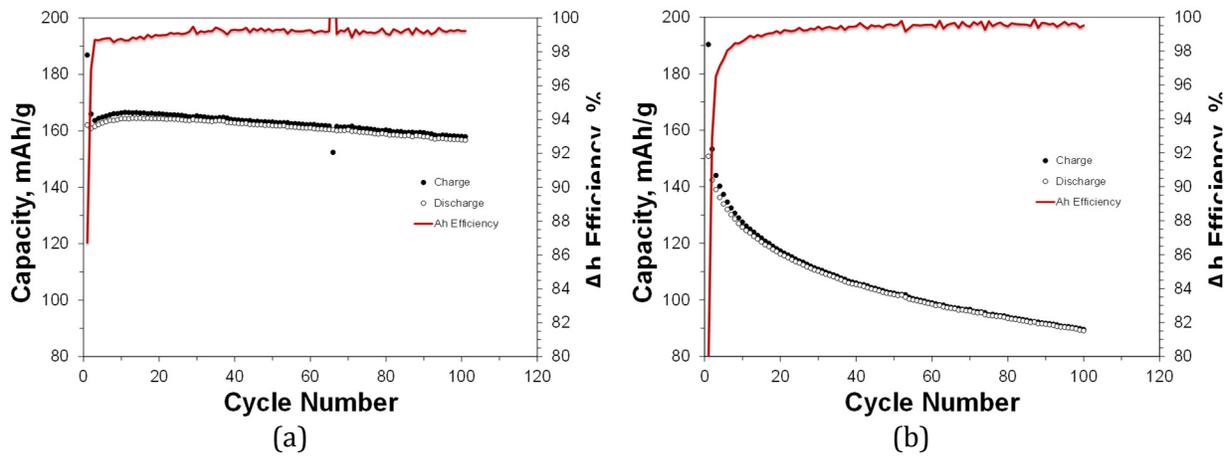
Figure 28: Cycle performance of pristine (a) and ball milled (b) powders and voltage profile (at 3rd cycle) comparison (c).

APPENDIX A – pH measurement studies

Solvent/active used

18MΩ Millipore water received on/at **Nitrogen purging started on/at**	**10/20/2015 @12:00 PM** **10/20/2015 @ 12:10 PM**	**pH = 5.98**
Duration of N_2 purge	**21 hours, 20 min** **10/21/2015 @ 9:30AM**	**pH =6.93 @ 9:45 AM**
Active material **PSA, (D10/D50/D90 and Dmean), µm**	NCM_523 (Toda_commercial) 6.39/11.01/19.08 µm and D_{mean} = 12.03 µm	

Tools/equipment descriptions

pH-meter/electrode	**Accumet excel XL15/Accucap ™ combination pH electrode; glass body, refillable silver free gel electrolyte**
pH buffer solutions	pH=4, 7 and 10 (Fisher Chemical, color-coded red, yellow and blue)
Filter paper	Cellulose nitrate filter paper, pore size = 1.2µm
Vacuum drying oven	Thermo Scientific; @-29.97 in.Hg; 20-24 hours
Sample vials	20 mL glass
Measuring cylinders	Glass, graduated, 10 mL (class A)

Experimental steps/details

1. All glass vials (20cc), filter funnels, petri dishes, measuring cylinders were washed with Millipore water and dried at 95°C overnight
2. 9 samples were prepared: Approximately 1 g of active material was mixed with 10 cc Millipore water. In the first 2 min, pH measurements were done and recorded. After each measurement the mixtures were shaken and left to settle till the next measurement. After the determined time of water soaking for a target sample was passed, it was filtered.
3. Prior to use the filter paper, rinse it with Millipore water (in order not to break into pieces), then fold it and place it to the funnel and let it dry.
4. After filtration there are solids remaining in the vial. Once the filtered liquid recovered and bottled for ICP analysis, rinse the vial and collect the remaining solids on the same filter paper. Put the filter paper in a glass petri dish and close the cover leaving a gap for water evaporation. Vacuum dry at 58°C for overnight. Duration~ 20-24 hours.
5. Recover the solids from filter paper after overnight vacuum drying. Weigh the solids. Sample for ICP analysis.

Experimental Plan – Second group of samples

Sample no	Virgin - 0	1	2	3	4	5	6	7	8
Time intervals	Initial	1 hour	3 hours	1 day	2 days	1 week	2 weeks	3 weeks	4 weeks
Date initiated	10/21/2015	10/21/2015	10/21/2015	10/21/2015	10/21/2015	10/21/2015	10/21/2015	10/21/2015	10/21/2015
Time Initiated	10:21 AM	10:18 AM	10:15 AM	10:12 AM	10:07 AM	10:04 AM	10:01 AM	9:58 AM	9:54 AM
Amount of active (g)	**1.07**	**0.995**	**1.025**	**1.007**	**1.032**	**0.996**	**1.011**	**1.066**	**0.998**
Date stopped	TBD	10/21/2015	10/21/2015	10/22/2015	10/23/2015	10/28/2015	11/4/2015	11/11/2015	11/18/2015
Time stopped	10:21 AM	11:18 AM	1:15 PM	10:12 AM	10:07 AM	10:04 AM	10:01 AM	9:58 AM	9:54 AM
pH @ 1-2 min	11.31 (@10:23am)	11.00 (@10:20 am)	11.04 (@10:17 am)	10.99 (@10:13 am)	10.97 (@10:09 am)	11.27 (@10:05 am)	11.17 (@10:02 am)	11.17 (@9:59 am)	11.28 (@9:56 am)
Active, g (dried)	TBM	0.919	0.958	0.945	0.962	0.9	0.962	0.969	0.935
Mass loss (g)	TBM	0.076	0.067	0.062	0.070	0.096	0.049	0.097	0.063

APPENDIX B – ICP analysis

Analysis of filtered liquid to examine Li and TM dissolution amounts

3 identical samples were prepared from each sample for measurement. And average data was recorded based on 3 readings.

- Calibration range for Li, Mn, Ni, Co = 0-200ppb (standards: 0, 2, 5, 20, 50, 100, 200 ppb)
- Dilution media consists of 2% HNO_3
- Dilution factor = 2500 (0-336 hours water soaked samples)

Analysis of vacuum dried solid to determine remaining Li and TM

3 identical samples were prepared from each sample for measurement. And average data was recorded based on 3 readings.

- Calibration range for Li, Mn and Co = 0-50 ppb (standards: 0, 2, 5, 20, 50 ppb)
- Calibration range for Ni = 0-100ppb (standards: 2, 5, 20, 50, 100 ppb)

First stock solution: ~75 mg of solid powder sample and 1 μL of aqua regia (3 mL HCL +1 mL HNO_3) were mixed and this mixture was then diluted into 100 mL of Millipore water.

Second stock solution: 30 μL of first stock was diluted into 100 mL Millipore water consisting 2% HNO_3.

APPENDIX C – High energy ball milling studies

Colloidal milling in IPA

	Material	ZrO$_2$ ball dia. (mm)	Ball-powder wt. (BPR) ratio	Duration (h)	Rotation speed (rpm)	D10/D50/D90 and Dmean	Remarks
#	*TODA 523 commercial*	*N/A*	*N/A*	*N/A*	*N/A*	*6.39/11.01/19.08 μm* *D_{mean} = 12.03 μm*	*-Tap density = 2.56 g/cc*
1	TODA 523	3 mm	**6.7:1**	4	300 rpm	0.05/0.22/0.96 μm **D_{mean} = 0.36 μm**	**- Zirconia contamination** - Close to target Action: Reduce BPR
2	TODA 523	1 mm	3.5:1	40	100 rpm for 20h, 150rpm for 10h, 200 rpm for 10h	0.06/0.26/1.11 μm **D_{mean} = 0.48 μm**	-No zirconia contamination, -Wide particle size distribution -Reduced BPR Action: Increase rotation speed
3	TODA 523	2 mm	3.5:1	4	300 rpm	0.05/0.22/0.99 μm **D_{mean} = 0.38 μm**	-No zirconia contamination, -Wide particle size distribution Action: Increase rotation speed and BPR
		5 mm	3.5:1	4	300 rpm	0.06/0.26/1.22 μm **D_{mean} = 0.53 μm**	
4	TODA 523	**2 mm**	**4:1**	**2**	**400 rpm**	0.05/0.20/0.93 μm **D_{mean} = 0.33 μm**	-No zirconia contamination, -Out of range for 5mm dia. Action: Use smaller ball diameters
		5 mm	4:1	2	400 rpm	0.06/0.30/1.92 μm **D_{mean} = 0.75 μm**	
5	TODA 523	1 mm	4:1	2	400 rpm	0.05/0.23/0.99 μm **D_{mean} = 0.39 μm**	-No zirconia contamination, -Close to target - 70% yield Action: Use a mixture of different ball diameters
		3 mm	4:1	2	400 rpm	0.05/0.23/1.04 μm **D_{mean} = 0.41 μm**	
6	TODA 523	**(1+3)mm**	**4:1**	**2**	**400rpm**	0.05/0.21/0.96 μm **D_{mean} = 0.35 μm**	-No zirconia contamination, -Hit the target - Try to reduce D90 -77% yield Action: Mix ball milled samples and re-run milling
		(1+2+3) mm	**4:1**	**2**	**400 rpm**	0.05/0.21/0.96 μm **D_{mean} = 0.36 μm**	
7	Mixture of ball milled powders from 4th and 6th experiment	**2 mm**	**4:1**	**2**	**400rpm**	0.05/0.18/0.89 μm **D_{mean} = 0.30 μm**	-No zirconia contamination, - Hit the target - Try to reduce D90 - 83% yield Action: Re-run for additional 2 hours to decrease D90
		(1+3) mm	4:1	2	400rpm	0.05/0.18/0.89 μm **D_{mean} = 0.30 μm**	
8	Mixture of ball milled powders from 4th and 6th experiment	2 mm	4:1	4	400rpm	0.05/0.21/0.94 μm **D_{mean} = 0.34 μm**	-No zirconia contamination, -81% yield Result: 4 hours milling is sufficient, further milling increases size of particles slightly.
		(1+3) mm	4:1	4	400rpm	0.05/0.20/0.91 μm **D_{mean} = 0.32 μm**	

Other Information/Results (Papers, Inventions, Software, etc.):

There were no publications, inventions, software, or presentations that resulted from this CRADA.

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