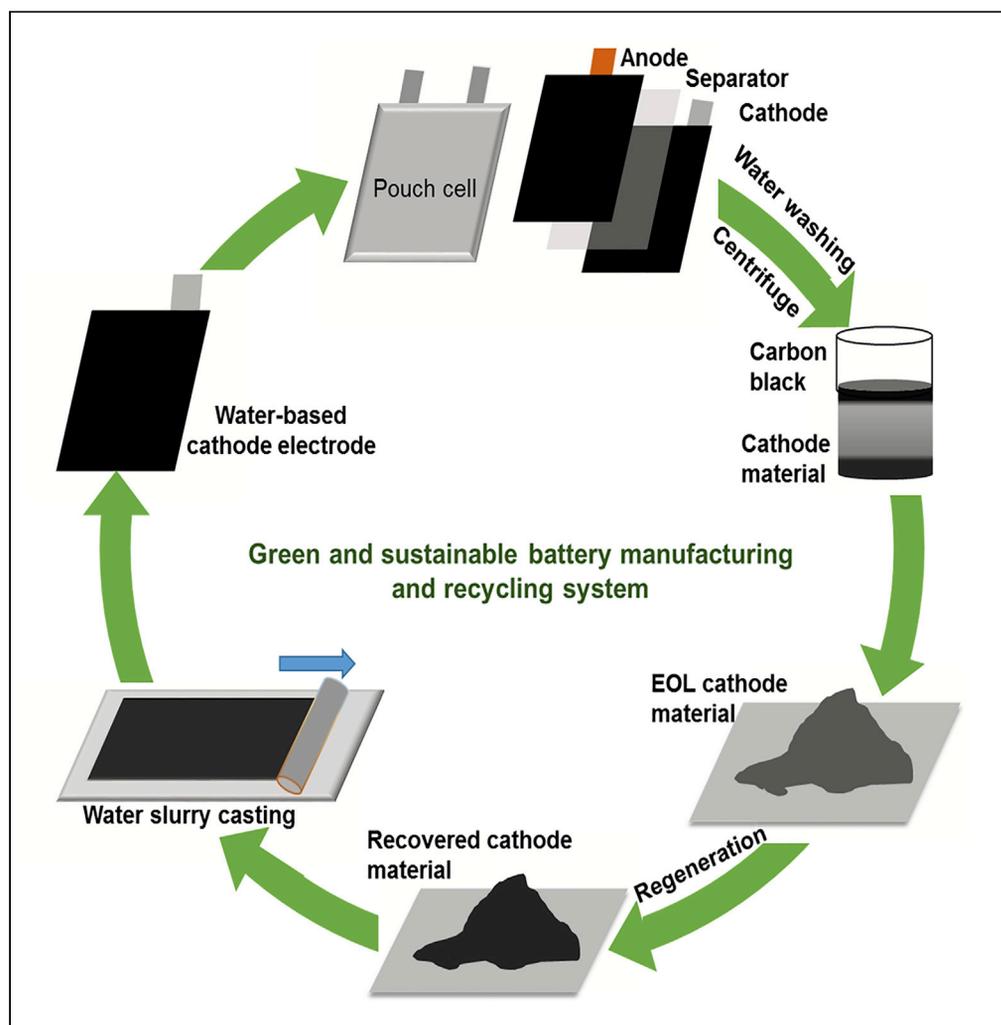


## Article

## Water-Based Electrode Manufacturing and Direct Recycling of Lithium-Ion Battery Electrodes—A Green and Sustainable Manufacturing System



Jianlin Li, Yingqi Lu, Tairan Yang, Dayang Ge, David L. Wood III, Zheng Li

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**HIGHLIGHTS**

Aqueous processed NCM523 cathodes show performance comparable with the NMP processed one

The spent NCM523 compound was separated from other cathode components in water

The spent NCM523 was successfully relithiated, restored and showed performance comparable with the pristine

This provides a potential path toward green and sustainable battery manufacturing

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## Article

## Water-Based Electrode Manufacturing and Direct Recycling of Lithium-Ion Battery Electrodes—A Green and Sustainable Manufacturing System

Jianlin Li,<sup>1,3,4,\*</sup> Yingqi Lu,<sup>2,3</sup> Tairan Yang,<sup>2</sup> Dayang Ge,<sup>2</sup> David L. Wood III,<sup>1</sup> and Zheng Li<sup>2,\*</sup>

## SUMMARY

It is critical to develop a low-cost and environmentally friendly system to manufacture and recycle lithium-ion batteries (LIBs) as the demand on LIBs keeps increasing dramatically. Conventional LIB cathodes are manufactured using N-methyl-2-pyrrolidone as the solvent, which is expensive, highly toxic, flammable, and energy intensive to produce and recover. Ideally, a close-loop industrial supply chain should be built, in which the batteries are manufactured, market harvested, and recycled with minimal external toxic solvent through the whole system. This work demonstrates a green and more sustainable manufacturing method for LIBs where no hazardous organic solvent is used during electrode manufacturing and recycling. The electrodes fabricated via water-based processing demonstrate comparable rate performance and cycle life to the ones from conventional solvent-based processing. Utilization of a water-soluble binder enables recovering the cathode compound from spent electrodes using water, which is successfully regenerated to deliver comparable electrochemical performance to the pristine one.

## INTRODUCTION

Widespread application of lithium-ion batteries (LIBs) in consumer electronics, electric vehicles (EVs), and grid storage continues to increase the demand for LIBs. It has been projected that the global LIB market will expand at a compound annual growth rate (CAGR) of 16.2% from 2014 to 2018 and reach \$92.2 billion by 2024 (Lithium Ion Battery Market, 2019). Mass production of LIBs can result in environmental concerns during battery manufacturing and disposal. Conventional LIB electrodes, especially cathodes, are manufactured through a slurry processing method where N-methyl-2-pyrrolidone (NMP) is used as a solvent (Li et al., 2012a). In fact, it is estimated that 4.1 million kg per year of NMP is used for depositing the cathode layers for a battery manufacturing plant producing 100,000 packs per year of 60 kW, 10 kWh plug-in hybrid vehicle (PHEV) batteries (Ahmed et al., 2016). Given that the global lithium ion battery production capability is ~400 GWh, enormous amount of NMP is needed. NMP is expensive and reprotoxic and has been added to the restricted substances list by the European Commission in 2018. In addition, about 47% of the total process energy in LIB manufacturing is consumed in the electrode drying process for evaporation and recovery of NMP solvent, a quarter of which can be reduced when replacing NMP with water (Wood et al., 2018). Another 29% of total energy is consumed by the dry room facility to support slurry mixing and casting operations for moisture and temperature control (Yuan et al., 2017). Thus, novel electrode manufacturing processes and/or a substitution of NMP need to be developed to reduce the processing cost and energy consumption (Li et al., 2017).

The booming LIB market not only continuously consumes scarce expensive metals but also brings a rapid growth in battery waste from end-of-life (EOL) LIB disposal. Improper disposal of EOL LIBs can generate enormous amounts of waste and poses a significant environment hazard as some components are toxic and carcinogenic in nature. There have been over 1.2 billion shipments of smartphones globally since 2014, which implies 24,000 tons of LIB cathode material waste in 2017 and roughly \$1 billion in market size for recycling these materials (Zheng, 2019). In addition, the first-generation EV batteries are approaching their EOL and generate roughly 20,000 tons of EOL LIB cathode materials. Thus, appropriate battery recycling processes need to be developed for economic viability and environmental sustainability. Currently the conventional recycling processes such as pyrometallurgy and hydrometallurgy are becoming

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undesirable because of the low lithium recovery and high energy input (Pagliaro and Meneguzzo, 2019; Diekmann et al., 2017). Direct recycling processes have attracted more attention since they can restore the cathode powder directly to yield battery grade material (Li, 2018; Sloop et al., 2018). Since polyvinylidene fluoride (PVDF) binder is currently widely used in the LIB electrodes, NMP is heavily used to dissolve the binder and separate out the cathode material from the aluminum foil. Undoubtedly, it will exacerbate the environmental and economic problems. Thus, novel methods are in urgent need to eliminate the dependence on this toxic solvent.

In this study, we report a green manufacturing process for LIB production and recycling where NMP was replaced by water in electrode fabrication and black mass (mixture of carbon black and active material) was separated from the current collector and recovered by dissolving the water-soluble binder in water. The active material was separated from carbon black and relithiated to generate battery-grade material. Although water-based processing for LIB manufacturing and direct recycle have been reported individually, to our best knowledge, integration of both processes has not been reported. This process enables numerous advantages and benefits in both economy and environment: (1) lower LIB manufacturing cost by eliminating NMP enabling ~2% cost reduction in the battery pack and \$3–6 million savings in capital investment from removing the entire emission control and solvent recovery system (Wood et al., 2018); (2) recovering black mass without using any organic solvents and direct recycling of the active material compound, which reduces the recycling cost and environmental impact while generating value-added compounds compared with elements. In comparison, organic binder was burned out in pyrometallurgical recycling and active material was separated from carbon black using NMP in hydrometallurgical recycling (Li et al., 2013a, 2013b); (3) reducing life cycle CO<sub>2</sub> equivalents emission for a 10-kWh battery by 1,000 kg (Zackrisson et al., 2010). Excellent electrochemical performance was achieved from the water-based processed electrodes used in this work, and comparable performance was obtained from the recycled materials. This methodology provides a green, sustainable process for LIB manufacturing and recycling if some underlying challenges can be resolved.

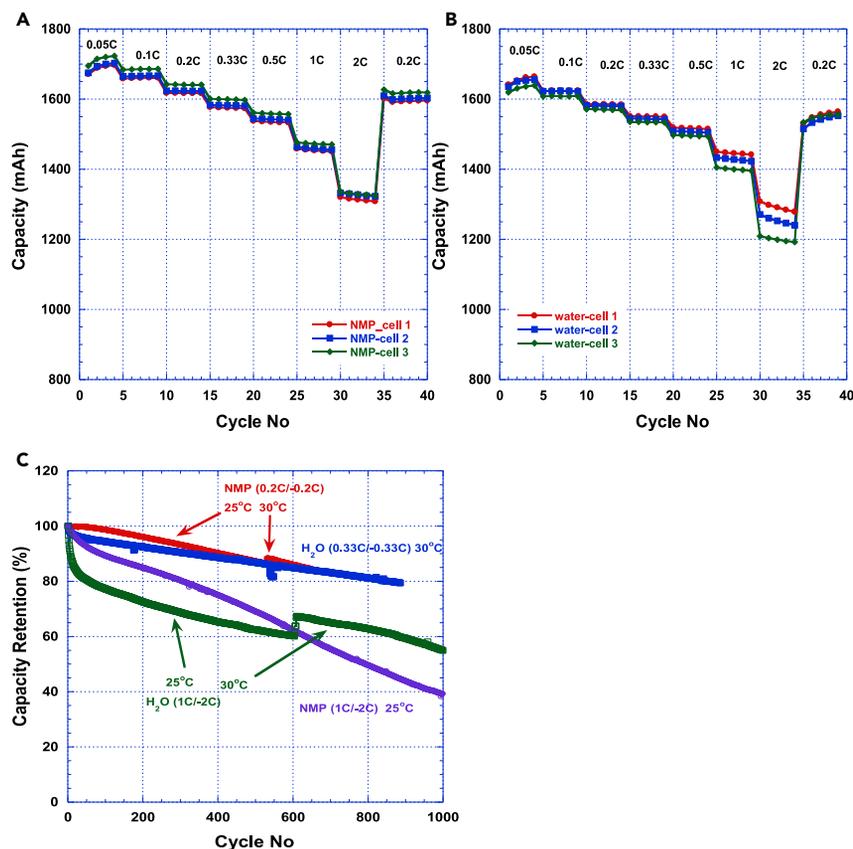
## RESULTS AND DISCUSSION

### Electrochemical Performance of Pristine Materials

Rate capability and cycle life was compared between NMP/PVDF baseline cells and cells with water-processed electrodes (NCM523 cathodes and graphite anodes) with three replicates for both tests. As shown in Figures 1A and 1B, the NMP- and water-processed electrodes exhibited excellent reproducibility and rate performance. When normalized to the capacity at C/20, the rate performance was identical up to 1C. When further increasing discharge rate, the water-based processed electrodes showed slightly lower performance and higher cell-to-cell variation. A similar phenomenon has been observed with NCM811, and it was attributed to a difference in binder coverage rather than structural changes to the active material (Wood et al., 2020). The cycle life testing shown in Figure 1C was started at 25°C in an environmental chamber where the temperature was raised to 30°C later to meet testing requirements for other projects, but the capacity was normalized to the initial value at the same rate. The NMP cells were cycled at 0.2C/-0.2C at 25°C before the temperature was increased to 30°C at the 530<sup>th</sup> cycle, which resulted in a 4% increase in capacity. The water-processed electrodes were cycled at 0.33C/-0.33C to reach 1,000 cycles in a shorter time, and it is seen in Figure 1C that their capacity initially faded at a higher rate. However, the fade rate subsequently decreased after 50 cycles, and the capacity retention was the same for both sets of cells at the 668<sup>th</sup> cycle. Considering the water-based cells were cycled at higher rates, their cycling performance can be considered superior to the NMP-based cells. It was found that the water-based cells retained 80% capacity after 864 cycles.

Cycle life at higher charge/discharge rates was also performed, and it was found that the water-based cells degraded quickly initially and slowed down afterward, as was the case for the lower cycling rates. The capacity retention was same for both sets of cells after 600 cycles before the temperature was increased to 30°C for the water-based cells. Based on the trend of the capacity retention curves up to the point of the temperature change, the water-based cells were on track to have better capacity retention through 1,000 cycles.

The chemical compositions of the pristine and EOL NCM523 are listed and compared with the target values in Table 1. The Ni fraction was normalized to 0.5, and other elements were scaled by the same factor. The experimental values of the pristine NCM523 agreed well with the target values, which validate the effectiveness of ICP-MS (inductively coupled plasma mass spectrometry). The EOL NCM shows a ratio of Li to transition metal of



**Figure 1. Electrochemical Performance Comparison**

(A–C) (A) Rate capability of the baseline NMP/PVDF cells; (B) rate capability of the cells with water-processed electrodes; and (C) comparison of cycle life between NMP/PVDF baseline cells and cells with water-processed electrodes. The 0.2C/-0.2C cycling data for NMP and 0.33C/-0.33C cycling data for the water-processed electrodes were replotted from reference (Wood et al., 2018).

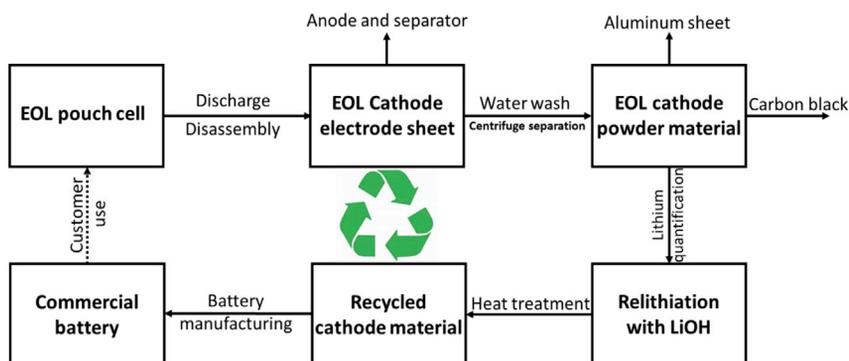
0.687, which was attributed to the capacity fade. In addition, the significant loss (~32%) of Li in the EOL sample indicates significant degradation to the NCM cathode and was the main reason for the cell degradation.

### Structure of NCM523

The schematic flow chart of the closed-loop recycling process is described in the Figure 2. Detailed information can be found in the Supplemental Information. Figure 3 shows the X-ray diffraction (XRD) patterns for the pristine NCM523, the  $\text{Li}_x\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  EOL LIBs, and recycled NCM523. All materials were indexed to the  $\alpha\text{-NaFeO}_2$  (space group:  $R\bar{3}m$ ) with no observed impurity peaks. Compared with the pristine material, the disappearance of the (006) diffraction peak and the merging of the (108) and (110) peaks in the EOL  $\text{Li}_x\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  pattern indicated a lithium deficiency and the degradation of the layered structure of the EOL battery cathodes (Valanarasu and Chandramohan, 2010). The (003) peak shifted to a lower angle after cycling corresponding to an increase in the  $c$  lattice parameter due to electrostatic repulsion between the oxygen layers in the Li-deficient state (Mohanty et al., 2013). The XRD pattern of the recycled

Sample Name	Li		Ni		Co		Mn		Li/Transition Metal	
	Actual	Target	Actual	Target	Actual	Target	Actual	Target	Actual	Target
EOL NCM	0.684	–	0.500	0.500	0.196	0.200	0.299	0.300	0.687	–
Pristine NCM	0.99	1.000	0.500	0.500	0.204	0.200	0.297	0.300	0.991	1.00

**Table 1. The ICP-MS Results for the Pristine and EOL NCM523**



**Figure 2.** The Process Flow Chart of the Direct Recycling Process

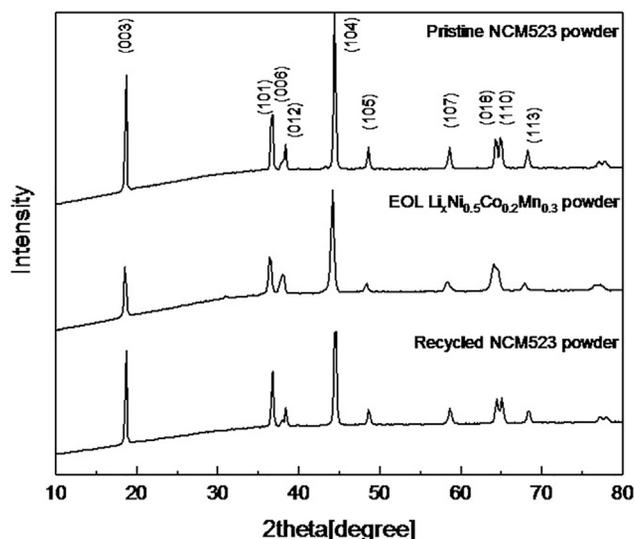
NCM523 matched that of the pristine sample, indicating full restoration of the crystal structure. Its XRD pattern shows a higher  $I_{003}/I_{104}$  ratio than that of the EOL as well as the pristine material, indicating less Li/Ni cation mixing in the recycled material, which is of great advantage to intercalation/deintercalation of  $\text{Li}^+$  and its good electrochemical properties (Nie et al., 2015).

### Morphology of NCM523

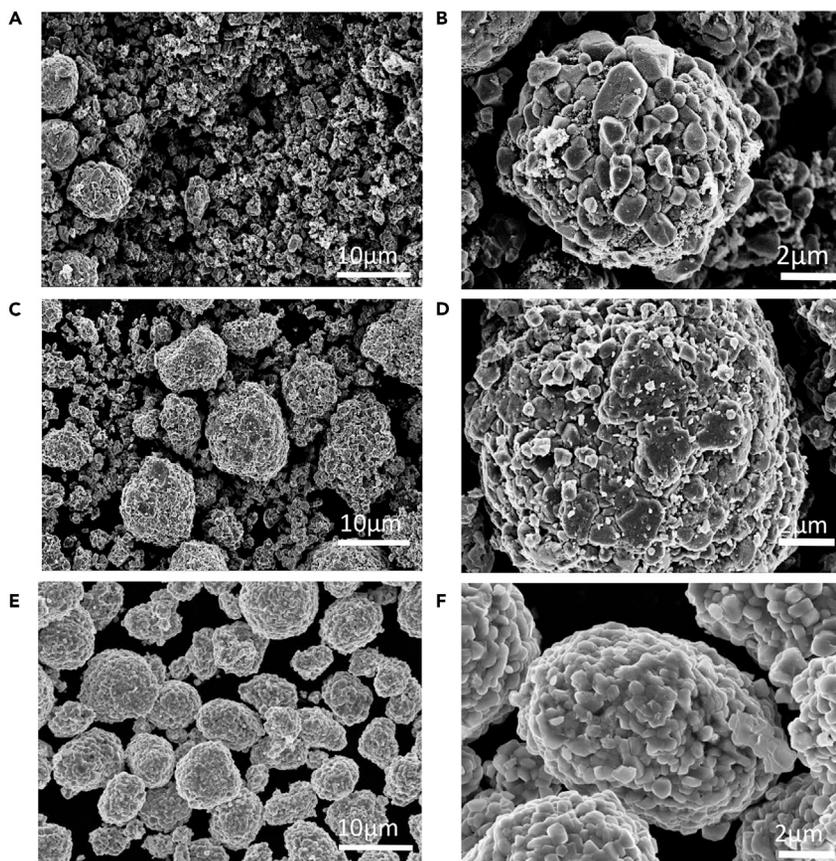
The scanning electron microscope (SEM) images in Figure 4 show the evolution of the cathode materials before and after recycling. Figures 4A and 4B show the EOL cathode materials washed from the current collector, and the observed agglomeration is possibly due to some binder residuals. The recycled materials in Figures 4C and 4D show well-distributed and enlarged particles in contrast to the EOL powder. Compared with the pristine powder shown in Figures 4E and 4F, the EOL and recycled powders had more small particles, which could be due to the fracture of secondary particles during calendaring and cycling (Xu et al., 2018). This phenomenon is common in the spent electrodes regardless of the recycle techniques. The fracture of cathode active material will likely lower the tap density of powder and affect the quality and performance of the recycled powder. More optimization on the annealing process is required to better reconstruct particle morphology and other properties, such as tap density and particle size.

### Electrochemical Behavior

The electrochemical performance of the recycled NCM523 cathode particles was evaluated in the voltage range of 2.7–4.2 V at 0.2C as shown in Figure 5. For direct comparison, a baseline electrode



**Figure 3.** Comparison of XRD Patterns for Pristine NCM523,  $\text{Li}_x\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  in EOL Pouch Cells, and Recycled NCM523

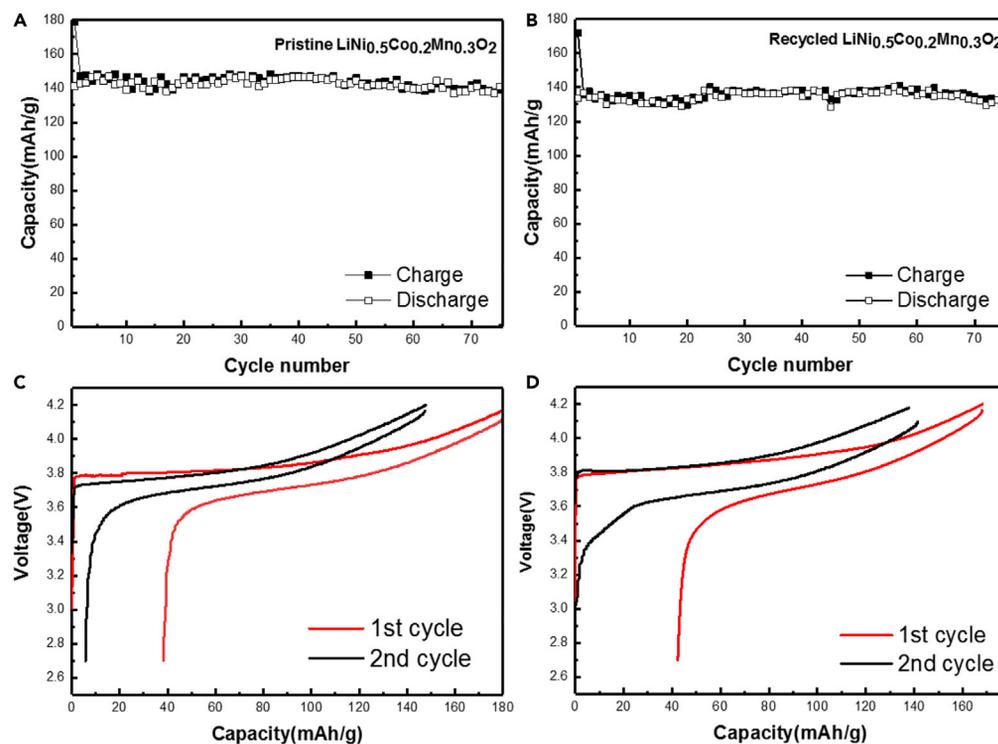


**Figure 4. Morphology of NCM523 Particles**

SEM images of (A and B) EOL NCM523 powder after DI water washing, (C and D) recycled NCM523 powder, and (E and F) pristine NCM523 powder.

was coated with pristine NCM523 and identical formulation and coating process. The recycled NCM523 showed stable cycling and comparable electrochemical performance with that of the pristine one, although its charge-discharge curve indicates higher hysteresis with slightly lower capacity. The irreversible capacity loss is mainly caused by kinetic inhibition except the initial capacity loss (Kasnatscheew et al., 2016). The recycled NCM523 was exposed to water during binder removal and then exposed to air during annealing. It is possible that some carbonate formed on the surface, which increased the electrode polarization. Therefore, detailed structural characterization and recycling process optimization are needed to further improve the electrochemical performance of the recycled NCM523. The process also needs to be scaled up to recycle enough materials for pre-pilot-scale coating to evaluate the performance of the recycled materials in large format cells for extended cycle life. Nevertheless, these promising preliminary results demonstrate the feasibility of the direct recycling of the NCM cathode materials. Since the Ni-rich NCM cathodes are less stable in water than Co-rich ones, the future strategy to optimize the aqueous recycling process is to use high-salt-concentration aqueous solutions during the washing process (Suo et al., 2015, 2017).

Switching from NMP-based to water-based processing in fabricating composite cathodes (Li et al., 2013a, 2013b; Memm et al., 2018; Ibing et al., 2019) has attracted great interest in the last decade. Although there are still challenges in realizing water-based processing for NCM cathodes, i.e., Al corrosion from high pH of the aqueous slurry (Bauer et al., 2019) and poor mechanical integrity in thick cathode (Du et al., 2017), great progress has been demonstrated, e.g., excellent cycle life (Wood et al., 2018, 2020). When successful, the water-based processing can significantly facilitate binder removal and recovery of black mass in the recycling process. In direct recycling, the binder removal process is particularly challenging. For conventional EOL LIBs with PVDF binder, toxic solvents such as NMP and dimethylformamide (DMF) are needed to re-dissolve the binder and extract the active



**Figure 5. Electrochemical Performance of NCM523 Electrodes**

Cycling performance of (A) Li/pristine LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> coin cell and (B) Li/recycled LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> coin cell at C/5. The voltage profiles of first two cycles (C) Li/pristine LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> coin cell and (D) Li/recycled LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> coin cell at C/5.

cathode materials in the black mass (Lv et al., 2018). Using water for the binder removal process will not only minimize the negative environmental impact caused by organic solvents, but also significantly reduce the cost for the binder removal unit operation. Meanwhile, using water instead of an organic solvent eliminates the solvent regeneration and reuse unit operation that further simplifies the overall process.

## Conclusions

A green manufacturing and direct recycling process were proposed where the organic NMP solvent was replaced by water during electrode fabrication and recovery of black mass during battery recycling. It was demonstrated that the water-processed electrodes exhibited electrochemical performance comparable with that of the ones from NMP-based processing. The cathode powder was successfully recovered from the spent electrodes, relithiated, and restored to stoichiometry, delivering comparable capacity to the pristine material. Although there are still many challenges to be resolved, this process provides a potential path toward green and sustainable manufacturing of lithium-ion batteries, which enables lower battery cost and much less environmental impact.

## Limitations of the Study

This work provides the first successful demonstration of a green close loop in battery manufacturing and recycling without using any organic solvents. The spent cells were from 1.6-Ah pouch cells with relevant chemistry, NCM523 and graphite. The whole process is still at laboratory scale but is scalable. Some steps were not optimized by any means, and more work is definitely required. For example, automatic separation and purification will need to be implemented. Additional processes will also be required when recycling other cell components, such as electrolyte salt.

## METHODS

All methods can be found in the accompanying [Transparent Methods supplemental file](#).

## SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at <https://doi.org/10.1016/j.isci.2020.101081>.

## ACKNOWLEDGMENTS

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## AUTHOR CONTRIBUTIONS

J.L. and Z.L. designed the experiment. J.L., Y.L., T.Y., D.G., and Z.L. conducted the experiment. J.L., Y.L., D.L.W., and Z.L. wrote the paper.

## DECLARATION OF INTERESTS

The authors declare no competing interest.

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## **Supplemental Information**

### **Water-Based Electrode Manufacturing and Direct Recycling of Lithium-Ion Battery Electrodes—A Green and Sustainable Manufacturing System**

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## Supplementary Information

### Transparent Methods

#### Battery cycling information

Pouch cells (~1.6 Ah) were assembled with  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  (NCM523) and graphite electrodes fabricated from NMP and water-based processing, respectively. The NMP-processed electrodes were used as a baseline to validate the performance of the water-based processed ones and were not used for recycling. The electrode fabrication and calendaring processes followed the standard procedures reported in our previous work (Li et al., 2016, Davoodabadi et al., 2018). Aluminum foil was treated by corona plasma at  $4.4 \text{ J/cm}^2$  to enhance slurry wetting on the current collector substrate (Li et al., 2012). Table S1 lists the detailed electrode information and the materials used in electrode fabrication are listed in Table S2. The electrode balance (n/p) ratio was ~1.2. The electrolyte was 1.2 M  $\text{LiPF}_6$  in ethylene carbonate/diethyl carbonate (EC/DEC in 3/7 wt), Celgard 2325 was used as the separator, and the electrolyte amount was 1.2 times the total pore volume of electrodes and separator. Electrochemical cycling took place between 2.5 V and 4.2 V. Pouch cells went through 4 formation cycles at C/20 (1C=1.6 A) charging and discharging rates followed by rate capability or cycle life testing, respectively. For rate capability testing, the pouch cells were charged at C/5 until 4.2 V followed by constant voltage charge until the current dropped to C/20. Discharge rates ranged from C/10 to 2C. Cycle life testing was evaluated at 0.2C/-0.2C, 0.33C/-0.33C, and 1C/-2C, respectively. The majority of the cycle life testing was performed at 25°C, but some cycles occurred at 30°C due to a change in temperature setting in the environmental chamber, which is specified in the experimental results. Two sets of cells were tested. One went through rate performance test followed by cycle life test at 1C/-2C. The other went through cycle life test at 0.2C/-0.2C or 0.33C/-0.33C. As shown in Figure 1, the pouch cells had at least 20% capacity fade. The cells with water-based processed electrodes aged for months at room temperature before being recycled (referred as EOL).

*Table S1. Electrodes information related to Figure 1*

Electrode	Solvent	Electrode Composition	Porosity	Loading
NCM523-NMP	NMP	NMC532/Denka CB/5130 PVDF in 90/5/5 wt%	37%	12.5 mg/cm <sup>2</sup>
NCM523-Water	Water	NMC532/Denka CB/CMC/PVDF Latex in 90/5/1/4 wt%	36%	12.5 mg/cm <sup>2</sup>
A12-NMP	NMP	A12/C65 CB/9300 PVDF in 92/2/6 wt%	33%	6.5 mg/cm <sup>2</sup>
A12-Water	Water	A12/C65 CB/CMC/SBR in 92/2/2/4 wt%	34%	6.5 mg/cm <sup>2</sup>

Table S2. Materials used in electrode fabrication related to Figure 1

Materials	Suppliers
LiNi <sub>0.5</sub> Mn <sub>0.3</sub> Co <sub>0.2</sub> O <sub>2</sub> (NMC532)	TODA America, Battle Creek, MI, USA
A12 graphite (A12)	ConocoPhillips, Houston, TX, USA
N-Methylpyrrolidone (NMP)	Sigma-Aldrich, St. Louis, MO, USA
Denka carbon black (Denka CB)	Denka, Tokyo, Japan
C-ENERGY Super C65 carbon black (C65 CB)	Imerys Graphite & Carbon, Bodio, Switzerland
carboxymethyl cellulose (CMC)	Sigma-Aldrich, St. Louis, MO, USA
styrene-butadiene rubber (SBR)	Targray, Kirkland, Canada
Solef® XPH-859 (PVDF latex)	Solvay S.A., Brussels, Belgium
Solef® 5130 (5130 PVDF)	Solvay S.A., Brussels, Belgium
Kureha w#9300 (9300 PVDF)	Kureha America, New York, NY, USA

#### Direct recycling of EOL cathode material

Figure 2 shows the schematic flow chart of the closed-loop recycling process where the EOL cells were discharged to 3.0 V at C/5 and sat for ~2 years at room temperature before being recycled. The pouch cells were first discharged to 2 V and then fully shorted below 0.5 V for safe disassembly. After deactivation, the cathode sheets were separated from the other cell components and thoroughly rinsed in dimethyl carbonate (DMC) to remove the electrolyte. Since water-soluble binders were used in the electrodes, the cathode sheets were then sonicated in DI water for 2-5 minutes in an electrode/H<sub>2</sub>O ratio of 3 g/50ml. After the sonication, the EOL cathode material was washed off from the aluminum current collector and suspended in water. The aqueous suspension composed of EOL cathode material and a small amount of carbon additives was then centrifuged to separate the cathode materials out. The extracted EOL cathode material was dried and its Li/transition metal (Li/TM) ratio was quantified by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Thermo Electron X-Series). The EOL cathode powders were mixed with LiOH using an agate mortar and pestle. The amount of LiOH added ensured a mixture with a Li/TM ratio of 1.05. The mixtures were pressed into pellets and sintered at 700°C for 6 h under air at a ramping rate of 10 °C/min in a muffle furnace.

#### Electrochemical test

The annealed pellets were ground and mixed with other components in NMP to prepare a cathode slurry (80 wt% active material/10 wt% TIMCAL carbon/10 wt% PVDF (MTI corporation)). The homogeneous slurry was coated onto an aluminum foil and dried at 100 °C overnight in a vacuum oven. Half coin cells were assembled in an argon-filled glove box with a lithium metal chip as the counter electrode, 1M lithium hexafluorophosphate (LiPF<sub>6</sub>) in a mixture of EC and dimethyl carbonate (DMC) with 3:7 volume ratio as the electrolyte, and Celgard 2325 as the separator. Electrochemical tests were performed on LAND battery tester using CR2032 coin cells.

#### Crystal structure and morphology characterization

The crystal structure of the materials was investigated by X-ray Diffraction (XRD) using a PANalytical X'Pert Pro multipurpose diffractometer equipped with Cu-K $\alpha$  radiation and X'Celerator detector. The morphology of the samples was examined by Environmental Scanning Electron Microscopy (SEM, FEI Quanta 600 FEG).

### Supplemental References

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