

Article

Performance of Cathodes Fabricated from Mixture of Active Materials Obtained from Recycled Lithium-Ion Batteries

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Abstract: The cathode performance of lithium-ion batteries (LIBs) fabricated from recycled cathode active materials is studied for three scenarios. These scenarios are based on the conditions for separation of different cathode active materials in recycling facilities during the LIB's recycling process. In scenario one, the separation process is performed ideally, and the obtained pure single cathode active material is used to make new LIBs after regeneration. In scenario two, the separation of active materials is performed with efficiencies of less than 100%, which is the actual case in the recycling process. In this scenario, a single cathode active material that contains a little of the other types of cathode active materials is used to make new LIBs after the materials' regeneration. In scenario three, the separation has not been performed during the recycling process. In this scenario, all types of cathode active materials are regenerated together, and a mixture is used to make new LIBs. The studies are performed through modeling and computer simulation, and several experiments are conducted for validation purposes. The cathode active materials that are studied are the five commercially available cathodes made of LiMn_2O_4 (LMO), LiCoO_2 (LCO), $\text{LiNi}_x\text{Mn}_y\text{Co}_{(1-x-y)}\text{O}_2$ (NMC), $\text{LiNi}_x\text{Co}_y\text{Al}_{(1-x-y)}\text{O}_2$ (NCA), and LiFePO_4 (LFP). The results indicate that the fabrication of new LIBs with a mixture of cathode active materials is possible when cathode active materials are not ideally separated from each other. However, it is recommended that the separation process is added to the recycling process, at least for the separation of LFP or reducing its amount in the cathode active materials mixture. This is because of the difference of the voltage level of LFP compared to the other studied active materials for cathodes.

Keywords: lithium-ion battery; recycling; cathode performance; mixture of cathode active materials; separation of cathode active materials



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1. Introduction

Lithium-ion batteries (LIBs) are storage systems for electrical energy. Their relatively high energy density, high power density, and long lifespan have led to the industry making them the first candidate for portable electronics, electric vehicles, and even renewable energy storage [1,2]. A commercial LIB consists of six components: (1) an anode or negative electrode; (2) a cathode or positive electrode; (3) an electrolyte; (4) a separator; (5) current collectors for positive and negative electrodes, which are usually aluminum and copper foils, respectively, and (6) the battery casing, which is usually stainless steel for cylindrical LIBs and polymer coated aluminum for pouch/prismatic LIBs [3]. The negative and positive electrodes are usually made of three materials: the active material for storage of lithium, the conductive material to enhance the electron conductivity of the electrode, and the binder to bond the active and conductive materials and to adhere the electrode to the current collector. Among the anode active materials, graphite is currently the most common one because of its relatively high energy density (372 mAh/g), good mechanical and chemical stabilities, and low cost [4]. Another anode active material is $\text{Li}_4\text{Ti}_5\text{O}_{12}$

(LTO), which is one of the promising anode active materials for LIBs because of its constant charge/discharge profile at 1.5 V versus lithium and its excellent Li-insertion/extraction reversibility with no structural change [5]. For cathode active materials, LiCoO_2 (LCO) is widely utilized due to its high specific energy [6]. Despite its success in the LIBs industry, it has some shortcomings such as the high cost (cobalt is not an abundant element on earth) and relatively lower specific power. These shortcomings have led the industry to adopt other materials such as LiFePO_4 (LFP), LiMn_2O_4 (LMO), $\text{LiNi}_x\text{Co}_y\text{Al}_{(1-x-y)}\text{O}_2$ (NCA), and $\text{LiNi}_x\text{Mn}_y\text{Co}_{(1-x-y)}\text{O}_2$ (NMC) [7]. Each of these cathode active materials has its own advantages and disadvantages. The electrolyte in LIBs is responsible for transferring lithium ions between the cathode and anode active materials. Most commercial LIBs currently use organic liquid electrolytes because of their relatively wide electrochemical stability. An organic liquid electrolyte is comprised of a lithium salt, such as lithium hexafluorophosphate (LiPF_6), dissolved in an organic solvent [8]. The separator is an electron non-conductive material that separates the positive electrode from the negative electrode to prevent the short circuit between them [9], while allowing rapid transport of ionic charges between the negative and positive electrodes. In most LIBs, separators are currently made of either microporous polymeric films or nonwoven fabrics. The microporous polymeric films (e.g., polyethylene (PP)) are the preferred separator for LIBs because of their thermal and mechanical stabilities [10].

Among all components/materials of LIBs, the cathode active material is usually expensive, as it may be valued at even 40% of the total material cost of LIBs [11]. Improvement of the energy density of active materials has been a pursuit of the scientific community for a long time [12]. Many researchers have studied the combination/mixture of two or three active materials to improve the electrode performance and reduce the cost of the cathode. For example, in a study, the authors have investigated the cathode mixture of LMO and NCA [13]. In fact, NCA shows a high energy density and a good lifetime, but it shows poor thermal stability at elevated temperatures. On the other hand, LMO shows a better thermal stability, higher nominal voltage, higher power density, and lower cost, but it has a lower energy density. Therefore, the performance of the cathode can be engineered when NCA and LMO are blended, and the cathode is made from a mixture of two active materials. The results of this research showed that, at low C-rates, NCA showed higher specific energy, while at high C-rates LMO showed higher specific energy. Another research has been conducted to investigate the blended electrode of two cathode active materials of LMO and NMC [14]. The results indicated that the low capacity of LMO is increased when it is blended with NMC. A research team has conducted a study on the ternary blend of NMC, LMO, and LMFP and showed the advantage of this blend [15]. Out of the many blended seniors, they showed that the blend of 75% NMC, 12.5% LMFP, and 12.5% LMO is comparable with NMC.

All prior blending studies have been conducted to either reduce the cost or enhance the electrochemical performance of the cathode. In contrast to prior studies, our focus in this paper is on the blended cathode materials that are obtained from the recycling of LIBs using the physical recycling method.

All LIBs that are produced today will be retired after about 10 years. If LIBs are landfilled, we may expect several environmental problems: (1) Contamination: chemicals found in batteries may leak from the casing once the battery is in a landfill and contaminate the area and groundwater. This is a serious threat to the environment, ecosystems, and human health. (2) Safety: the landfilled lithium-ion batteries may catch fire and an explosion may happen. (3) Sustainability: several rare materials such as lithium and cobalt are wasted in landfills and new materials will need to be extracted from mines. In general, three methods are available to recycle LIBs. Hydrometallurgy (melting), pyrometallurgy (chemicals), and physical or direct methods. The direct method is the most cost-effective and environmentally friendly method for recycling LIBs, and it is also the most promising recycling method for these batteries. One advantage of the physical method is that the electrode active materials can be separated without changing the morphology of the

materials. Hence, the recycled electrode materials can be regenerated and reused to make new LIBs. In recycling plants that operate based on the physical method, all types of LIBs are usually recycled together without sorting them out based on the battery chemistry. In fact, sorting LIBs is not usually logistically possible. Therefore, the obtained cathode active materials are a blend of different active materials. This motivated us to look at the blend of different cathode materials from the angle of the obtained materials from LIB recycling with the physical method.

In this study, we decide to show how the battery performance can be affected if it is built with a blend of recycled cathode active materials. The focus will be on the electrochemical performance of the blended/mixture of the five most commercially available cathode types: LFP, LMO, NMC, NCA, and LCO. This study is the continuation of the studies conducted by the authors for recycling LIBs [16–19]. The authors' results have already indicated that the complete separation of the five cathode active materials is achievable. However, there is still a concern or uncertainty about the performance of separation that cannot reach 100% in practice. Therefore, we study the performance of LIBs made from the recycled cathode materials based on the following three scenarios:

- (I) The separation process is performed ideally. In this scenario, a pure single regenerated cathode active material is used to make new LIBs.
- (II) The separation process is performed with an efficiency of less than 100%. This is the actual scenario in the recycling process with the physical method. In this scenario, a single regenerated cathode active material that contains a little of the other types of cathode active materials is used to make new LIBs.
- (III) The separation has not been performed. In this scenario, all types of cathode active materials are regenerated together and used to make new batteries.

In this paper, the results of both mathematical modeling and experiments are presented. For the modeling, a pseudo-two-dimensional (P2D) model based on the porous theory proposed by Newman [20] has been adopted. The computer simulation has been carried out in the COMSOL Multiphysics software package for all three scenarios. The experiments have been conducted to validate the simulation results.

2. Model

Since the objective is to study the performance of the cathode active material, we modeled a half-cell of the LIB. As shown in Figure 1, a half-cell consists of a lithium foil anode, separator, cathode (positive electrode), aluminum current collector, and liquid electrolyte, which is available in the separator and the cathode.

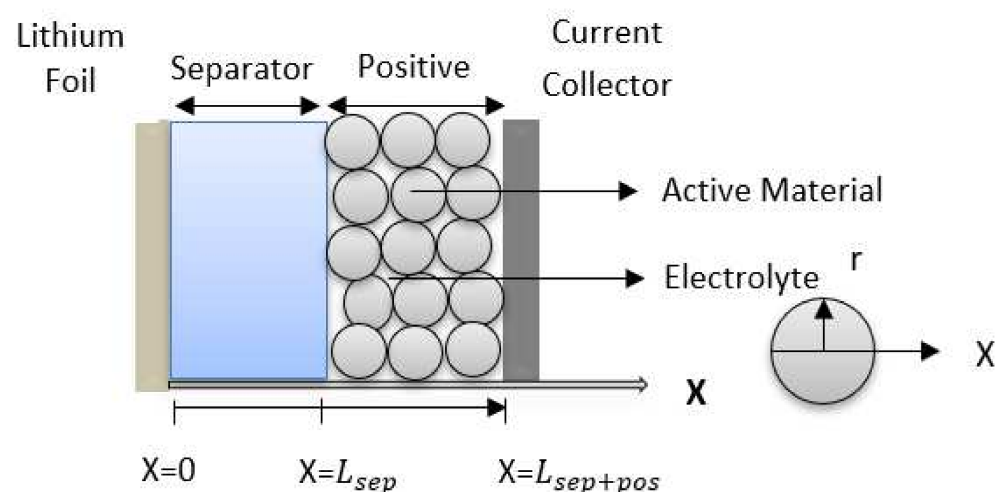
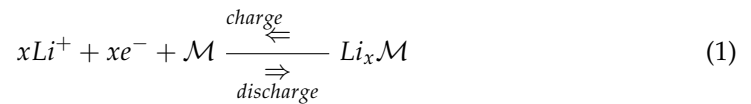


Figure 1. Schematic of the half-cell lithium-ion battery made from a single cathode active material.

The electrochemical reaction during charging and discharging of the half-cell can be expressed as Equation (1) [21]. During discharging, the lithium ions move from the lithium foil to the cathode particles. During charging, the lithium ions move back from the cathode to the lithium foil.



2.1. Half-Cell Made from a Single Cathode Active Material

The model considers one active material for the cathode, as seen in Figure 1. The negative electrode in the half-cell works as a reference electrode for the battery. For the modeling, we consider the: (a) electric charge transfer in the cathode; (b) ionic charge transfer in the cathode; (c) lithium-ion mass transfer in the cathode; (d) lithium mass transfer in the cathode active material particles (intercalation); (e) ionic charge transfer in the electrolyte; (f) lithium-ion mass transfer in the separator, and (g) electrochemical reaction at the active sites of the cathode. The modeling equations and their boundary and initial conditions are summarized in Table 1. Several assumptions have been made for the modeling. The main assumptions are that the battery is fresh and there is no sign of materials degradation, the cathode active materials are solid spheres with uniform size, the Bruggeman assumption is valid for calculation of the effective conductivities and diffusivities, there is no volume change in the cathode active materials during charging and discharging, no SEI layer is formed on the lithium foil, the entire surface of all cathode active material particles is an active site for electrochemical reactions, the voltage drop in the aluminum current collector is negligible, and the half-cell temperature is kept constant during charging and discharging. In addition, the half-cell model is pseudo-two-dimensional (1D + 1D). This means that the lithium mass transfer equation in the cathode active material particles is solved only in r direction, and all other transport equations are solved in only x direction. See Figure 1 for the r and x directions.

2.2. Half-Cell Made from a Mixture of Cathode Active Materials

The modeling of the cathode performance made from a mixture of cathode active materials (see Figure 2) is similar to the modeling of the cathode made from a single cathode active material. However, there are some differences. The differences are discussed here.

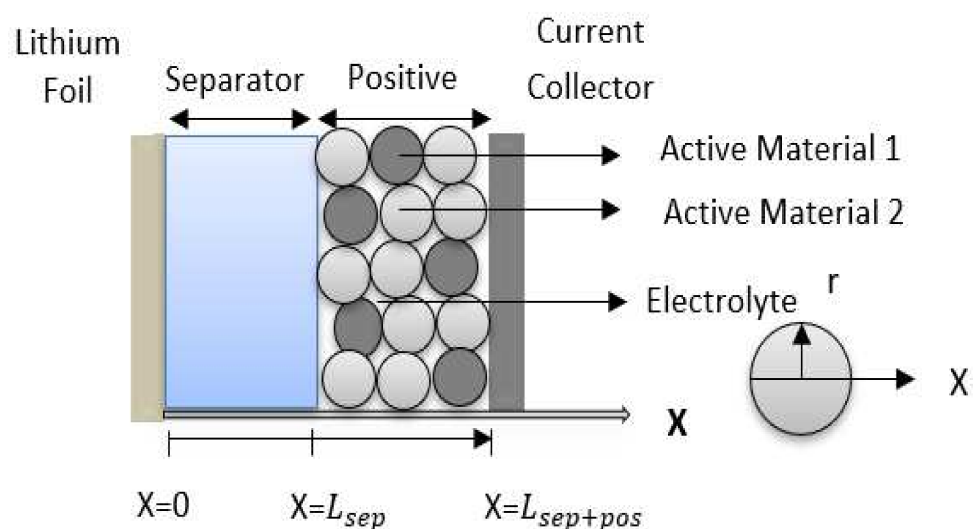


Figure 2. Schematic of the half-cell lithium-ion battery made from a mixture of cathode active materials.

Table 1. The modeling equations for performance simulation of a cathode made from a single active material [20].

Equations	Initial and Boundary Conditions
Li mass transfer in cathode active material particles	
$\frac{\partial c_s}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 D_s \frac{\partial c_s}{\partial r} \right)$ Solution of this equation gives the distribution of lithium in r direction in the cathode particle, which is located at any x, at any time t	$\frac{\partial c_s}{\partial r} = 0 \text{ at } r = 0$ $\frac{\partial c_s}{\partial r} = -\frac{i_{local}}{FD_s} \text{ at } r = r_p$ $c_s = c_{s,0} \text{ at } t = 0$
Electric charge transfer in the cathode	
$\nabla \cdot i_s = -S_{a,cat} i_{local}$ $i_s = -\sigma_{s,cat,eff} \nabla \phi_s$ $\sigma_{s,cat,eff} = \sigma_{s,cat} \varepsilon_{s,cat}^{1.5}$ $S_{a,cat} = \frac{3}{r_{p,cat}}$ Solutions of these equations give the distribution of electric current along the cathode thickness at any time t	$i_s = 0 \text{ at } x = L_{sep}$ $\phi_s = 0 \text{ at } x = L_{sep}$ $i_s = \frac{I_{applied}}{A} \text{ at } x = L_{sep} + L_{pos}$
Ionic charge transfer in the electrolyte within the cathode	
$\nabla \cdot i_l = S_a i_{local}$ $i_l = -\sigma_{l,cat,eff} \nabla \phi_l + \frac{2RT}{F} \sigma_{l,cat,eff} (1 - t_+^0) \left(1 + \frac{d \ln f}{d \ln c_l} \right) \nabla \ln c_l$ $\sigma_{l,cat,eff} = \sigma_l \varepsilon_{l,cat}^{1.5}$ Solutions of these equations give the distribution of ionic current along the cathode thickness at any time t	$i_l = 0 \text{ at } x = L_{sep} + L_{pos}$ $i_l = \frac{I_{applied}}{A} \text{ at } x = L_{sep}$
Li ⁺ mass transfer in the electrolyte within the cathode	
$\varepsilon_{l,cat} \frac{\partial c_l}{\partial t} + \nabla \cdot N_l = 0$ $N_l = -D_{l,cat,eff} \nabla c_l - \frac{i_l t_+^0}{F}$ $D_{l,cat,eff} = D_l \varepsilon_{l,cat}^{1.5}$ Solutions of these equations give the distribution of lithium-ion concentration along the cathode thickness at any time t	$N_l = 0 \text{ at } x = L_{sep} + L_{pos}$ $c_l = c_{l,0} \text{ at } t = 0$
Ionic charge transfer in the electrolyte within the separator	
$\nabla \cdot i_l = 0$ $i_l = -\sigma_{l,sep,eff} \nabla \phi_l + \frac{2RT}{F} \sigma_{l,sep,eff} (1 - t_+^0) \left(1 + \frac{d \ln f}{d \ln c_l} \right) \nabla \ln c_l$ $\sigma_{l,sep,eff} = \sigma_l \varepsilon_{l,sep}^{1.5}$ Solutions of these equations give the distribution of ionic current along the separator thickness at any time t	$i_l = \frac{I_{applied}}{A} \text{ at } x = 0$
Li ⁺ mass transfer in the electrolyte within the separator	
$\varepsilon_{l,sep} \frac{\partial c_l}{\partial t} + \nabla \cdot N_l = 0$ $N_l = -D_{l,sep,eff} \nabla c_l - \frac{i_l t_+^0}{F}$ $D_{l,sep,eff} = D_l \varepsilon_{l,sep}^{1.5}$ Solutions of these equations give the distribution of lithium-ion concentration along the separator thickness at any time t	$N_l = 0 \text{ at } x = 0$ $c_l = c_{l,0} \text{ at } t = 0$
Electrochemical reaction in the cathode (Butler–Volmer kinetics)	
$i_{local,cat} = i_{0,cat} \left[\exp \left(\frac{F}{2RT} \eta_{cat} \right) - \exp \left(-\frac{F}{2RT} \eta_{cat} \right) \right]$ $i_{0,cat} = F k_{cat} \left(c_{s,max} - c_{s,surf} \right)^{0.5} c_{s,surf}^{0.5} \left(\frac{c_l}{c_{l,ref}} \right)^{0.5}$ $\eta_{cat} = \phi_s - \phi_l - E_{eq,cat}$ Solutions of these equations give the local current generation along the cathode thickness at any time t as well as the local activation + concentration polarizations along the cathode thickness at any time t	

The mixture of cathode active materials consists of spherical particles from different active materials that are mixed homogenously before the cathode slurry is coated on the aluminum current collector. For the modeling, it is assumed that the mixture is homo-

geneous, while each type of cathode active material can have its own particle sizes. For the mixture of cathode active materials, the equation of lithium mass transfer should be solved for each cathode active material. The electrochemical reaction equation should also be solved separately for each cathode active material, and the total local current should be obtained from the summation of the local current generated by each cathode active material. The additional modeling equations and their boundary and initial conditions to simulate the behavior of a mixture of cathode active materials are summarized in Table 2.

Table 2. The additional modeling equations required for performance simulation of a cathode made from a mixture of active materials [13].

Equations	Initial and Boundary Conditions
Li mass transfer in the particles of each cathode active material	
$\frac{\partial c_{s,i}}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 D_{s,i} \frac{\partial c_{s,i}}{\partial r} \right) \quad \text{for } i^{th} \text{ cathode active material}$ Solution of this equation gives the distribution of lithium in r direction in the particles of the cathode active material i, which is located at any x, at any time t	$\frac{\partial c_{s,i}}{\partial r} = 0 \text{ at } r = 0$ $\frac{\partial c_{s,i}}{\partial r} = -\frac{i_{local,i}}{F D_{s,i}} \text{ at } r = r_{p,i}$ $c_{s,i} = c_{s,i,0} \text{ at } t = 0$
Electrochemical reaction in the cathode (Butler–Volmer kinetics)	
$i_{local,cat,i} = i_{0,cat,i} \left[\exp\left(\frac{F}{2RT} \eta_{cat,i}\right) - \exp\left(-\frac{F}{2RT} \eta_{cat,i}\right) \right] \quad \text{for } i^{th} \text{ cathode active material}$ $i_{0,cat,i} = F k_{cat,i} \left(c_{s,i,max} - c_{s,i,surf} \right)^{0.5} c_{s,i,surf}^{0.5} \left(\frac{C_l}{C_{l,ref}} \right)^{0.5}$ $\eta_{cat,i} = \phi_s - \phi_l - E_{eq,cat,i}$ $i_{loc,total} = \sum_{i=1}^N i_{loc,i}$ Solutions of these equations give the total local current generation along the cathode thickness at any time t as well as the local activation + concentration polarizations for each cathode active material along the cathode thickness at any time t	

The capacity of the cathode made from a mixture of cathode active materials can be obtained from Equation (2):

$$Q_{cat} = F \varepsilon_{s,cat} L_{pos} \sum_{i=1}^N Y_i c_{s,i,max} (SOC_{i,max} - SOC_{i,min}) \quad (2)$$

where the state-of-charge (SOC) of each active material can be obtained from Equation (3):

$$SOC_i = \frac{c_{s,i,surf}}{c_{s,i,max}} \quad (3)$$

Based on this mathematical modeling, the simulation of half-cell LIBs was carried out in the COMSOL Multiphysics software package, version 5.2a.

3. Experiment

3.1. Cathode Groups

The cathodes for the experiments are divided into three groups. The first group is the cathodes that were made of a single cathode active material to simulate the performance of the battery in case the separation of active materials during the recycling process is ideal. This group is for the study of scenario I. The second group is the cathodes that were made of a mixture of active materials with one dominant cathode active material to simulate the conditions that the separation process is not ideal and there are some impurities from other types of cathode active materials. This group is for the study of scenario II. The cathodes in this group are made from a dominant cathode active material and the minor percentage of the other four types of cathode active materials that are equally mixed. The third group is the cathodes that were made of the equally mixed five types of cathode active materials to simulate the battery performance in the case that no separation happened in the battery recycling. This group is for the study of scenario III.

3.2. Half-Cell Fabrication

To study the performance of cathodes, several cathodes from each of the three groups were made. The cathode active material was acetylene black (MTI corporation), and the binder was PVDF (MTI corporation). The cathode active materials were mixed homogeneously with PVDF and acetylene black with a weight ratio of 92:4:4, respectively. The solvent to make the cathode slurry was NMP (Sigma-Aldrich) that was mixed at a solid-to-liquid ratio of 1:2 before the cathode slurry was coated on the aluminum current collector. After making the cathodes, several coin half-cells (3032-type) were assembled in the order shown in Figure 3 in an argon-filled glovebox in the laboratory. Lithium foil was used as a reference electrode for all half-cells. The electrolyte used in the half-cells was 1 M LiPF₆ salt in 1:1 EC:DEC (by weight) solvent (Sigma-Aldrich).

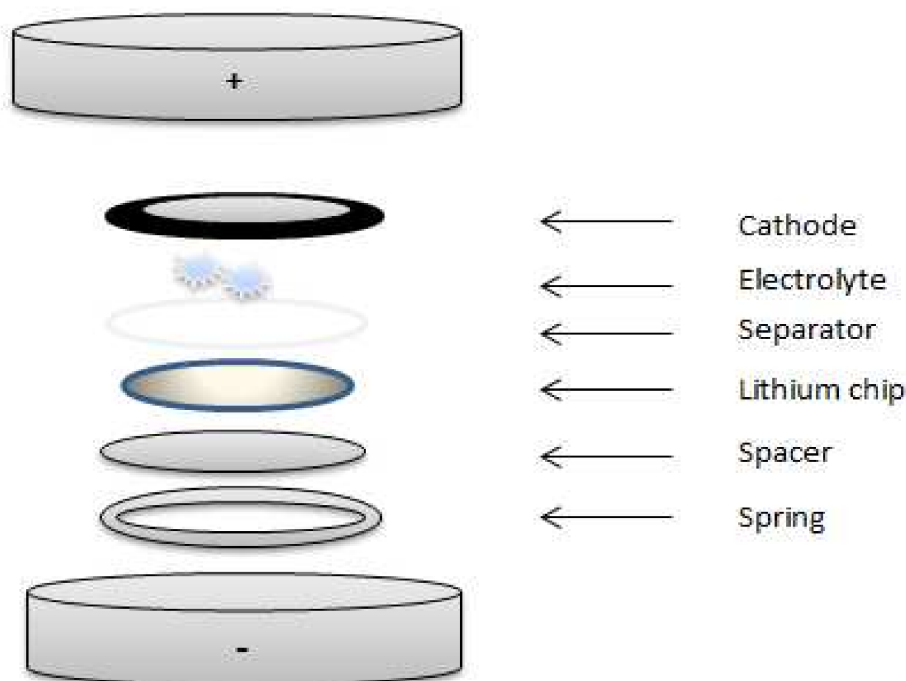


Figure 3. The schematic of the half-cell assembly of coin cells in glovebox.

4. Results and Discussion

In this section, the results of the computer simulation and experiments for scenarios I to III are presented. The results are generated based on one important assumption, that the efficiency of the regeneration process to recover the recycled cathode active materials is 100%. This means that the regeneration process is ideal and the capacity of the recycled active material after the regeneration reaches the capacity of the fresh material. This assumption was made to reduce the degree of freedom of the study to only focus on the effect of blending cathode materials on the cathode performance.

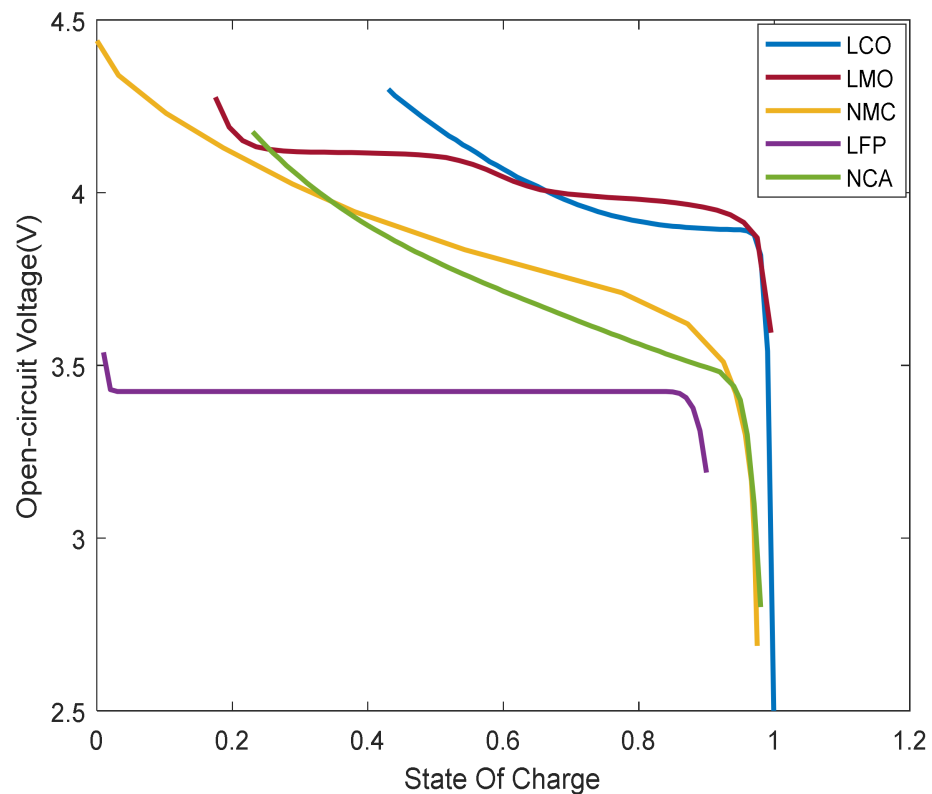
4.1. Scenario I

In this scenario, the separation process is assumed to be performed ideally. This means that a pure single regenerated cathode active material can be used to make new LIBs. The modeling was carried out for five of the most common cathode active materials: LCO, LMO, NCA, NMC, and LFP. The modeling parameters for each of the cathode active materials are listed in Table 3.

Table 3. Model parameters of the commonly used cathode active materials in LIBs [22–27].

Active Material	Density (kg/m ³)	D_{50} (μm)	Maximum State of Charge (mol/m ³)	Initial State of Charge (mol/m ³)	Reaction Rate COEFFICIENT, k_i (mol/s.m ²)	Theoretical Capacity (mAh/g)
LMO	4280	25	23,670.6	6000	5×10^{-10}	148.2
LCO	5050	12	51,555	23,750	1×10^{-7}	273.8
NMC	4770	10.5	51,385	21,500	1×10^{-11}	279.5
NCA	4450	13.6	46,319	8067.9	1×10^{-10}	278.9
LFP	3600	3.5	22,806	1000	3.63×10^{-11}	169.9

The open circuit voltage (OCV) profile of each cathode active material is shown in Figure 4. As seen, each material has a different nominal voltage. The OCV profile represents the ideal discharge performance of the half-cell.

**Figure 4.** Open circuit voltage of some commercially available cathode active materials for LIBs versus the active material's state of charge at 25 °C.

The performance of half-cells with single cathode active materials at 1C discharge is shown in Figure 5. The actual capacity of the battery is lower than the theoretical capacity. The discrepancies of the actual and the theoretical capacity of cathode active materials are due to several factors. One of the factors is the discharge C-rate. As the C-rate increases, the capacity of the battery decreases [28]. In this study, we chose 1C because it is an appropriate indicator for the battery performance, especially for batteries used in hybrid electric vehicles and aircrafts. Another factor is the crystal structure of the active materials. As shown in Figure 5, the actual capacity of batteries, which is obtained from mathematical modeling, is in the range of the experimental results reported in the literature [29,30]. In addition, the modeling and experimental profiles are very close to each other, indicating the validity of the adopted mathematical model.

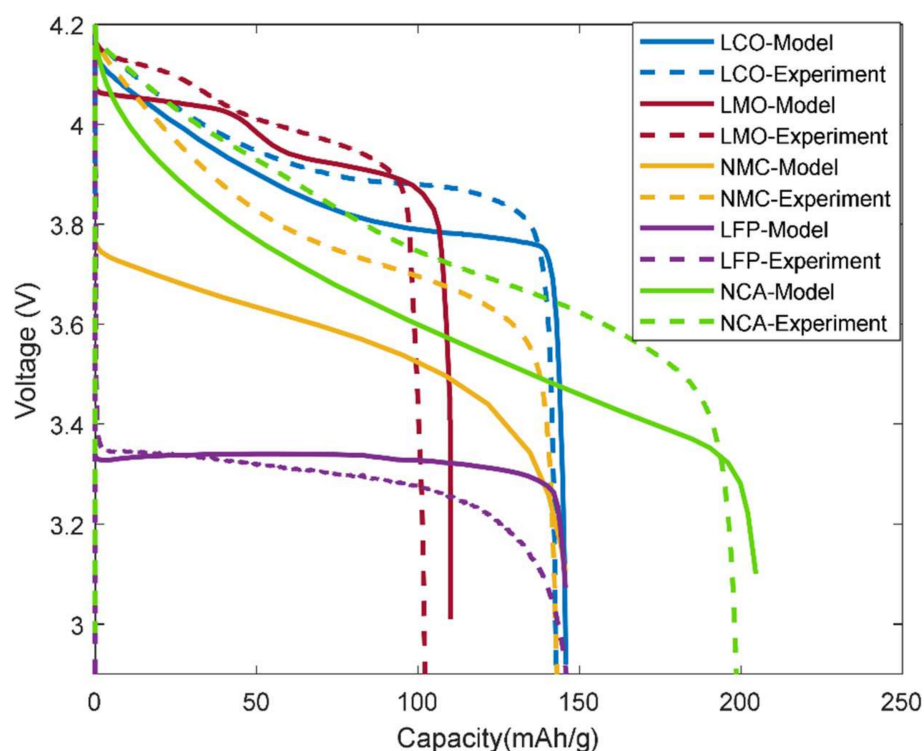


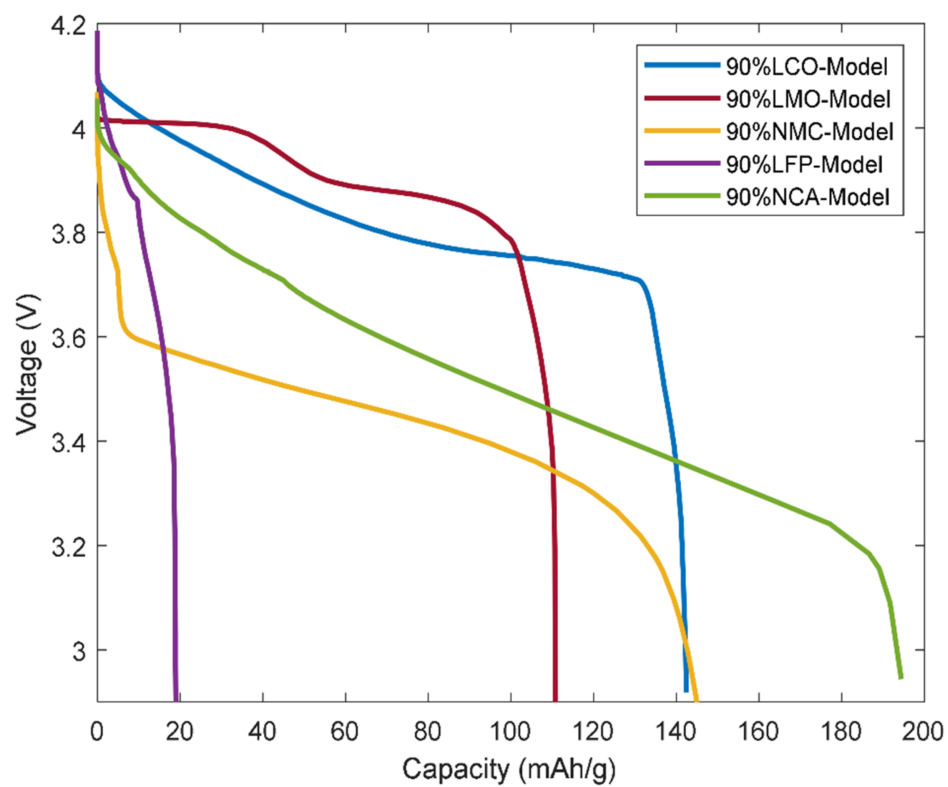
Figure 5. Discharge profile (1C and 25 °C) of half-cells made from cathodes with a single cathode active material.

4.2. Scenario II

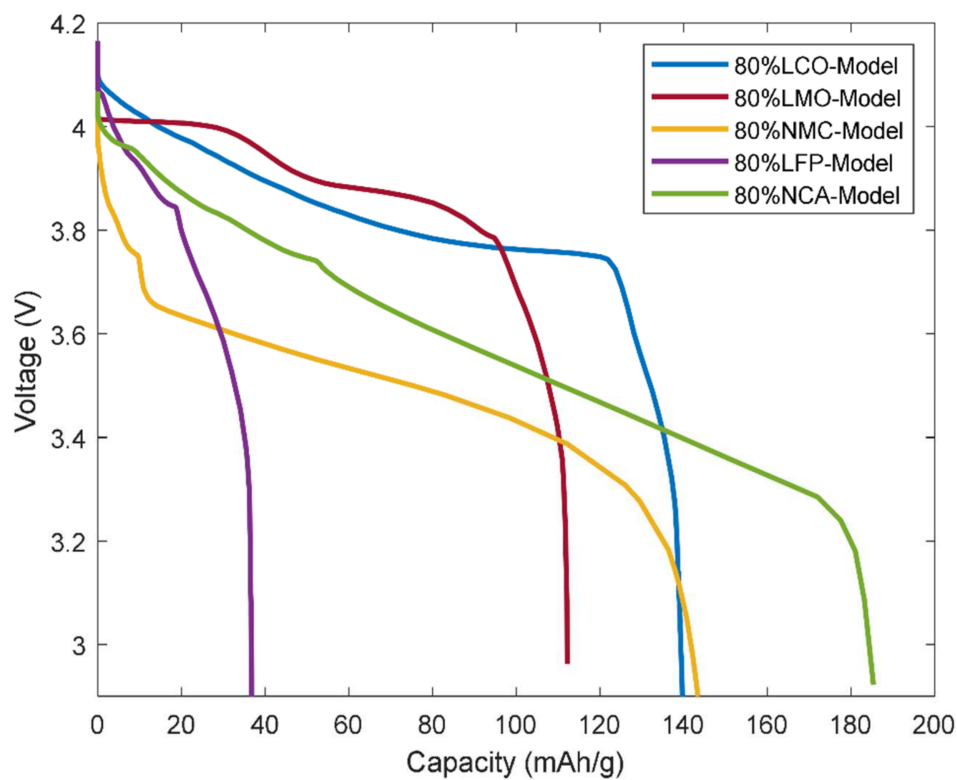
In this scenario, the separation process is performed with an efficiency of less than 100% (actual separation process). Therefore, the single regenerated cathode active material contains a little of the other types of cathode active materials.

To obtain the electrochemical performance of the half-cells made from these regenerated cathode active materials, pure LCO, LMO, NMC, NCA, and LFP powders were mixed homogeneously in different mass ratios. Five different mass ratios of 90%, 80%, 70%, 60%, and 50% were considered for the dominant active materials, and 2.5%, 5%, 7.5%, 10%, and 12.5% of each of the other four active materials were mixed with the dominant material, respectively. For example, for the dominant LCO cathode, we mixed 90 wt% LCO with 2.5 wt% NMC, 2.5 wt% LMO, 2.5 wt% NCA, and 2.5 wt% LFP for sample cathode one. For sample cathode two, we mixed 80 wt% LCO with 5 wt% NMC, 5 wt% LMO, 5 wt% NCA, and 5 wt% LFP. Similarly, we made sample cathodes three, four, and five for the dominant LCO of 70%, 60%, and 50%. We also carried out the same for the dominant LMO, NMC, NCA, and LFP cathode samples one to five. Obviously, in each half-cell, the dominant cathode active material has a higher percentage than the other four cathode active materials. After preparation of all samples and finishing the formation process, the half-cells were discharged between the voltage limits of 4.2 V and 2.9 V at a 1C rate and 25 °C.

Figure 6 shows the performance of the half-cells for five cathode active materials. As seen, when the NCA is the dominant active material, the capacity of the battery decreased with the decreasing percentage of NCA. The reduction in the capacity is because of the higher capacity of NCA among the other four types of the cathode active materials. When the LCO and NMC are the dominant materials, there is a slight reduction in the capacity when the percentage of the dominant active material reduces. This insignificant reduction of the capacity happens because these two cathode materials have a capacity in the average range among the other cathode active materials.

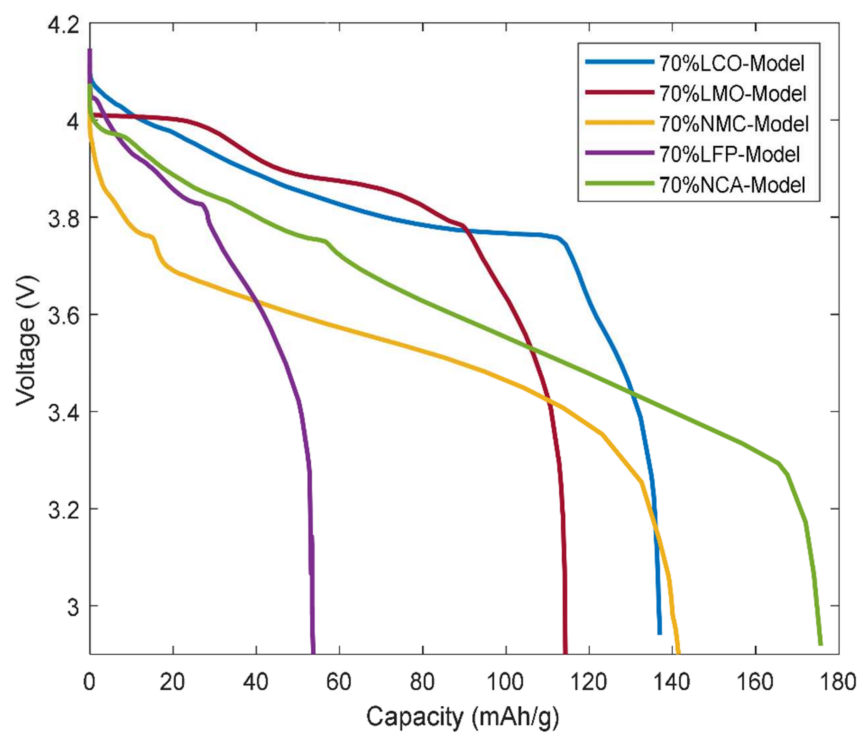


(a)

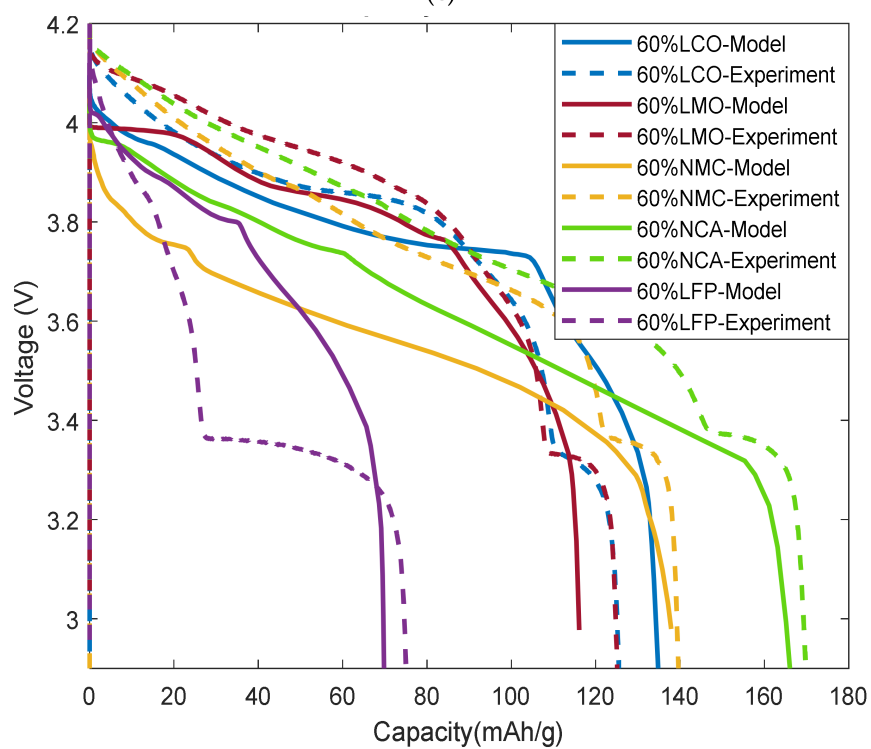


(b)

Figure 6. Cont.



(c)



(d)

Figure 6. Cont.

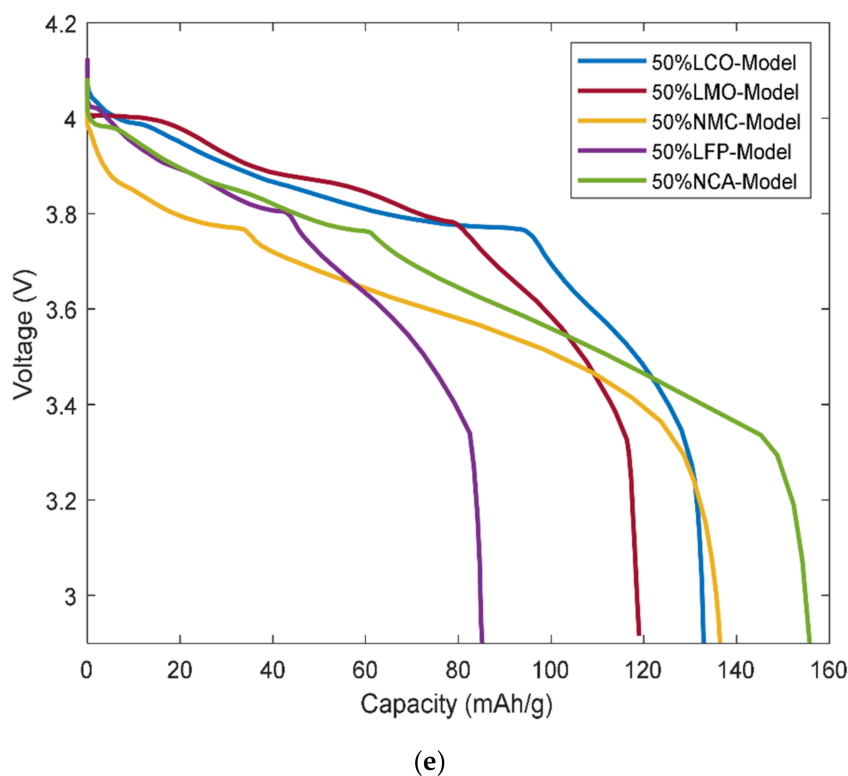


Figure 6. Discharge profile (1C and 25 °C) of half-cells made from a dominant cathode active material. (a) 90% dominant active material mixed with 10% other active materials (2.5% each), (b) 80% dominant active material mixed with 20% other active materials (5% each), (c) 70% dominant active material mixed with 30% other active materials (7.5% each), (d) 60% dominant active material mixed with 40% other active materials (10% each), and (e) 50% dominant active material mixed with 50% other active materials (12.5% each).

When the dominant material is LMO, the capacity of the half-cells is increased with the decreasing percentage of LMO. This increase is due to the difference between the capacity of the LMO and the other four cathode active materials. In fact, LMO has the lowest capacity among the other four materials, while it has the highest nominal voltage of 3.9 V.

The worst-case scenario was found when the dominant material is LFP. The capacity of the half-cells decreased significantly. This reduction of the capacity is due to the fact that the LFP has the lowest nominal voltage (3.2 V) compared to the other four cathode materials, as seen in Figure 4. Thus, the performance of the cathode with a dominant active material is dependent on the nominal voltage of the other mixed active materials. Therefore, all other active materials should be completely separated from the LFP.

For validation purposes, we made half-cells with 60% of the dominant cathode active material and 10% of each of the other four active materials and compared the modeling results with the experimental results. This comparison is shown in Figure 6d. As seen, there is a good agreement between the experiments and modeling in terms of the prediction of the cathode capacity. However, discrepancies are evident for the prediction of voltages, especially for the case when LFP is the dominant active material. Since our focus in this paper is the evaluation of the electrode capacity, the current model is valid. However, a more accurate model is required for studying the voltage trends.

4.3. Scenario III

In this scenario, the separation has not been performed during the recycling process, all types of cathode active materials are regenerated together, and a mixture of cathode active materials is used to make new LIBs. Three samples were prepared for this scenario.

For sample one, we made the half-cells from cathodes with equal weight percentages of the five cathode materials (20 wt% LCO, 20 wt% LMO, 20 wt% NMC, 20 wt% NCA, and 20 wt% LFP). Since from the results of scenario II we learned that LFP is not suitable to be in the mixture of cathode active materials, we made two more samples that have only 5 wt% and 0 wt% LFP. These two samples simulate the case that the separation is performed only for LFP. For sample two, we made the half-cells from cathodes with equal weight percentages of 23.75% for LCO, LMO, NMC, and NCA and 5 wt% LFP. For sample three, we made the half-cells from cathodes with equal weight percentages of 25% for LCO, LMO, NMC, and NCA. No LFP exists in sample three. The composition of samples one to three are listed in Table 4.

Table 4. Mass fraction of active materials in the cathode samples made for scenario III.

Cathode in the Half-Cells	LCO wt%	LMO wt%	NMC wt%	NCA wt%	LFP wt%
Sample 1 (20% each)	20	20	20	20	20
Sample 2 (5% LFP, 23.75% each)	23.75	23.75	23.75	23.75	5
Sample 3 (0% LFP, 25% each)	25	25	25	25	0

As seen in Figure 7, the best performance was found for the half-cells made from sample three, which has 0% LFP. The capacity of the half-cell made with a 5 wt% LFP (sample two) does not have noticeable a difference in comparison to the half-cell made from sample three. Therefore, we can conclude that a small fraction of LFP (typically less than 5 wt%) does not have a significant impact on the cathode capacity. However, the half-cell capacity decreases significantly when the weight percentage of LFP in the cathode active material mixture reaches 20% (sample one).

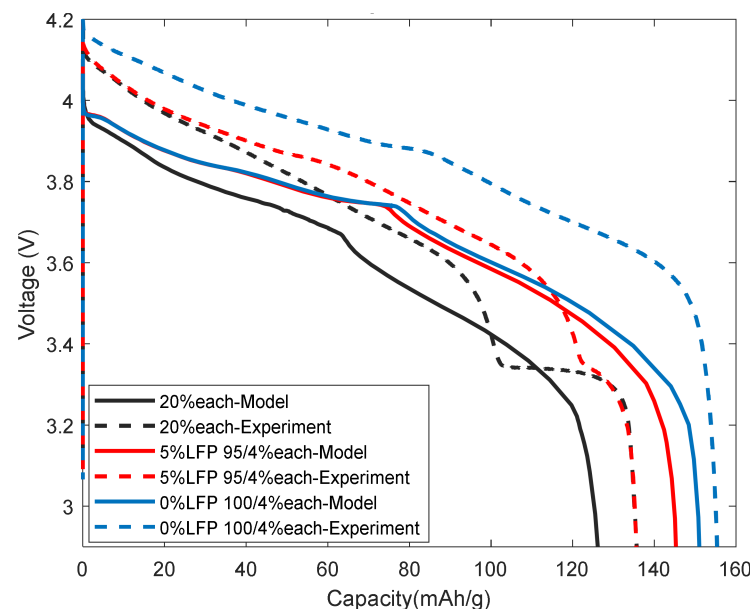


Figure 7. Discharge profile (1C, 25 °C) of cathodes made from the mixture of regenerated cathode active materials. Black curves: 20 wt% of each of the five types of cathode active materials (sample 1). Red curves: 5 wt% LFP and 23.75 wt% of each of the other four active materials (sample 2). Blue curves: 0 wt% LFP and 25 wt% of each of the other four cathode active materials (sample 3).

5. Conclusions

The performance of cathodes made from recycled cathode active materials for three scenarios of the active materials' separation was studied. In scenario one, the separation process in the recycling facility was ideal, and a pure single cathode active material was used

to make new batteries. In scenario two, the separation process for active materials in the recycling facility was realistic, with an efficiency of less than 100%. In this scenario, a single cathode active material that contains a little of the other types of cathode active materials was used to make new batteries. In scenario three, the separation was not performed, and all types of cathode active materials were regenerated together and used to make new batteries. The results were generated through modeling and computer simulation and several experiments were conducted for validation of the model. The cathode active materials that were studied are five commercially available cathode active materials: LMO, LCO, NMC, NCA, and LFP. The results indicated that the fabrication of new LIBs with a mixture of regenerated cathode active materials is possible when the cathode active materials are not separated from each other. However, it is better that the separation process is added to the recycling process, especially for minimization of the amount of LFP in the mixture of cathode active materials. It is not necessary that the separation process is ideal. However, more studies are still required to show that making new LIBs with a dominant cathode active material is technically and economically feasible.

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Nomenclature

A	Apparent surface area of electrode (m^2)
c	Concentration (mol/m^3)
D	Diffusivity (m^2/s)
D_{50}	Mean diameter of particles (m)
E_{eq}	Equilibrium potential (V)
f	Mean molar activity coefficient of inorganic salt in electrolyte
F	Faraday's constant ($96,485 \text{ C}/\text{mol}$)
i	Current density (A/m^2)
$I_{applied}$	Applied current to battery (A)
i_0	Exchange current density (A/m^2)
i_{local}	Local current density generation (A/m^2)
k	Electrochemical reaction rate coefficient (m/s)
L	Thickness (m)
N	Flux ($\text{mol}/\text{m}^2 \cdot \text{s}$)
Q	Capacity (Ah/m^2)
r	Radial direction in spherical coordinate system (m)
R	Universal gas constant ($8.314 \text{ J}/\text{mol K}$)
r_p	Average radius of active material particles
S_a	Surface area per unit volume (m^2/m^3)
SOC	State of charge of the active material
t	time (s)
t_+^0	Lithium-ion transference number
T	Temperature (K)
x	x direction in cartesian coordinate system (m)
Y	Mole fraction of an active material in the mixture of active materials

Greek Letters

ε	Volume fraction
η	Polarization (V)
σ	Conductivity (S/m)
ϕ	Potential (V)

Subscripts

0	Initial
<i>i</i>	Index for <i>i</i> th cathode active materials in the cathode mixture
<i>l</i>	Liquid phase (electrolyte)
<i>cat</i>	Cathode
<i>eff</i>	Effective
<i>max</i>	maximum
<i>min</i>	minimum
<i>pos</i>	Positive electrode (cathode)
<i>ref</i>	Reference
<i>s</i>	Solid phase of electrode (active/conductive material)
<i>sep</i>	Separator
<i>surf</i>	Surface

Abbreviations

DEC	Dimethyl carbonate
EC	Ethylene carbonate
LCO	LiCoO ₂
LFP	LiFePO ₄
LIB	Lithium-ion battery
LMO	LiMn ₂ O ₄
NCA	LiNi _x Co _y Al _(1-x-y) O ₂
NMC	LiNi _x Co _y Mn _(1-x-y) O ₂
NMP	N-Methyl-2-pyrrolidone
OCV	Open circuit voltage
PVDF	polyvinylidene fluoride

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