

Regeneration of Polyolefin Separators from Spent Li-Ion Battery for Second Life

Subramanian Natarajan,^[a, c] Krishnan Subramanyan,^[a] R. Baby Dhanalakshmi,^[b] A. Manuel Stephan,^{*[b]} and Vanchiappan Aravindan^{*[a]}

The increased usage of Lithium ion batteries and dominance in the consumer applications bring out a vast quantity of hazardous spent LIBs into the waste stream. Current recycling industries/technologies have engrossed only to recover the maximum valuable metal sources from the spent LIBs and the ignorance of harmful polyolefins (separators/polymers) in a huge amount would earn environmental hazards and impedes the reuse applications. In this study, for the first time, we have simply recovered the used separator from spent LIBs, cleaned with de-ionized water and reutilized the separator without any modification for new battery fabrication to emphasize "3R" principles in green chemistry. First, the recovered separator has been examined by characterization techniques including tensile strength, differential scanning calorimetry, ionic conductivity, electrolyte uptake, and interfacial resistance, etc. to validate the suitability for re-use and compared with a commercial separator of Celgard. The obtained results endorsed to reuse the separator in a half-cell configuration by employing LiMn_2O_4 as a cathode and Li metal as an anode. The test cell displayed almost equal capacity of $\sim 123 \text{ mAh g}^{-1}$ at 25 mA g^{-1} using the recovered separator and achieved better cycling life. These outcomes evidently prove that the recovered separator from spent LIBs would replace the commercial separator for the battery application in the near future that helps to accomplish the complete recycling process of spent LIBs for the industries where the recovery of metals only being effectively recycled.

1. Introduction

In this era of the modern technological advancements, high energy and power density of lithium-ion batteries (LIBs) mostly knock out other batteries in power tools, portable electronics applications, also likely awaited to increase in the hybrid/full

electric vehicles as a consequence of the recent shocking rate of green-house emissions.^[1–3] As a pioneer, numerous countries have planned and some countries like Norway, France, and India declared plans to ban the vehicles based on the internal combustion engines in the near future.^[4–6] Thus, LIBs are of phenomenal interest in research to further develop the electrochemical performance in view of creating the choice to make technology for electric vehicles applications.^[1,2,7] Additionally, the constant growth of lithium-ion batteries in the energy market paves the way to make a demand for the separators which plays a crucial role in the batteries by executing two main functions effectively.^[8] The separator places between the positive and negative electrodes to avert the short circuits and simultaneously permit swift transport of ions effectively in an electrochemical cell as a good electronic insulator.^[9] Generally, the cathode of LIB holds intercalated Li-based compounds on the Al foil including LiCoO_2 , LiMn_2O_4 , $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$, LiFePO_4 , and $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$, etc. and graphite flakes on the Cu foil as an anode. The microporous polyolefin membranes (polypropylene (PP), polyethylene (PE) or PP/PE/PP) permit to travel Li-ions which is offered by the electrolyte (lithium salt in aprotic organic solvents) during the charging-discharging process in the LIBs.^[1,9]

Upon the exploration of various separator materials, the polyolefin materials find an unprecedented place owing to their outstanding mechanical properties, compatibility, chemical stability, and low-cost.^[9–13] Also, different composition of polyolefin separator is being used as a single layer and multilayer in the LIBs offers by different manufacturers. Generally, the separator placed in the LIBs has a pore size in the range of $\sim 0.03\text{--}0.1 \mu\text{m}$ along with 30–50% porosity. However, the single layer of PP and PE porosity will be lost if the temperature reaches their melting points of 165°C and 135°C , respectively. Consequently, Celgard had established the trilayer material through PP/PE/PP that helps to maintain the integrity of film using the layer of PP and the PE layer shutdown the cell when observed the over-temperature condition.^[9,10] Also, the battery industry needs to construct the LIBs using low-cost separator with general requirements such as pore size, thickness, porosity, tensile strength, electrical resistance, wettability, and electrochemical stability, etc.^[9,11] Besides, the global market for LIB separator would raise by \$2.02 billion in the forecast period of 2018–2022^[12] whereas it will increase at an 18.01% compound annual growth rate during 2019–2024^[13] owing to the nonstop requirement of LIBs for the various applications.

[a] Dr. S. Natarajan, K. Subramanyan, Dr. V. Aravindan
Department of Chemistry
Indian Institute of Science Education and Research (IISER)
Tirupati – 517507, India
E-mail: aravind_van@yahoo.com

[b] R. B. Dhanalakshmi, Dr. A. M. Stephan
CSIR-Central Electrochemical Research Institute (CECRI)
Karaikudi – 630006, Tamil Nadu, India
E-mail: amstephan@cecri.res.in

[c] Dr. S. Natarajan
Nanomaterials & System Laboratory
Major of Mechatronics Engineering, Faculty of Applied Energy System
Jeju National University, Jeju 63243, Republic of Korea

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Most of the present recycling strategies at both lab and industrial scale have been only focusing on the recovery of metals from the cathode due to their demand and it is hardly ever on the anode part.^[1,2,14–17] Also, some techniques the anode part by burning or left as a residue after filtration at the end.^[2,18–20] Similarly, the polymers which play as a separator in the LIBs are also not getting consideration during the recycling that obstacle the goal of the recycling process.^[2,8,18,21] It should be noted that the other spent batteries components become relatively lower values after the removal of the metal-rich cathode part.^[22,23] Consequently, anode and separator could not seek out their place as a valuable product at the end of the recycling process.^[20,24] Even the current battery recycling industries such as Umicore, Sumitomo-Sony, Toxco, and Litho-Rec process, etc. follow the pyrometallurgy, hydrometallurgy or combination of those techniques to recycle the spent LIBs. However, these recycling technologies end up with metal oxide/salt/powder or alloy as the main products, neglecting the remaining parts of the spent LIBs including an anode, electrolyte, and separator.^[1,2,7,18] Recently, researchers have turned into the electrolyte components to extract the electrolyte effectively by involving supercritical CO₂ extraction as it has a good dissolving capacity for the organic compounds present in the electrolyte complex.^[25,26] Similarly, the graphite from the anode is receiving a lot of attention recently due to the presence of Li residue in the form of solid electrolyte interface as well as owing to their wide applications.^[27–31]

However, the separator still remains as an ignored component in the spent LIBs and the recycling of separator is needed before entering into the waste stream in large volumes. The separator can be reused for a wide range of applications if recycled acceptably which the companies/researchers failed to do it.^[19,20,32–34] For example, the preliminary process like sieving eliminates the separator part in the coarse fraction (>1 mm) along with plastic, Al foil, and Cu foil during the recycling of spent LIBs.^[2] In magnetic separation technique, the separator is being considered as a non-magnetic impurity and removes with plastics eventually.^[35,36] Unfortunately, the industrial recycling technique, for instance, LithoRec battery recycling process rejects the separator in the coarse fraction (>1 mm) through gravity type zig-zag air classifier, which separates electrodes from remaining parts of the spent LIBs.^[2,27] Yet, there is no evidence after the separation for the reuse of separator in that kind of technologies, emphasizes the industries/researchers recycle/reuse properly for more suitable applications. Taking this advantage, we have attempted for the first-time to reuse the separator in the H₂ and CO₂ storage applications *via* a simple one-step carbonization technique, as well as in the synthesis of polymer–graphite nanocomposite thin films.^[8,21] In our recycling process, the separator has been examined as such for the battery fabrication and compared with a fresh separator in the electrochemical studies. The resultant electrochemical performance also impressed and guarantees that the separator can be reused efficiently for the fabrication of commercial lithium-ion batteries in the near future.

2. Results and Discussion

FE-SEM analysis was executed to examine the morphology of both used separator of spent LIBs and fresh separator from Celgard. It is very clear from the obtained images (Figure 1) that the stripe-like morphology was determined in both used and fresh separator with uniform distribution of pores and no difference was observed in the surface of the separators.^[8,9] The presence of particles on the used separator might arise from the precipitation of electrolyte reduction products. Moreover, the mechanical strength of the used and fresh separators was checked by plotting stress-strain curves (Figure 2a), in that, fresh separator from spent LIBs exposed the maximum tensile strength of 13.3 kg mm⁻² whereas used separator could reach only the tensile strength of 7.7 kg mm⁻² as it is already permitted the “n” number of ionic charge carriers rapidly through their porous membrane when placed in the LIBs that decreased the mechanical properties of the used separator. Separator shutdown is a vital mechanism in order to limit the temperature and also to stop the venting in a short-circuited battery which happens near to the melting point of the separator, thus the melting point of the separator decides the separator shutdown temperature. The formation of the nanoporous film (insulating layer) between the positive and negative electrodes because of the pores collapse when the separator reaches near to the melting point restricts the electrochemical activity before the explosion of the battery, can be identified by DSC analysis.^[9,37] The melting curve of the used separator clearly showed the material is comprised of polyethylene and polypropylene by displaying the peak temperatures of ~137 °C and ~161 °C, well-matched with the fresh separator temperature range which indicates the material may belong to the Celgard 2325 (PP/PE/PP) or PP/PE (Figure 2b).^[9,38] The trilayer kind of material plays a dual role wherein one material can be used for the shutdown response and another material will be utilized for the mechanical properties.^[9]

The electrolyte uptake of the separator is a significant physical property and considered as a decisive factor in the performance of the battery, its main role is able to well-absorb the electrolyte in a substantial quantity and should hold the consumed electrolyte when the battery is in the electrochemical process lead to attain minimum cell resistance.^[39] Figure 2c compares the electrolyte uptake behaviour of used and fresh separators after soaking in 1 M LiPF₆ in 1:1 v/v of EC: DMC. It should be noted that the electrolyte uptake of used separator increases from ~147 to ~338% when the time increased from 1 to 10 min, whereas fresh separator showed only ~110 to ~233% during the same time interval specifies that the used separator has the capability to replace the fresh separator in the practical cell fabrication. Also, the reason for the lower percentage electrolyte uptake of fresh separator compared to the used separator might be due to the processing parameters/conditions of the membranes. As well, the good-electrolyte uptake property of the separator reflects in the achievement of excellent ionic conductivity and performance of the battery. Ionic conductivity of the both used and fresh electronically insulating membranes were checked by

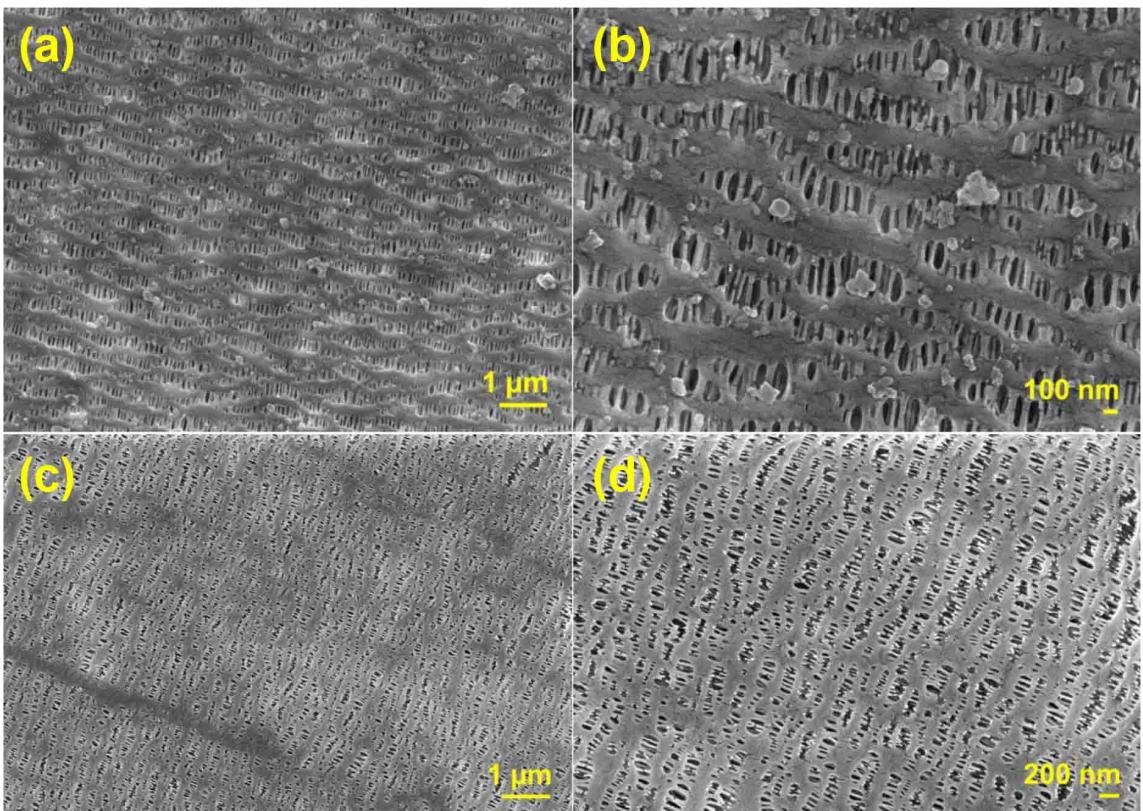


Figure 1. FE-SEM images of (a and b) used separator from spent LIBs; (c and d) fresh separator (Celgard).

plotting inverse temperature as a function (Figure 2d), exhibited the order of $\sim 10^{-4} \text{ S cm}^{-1}$ even the temperature increased in the range of 0–70°C. The comparable ionic conductivity results evidently prove both used and fresh separators allowed similar kinds of transportation of Li-ions through the interconnected porous structure. The Li-based electrolyte salts in a mixture of organic compounds form the solid electrolyte interface (SEI) layer with the anode not only governs the Li-ion conduction and electrochemical performance but also the safety issues of the batteries eventually.⁴⁰ However, the thickness of the SEI layer during this process can be formed in the range of few to hundreds of angstroms that can be identified by impedance spectroscopy. To compare the interfacial stability of used and fresh separator with metallic lithium electrodes, a symmetric cell was constructed and measured at 25°C which is shown in Figure S1. The interfacial resistance values were constant up to five days, then showed in a zig-zag manner for the used separator whereas fresh separator had shown constant resistance than the used separator. Nevertheless, both used and fresh separator displayed almost the same interfacial resistance values which approve the used separator to be employed for the battery applications.

2.1. Electrochemical Performance

In order to evaluate the feasibility of using the spent battery separator for practical LIB application, the coin-type cell was

assembled using LiMn_2O_4 as the cathode and metallic Li as an anode in the organic electrolyte at a current density of 25 mA g⁻¹. For the comparison, fresh separator (Celgard) was examined in the half-cell configuration separately at the same current density by employing the same electrodes. Figure 3a and b display very analogous charge-discharge profiles involved two potential plateau features associated with the intercalation-deintercalation process that revealed the initial discharge specific capacities of ~ 123 and $\sim 118 \text{ mAh g}^{-1}$ for the used and fresh separator, respectively. However, the capacity slightly decreased when the cycle number was increased as shown in Figure 3a and b. Subsequently, the cycling test was performed between 3.5 to 4.3 V vs. Li to check the stability of the used separator and the result was compared to the fresh separator cycling performance. Figure 3c illustrates that the used separator slightly dominated without compromising the capacity up to 60 cycles however it could not meet 100 cycles where the fresh separator delivered $\sim 85 \text{ mAh g}^{-1}$ after 120 cycles. As well, high coulombic efficiency was noticed for the used separator compared to the fresh separator (Figure 3d). This result proves that there is no much variance in the capacity and cycling capacity between the fresh and used separator which clearly underlines that the separator can be employed successfully for the battery applications. Further, the study has to be conducted to ensure the possibility of re-using the spent battery separator. Currently, we are in the process of purifying the spent battery separator to see the electrochemical activity towards the battery applications.

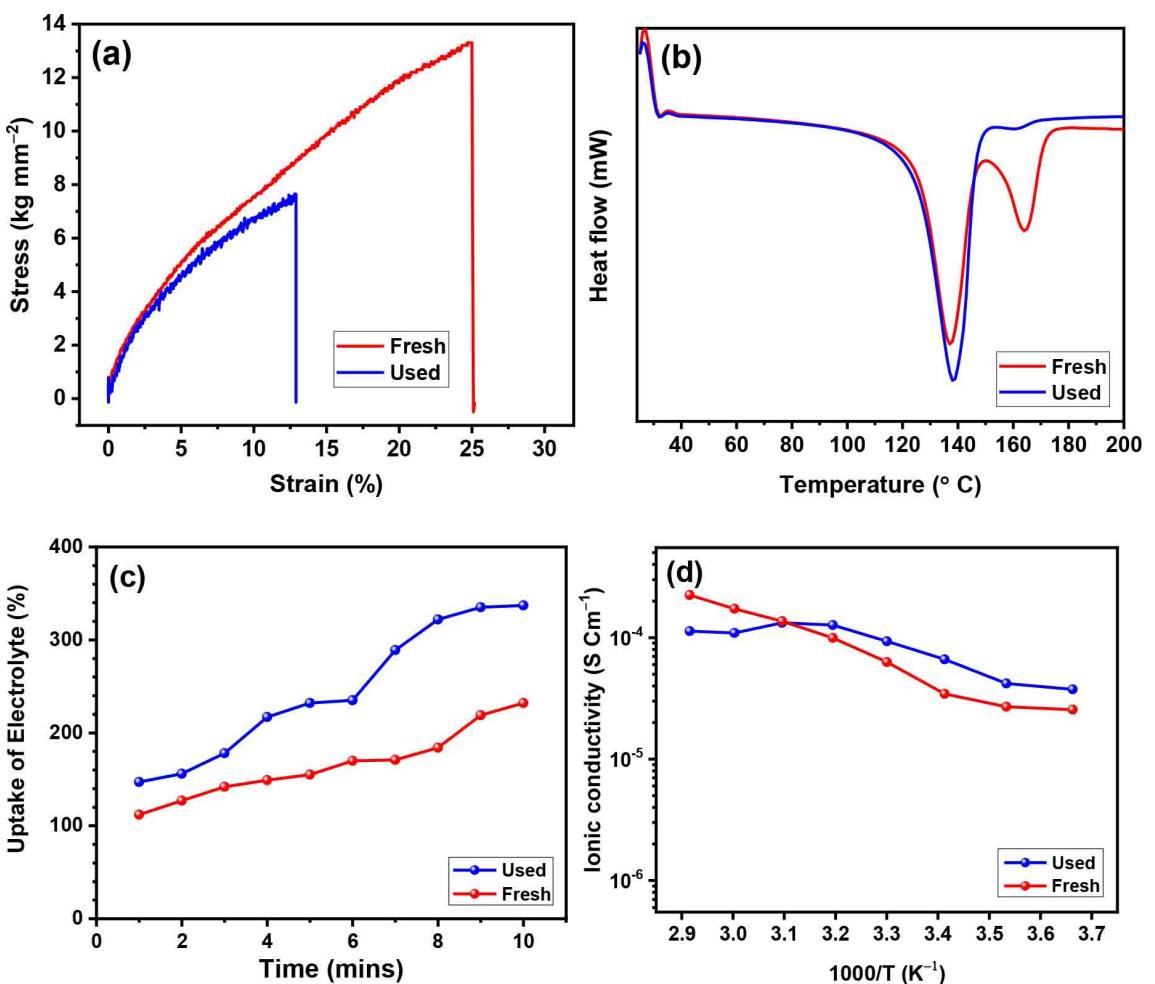


Figure 2. a) Stress-strain curves, b) DSC thermograms, c) electrolyte uptake behaviour, d) ionic conductivity of the used separator from spent LIBs and commercial separator (Celgard).

3. Conclusions

The separator from spent LIBs has been reused for the first time for the new battery fabrication in this present work. The recovered separator met the essential requirements to be a good separator is confirmed by the characterization techniques and with the comparison of the commercial separator. The mechanical properties, electrolyte uptake behaviour, ionic conductivity, and the interfacial resistance, etc., ensured the reuse of spent LIB separator in a new battery fabrication that showed high capacity and decent cycling life in the half-cell assembly. Therefore, the obtained results of the used separator emphasize the recycling industries and researchers so as to reuse the waste separator in the battery applications in the near future to build cost-effective LIBs in an effective way. As well, this “waste-to-wealth” initiative could preserve the environment from the upcoming massive amount of non-degradable plastic waste.

Experimental Section

Recovery of the separator from spent LIBs

Spent LIBs were collected and discharged using NaCl solution regardless of manufacturers from local vendors in Tirupati, Andhra Pradesh, India. Subsequently, the LIBs were disassembled manually and detached the wrapped-up separators from both positive and negative electrodes. Then, the collected separators without any modification have been immersed into water under the sonication for five minutes to remove any impurities present in their surface. Further, the separators were dried at 70 °C, characterized and reused as-such for lithium-ion battery studies (charge-discharge process). Besides, the recovered parts of cathode, anode and metallic cases were stored to reuse for energy storage applications.

Material characterization

The surface morphology of the recovered separator from spent LIBs and fresh separator (Celgard 25 micrometer Trilayer polypropylene–polyethylene–polypropylene membrane) were observed on a field-emission scanning electron microscope (JSM-7100F instrument). The thermal properties of both recovered and fresh separators were examined using a differential scanning calorimeter (DSC 214 polyma). The ionic conductivity was meas-

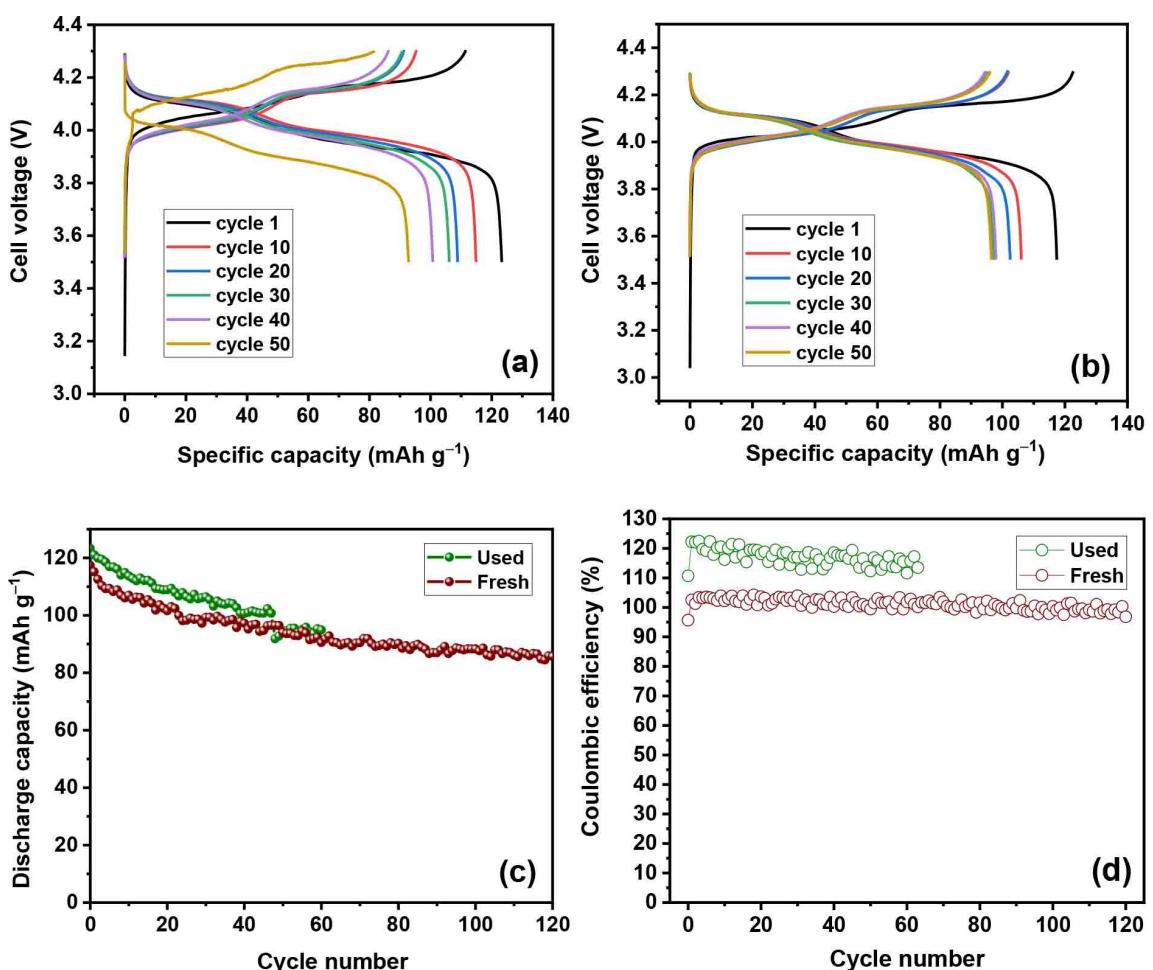


Figure 3. Galvanostatic charge-discharge profiles of LiMn_2O_4 vs. Li at a current density of 25 mA g^{-1} in half-cell assembly for a) used separator, b) fresh separator, c) cycling profile for used and fresh separator, and d) Coulombic efficiency of the cell using recovered/used and fresh separator.

ured for the separators using an electrochemical impedance analyzer (Biologic Model, VSP France) in the temperature ranges from 0 to 70°C between the frequencies 1 kHz and 50 mHz. The electrolyte uptake was measured by employing the formula by soaking the known weight of the separators in the non-aqueous electrolyte and compared their efficiency by weighing after 24 h. The interfacial property of fresh and used separator was tested by constructing a symmetric non-blocking cell using lithium metal anode, and the impedance analysis calculated based on the time was measured at 25°C . Mechanical properties of both separator samples were executed in the ASTM D882 by loading the sample at a test speed of 500 mm min^{-1} .

The uptake percentage of the electrolyte solution was measured using the following equation

$$\text{Uptake (\%)} = [(M_1 - M_0)/M_0] \times 100$$

Where M_0 and M_1 respectively represent the initial and final weight of the membrane.^[41]

The composite cathode was prepared by mixing 80 wt.% of the LiMn_2O_4 (Sigma-Aldrich, USA)(LMO), 10 wt.% of Teflonized acetylene black (TAB-2, binder), and 10 wt.% of acetylene black (conductive additive) and prepared as a film using ethanol, subsequently placed in the stainless-steel mesh and dried at 75 degree celsius in a vacuum oven for 4 hours. The used and fresh

separator was separately placed between LMO cathodes and lithium metal foil anode with 1 M LiPF_6 electrolyte in ethylene carbonate Ec:DMC (1:1 vol.%) which was assembled in an argon-filled glove box (MBraun, Germany) using 2016 type coin cell.

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Conflict of Interest

The authors declare no conflict of interest.

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