Semi-interpenetrated polymer networks based on modified cellulose and starch as gel polymer electrolytes for high performance lithium ion batteries

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Abstract Poly(ethylene oxide) (PEO) is one of the most famous polymer electrolytes; however, its low conductivity and capacity have prevented its commercial applications. This study utilizes carboxymethyl starch (CMS) and oxidized carboxymethyl cellulose (OCMC) natural polymers with a high potential to dissolve lithium ions (Li+) in to help PEO ionic conductivity. The semi-interpenetrating polymer networks (semi-IPNs) consist of crosslinked poly(ethylene glycol) methyl ether methacrylate (PEGMA) with poly(ethylene glycol) diallyl (PEGDA) and free CMS/OCMC chains. Effect of increasing the amount of natural polymer on the electrochemical properties of semi-IPNs is investigated. Semi-IPN CMS50% and semi-IPN OCMC50% deliver excellent results such as high conductivity (in order $10^{-2}$ S cm$^{-1}$) at room temperature, electrochemical stability window higher than 4.5 V, high Li$^+$ transfer number, high discharge capacities (191 and 203 mAh g$^{-1}$ with capacity retention of 85 and 88.5% after 100 cycles at 0.2 C, respectively), and stable cyclic behavior.

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Graphical Abstract

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Introduction

Lithium ion batteries (LIBs) are widely utilized in electrical industry and energy storage devices because of their high energy density, lightweight, and stability (Hassoun et al. 2009; Zhou et al. 2014; Manthiram et al. 2017). Typical LIBs use a highly conductive carbonate liquid as the electrolyte, whereas escape from these toxic and flammable solvents ends up in issues such as safety and contamination (Liu et al. 2018a, b; Lisbona et al. 2011). Gel polymer electrolytes (GPEs) are one of the foremost effective ways that researchers have developed thus far for this downside besides increasing flexibility and mechanical properties of LIBs (Cho et al. 2019; Thakur et al. 2012; Lee et al. 2014). Poly(ethylene oxide) (PEO) is one of the most popular polymers used in GPEs (Zhang et al. 2019; Chan et al. 2018; Li et al. 2017), that has been studied a lot. However, because of its low ionic conductivity, deficient environmental friendly, and poor mechanical properties, it is not nevertheless become an acceptable alternative to liquid electrolytes (Zhou et al. 2019a, b; Naderi et al. 2016). The solutions planned by the researchers are to use natural polymers with high electron donor atoms in their structure (Baskoro et al. 2019), equivalent to cellulose and its derivatives, and to blend them with synthetic polymers such as PEO, or to composite them with different polymers and fillers. Cellulose/PEG based GPE (Zhao et al. 2020a, b), and GPE based on cellulose triacetate and poly(polyethylene glycol methacrylate) p(PEGMA) employing a photopolymerization technique (Nirmale et al. 2017), are instances of the blending approach. A cross-linked nanocomposite polymer electrolyte (CNPE) based on poly(propylene oxide)-poly(ethylene oxide)- poly(propylene oxide) triblock chains and surface-modified SiO2 nanoparticles (Tang et al. 2020), nanocellulose/ hydroxypropyl methylcellulose composite matrix as biodegradable, flameproof, and self-standing GPE (Gou et al. 2021), sandwich composite of PEO@ (Er0.5Nb0.5)0.05Ti0.95O2@cellulose electrolyte (Zheng et al. 2021), cross-linked nano-SiO2 and cellulose acetate (Hu et al. 2020), and GPE based on pure natural polymer matrix of potato starch composite lignocellulose (Song et al. 2017) are examples of composites. In a motivating study, Zhu et al. (Zhu et al. 2015) synthesized a porous membrane of carboxymethyl cellulose (CMC) by a simple nonsolvent evaporation method as a host of a GPE for LIBs. Despite these studies, the absence of an effective and environmental friendly GPE for LIBs continues to be felt. Carboxymethyl starch
(CMS) and oxidized carboxymethyl cellulose (OCMC) are two offered and environmental friendly natural polymers with high mechanical strength (due to high glass transition temperature \(T_g\)) (Heinze et al. 2005; Jiang et al. 2016; Cheng et al. 2008). These two polymers have high potential for GPEs applications because of the large number of electron donor atoms in their repeating units. However, their smooth and nonporous surface prevents the whole uptake of lithium salt solution (Zhu et al. 2015; Minaev et al. 2016). As a result, these two polymers cannot show their potential in dissolving and transporting lithium salts as GPEs. To overcome this challenge, blending CMS/OCMC with other polymeric phases with high ability to uptake lithium salt solution such as cross-linked PEO is an effective approach (Dragan et al. 2014).

To require advantage of the utmost swelling properties of PEO and ionic conductivity of CMC/OCMC, this study synthesizes a GPE based on semi-interpenetrating polymer network (semi-IPN) structure. This consists of a crosslinked network of poly(ethylene glycol) methyl ether methacrylate (PEGMA)/poly(ethylene glycol) diallyl (PEGDA) (as a protracted chain crosslinker), and CMS/OCMC free chains. Herein, P(PEGMA) network helps uptaking lithium salt solution and CMS/OCMC additionally improves ion transfer beside mechanical properties of the ultimate GPE. Furthermore, effect of amount of natural polymers (CMS/OCMC) in the P(PEGMA)-PEGDA networks on the electrochemical properties similar to solvent uptake and conductivity is investigated. Finally, electrochemical properties and performance of fabricated lithium ion batteries are investigated.

**Experimental section**

Synthesis of carboxymethyl cellulose (CMC) and oxidative carboxymethyl cellulose (OCMC)

Firstly, cellulose was extracted from cotton gin waste in 4 steps: treatment of cotton gin waste with NaOH (20 wt. %), bleaching with \(\text{H}_2\text{O}_2\) (1.5 wt. %), adjusting the pH at 7 by dilute HCl, and acid treatment with \(\text{H}_2\text{SO}_4\) (10 wt. %). Then, cellulose was converted to CMC after alkalization and etherification with monochloroacetic acid and NaOH (Haleem et al. 2014). Subsequently, periodic acid was added to a clear solution of CMC and distilled water under stirring. Finally, the pH of the solution was adjusted to about 3.5 by using dilute \(\text{H}_2\text{SO}_4\) and sodium bicarbonate at 45 °C to obtain OCMC (Anjali et al. 2012).

Synthesis of carboxymethyl starch (CMS)

Starch and sodium monochloroacetate (1:1 w/w) were dissolved in NaOH solution (15%). Then, isopropyl alcohol was added to the solution under stirring and nitrogen purging at 40 °C. After filtration, it was suspended in methanol and neutralized with acetic acid. At the end, the obtained slurry was dried in a vacuum oven at 40 °C for 48 h (Lawal et al. 2007).

Synthesis of poly(ethylene glycol) diallyl (PEGDA)

PEG 600 (2 g, 1 mmol) was dissolved in THF (70 mL). Then, allyl bromide (173 μL, 2 mmol) was added dropwise to the reaction mixture at room temperature. Afterward, powder NaOH (200 mg, 5 mmol) was added to the mixture, and the resulting suspension was stirred at 80 °C for 24 h. After cooling at room temperature, it was filtered and washed several times with THF to eliminate the catalyst. Subsequently, the aqueous solution was dried under vacuumed oven at room temperature (Mauri et al. 2015). Scheme S1 shows the synthetic approach of PEGDA.

Preparation of semi-IPN-PEGMA/OCMC and semi-IPN-PEGMA/CMS

PEGMA and OCMC in different molar ratios of 90/10, 70/30, and 50/50 were dissolved in distilled water. Then, synthesized PEGDA (10 mol. % of total

| The ratio of semi-IPN-PEGMA/ Polymer(w/w) | CMS | OCMC |
|------------------------------------------|-----|------|
| 100/0 PEGMA                              | PEGMA | PEGMA |
| 90/10 semi-IPN CMS10%                   | semi-IPN | OCMC10% |
| 70/30 semi-IPN CMS30%                   | semi-IPN | OCMC30% |
| 50/50 semi-IPN CMS550%                  | semi-IPN | OCMC50% |
monomer) was added to the reaction mixture. Subsequently, in situ polymerization was initiated by introduction of KPS (1 mol. % of total monomer) and mixtures were casted in Teflon molds. The reaction was continued for 5 h in an oven at 65 °C. The obtained films were dried in a vacuumed oven at 35 °C overnight. The preparation of SIPN-PEGMA/CMS procedure was performed as SIPN-PEGMA/OCMC.

Preparation of GPE

The obtained films were swollen in 1 M solution of LiPF6 in diethyl carbonate (DEC)/dimethyl carbonate (DMC) (1:1 V/V) for 1 h in a glove box and then utilized for further characterizations. Table 1 shows the coding of different GPEs.

Electrochemical characterizations

Electrochemical impedance spectroscopy (EIS) was carried out using a PGE-18 electrochemical workstation to measure ionic conductivity of GPEs within a frequency range from 1 MHz to 0.1 Hz at an AC potential amplitude of 10 mV. The ionic conductivity of electrolytes was calculated according to Eq. (1):

\[ \sigma = \frac{h}{R_p A} \]  

(1)

where \( \sigma \) is the ionic conductivity, \( R_p \) is the bulk resistance of polymer which is obtained by fitting the appropriate circuit on the Nyquist curves by ZsimpWin software, \( A \) is the area of the electrode–electrolyte interface, and \( h \) is the thickness of the polymer film. Also, temperature dependent conductivity was carried out at different temperatures. GPEs were sandwiched between two electrodes made up of stainless-steel (SS) for measurement of impedance. The cyclic voltammetry (CV) and the charge–discharge tests were performed by means of an Atomlab electrochemical workstation. CV curves were operated from 0.0 to 6.0 V for the LiCoO2/GPE/Li cell at a scan rate of 0.1 mV s⁻¹. The galvanostatic charge and discharge (constant current) cycling tests were performed at ambient temperature in the potential window of 2.50 to 4.50 V at different rates on a Li/GPE/LiCoO₂. The cathode was used for CV and charge–discharge tests, comprised 80 wt. % LiCoO₂, 5 wt. % PVDF, and 15 wt. % super-P carbon black.

All these materials were dissolved in NMP as solvent, then, the obtained slurry was coated on aluminum foil and vacuum-dried at 80 °C for 24 h. Cell fabrication was accomplished in a glovebox filled with argon gas. To prepare cells, GPEs (\( A = 25 \) mm², \( h = 1.5 \) mm) were sandwiched between the above prepared LiCoO₂ cathode and lithium foil without any adhesion. DC polarization and impedance analysis were utilized to measure the transference number (\( t^{+} \)) of GPEs at 10 mV DC voltage which was applied to Li/GPE/Li cell. \( t^{+} \) of electrolytes was calculated according to the Eq. (2):

\[ t_{Li^+} = \frac{I_{ss}(\Delta V - I_0 R_{b,0})}{I_0(\Delta V - I_{ss} R_{b,ss})} \]  

(2)

where \( I_0 \) is initial current, \( I_{ss} \) is steady state currents, \( R_{b,0} \) is initial resistance, and \( R_{b,ss} \) is final resistance which were measured by AC impedance spectroscopy. Electrochemical measurements, except for the temperature dependent conductivity were carried out at room temperature.

Results and discussion

The synthesis of GPEs have been carried out according to the procedure mentioned in the Experimental Section and graphical illustration shown in Scheme 1. To ensure correct synthesis of semi-IPNs, Figure S1 shows the FT-IR spectra for PEGDA, PEGMA cross-linked networks (PEGMA-PEGDA), CMS, OCMC, semi-IPN CMS 50%, and semi-IPN OCMC 50%. PEGDA and PEGMA have similar FT-IR spectra because of their similar structures. In the spectra of PEGMA-PEGDA and PEGDA, the absorption peak at 1030 cm⁻¹ is related to C-O stretching, 2869 cm⁻¹ corresponded to CH vibration, and absorption peak at 3541 cm⁻¹ is associated with absorbed humidity (Banaei et al. 2018; Modarresi-Saryazdi et al. 2018). In PEGMA-PEGDA spectra, peak at 1746 cm⁻¹ belongs to the carbonyl end group of PEGMA monomers, and loss of PEGDA absorption peak at 951 and 1661 cm⁻¹ in PEGMA-PEDGA related to = C-H out of plane bending and C= C starch, respectively, is a sign of the formation of PEGMA-PEGDA network. CMS and OCMC joint absorption peaks occur in 1102 cm⁻¹ and 1030 cm⁻¹ (C-O stretching).
1464 cm⁻¹ (CH₂ scissoring), 2869 cm⁻¹ (CH vibration), 3500 cm⁻¹ (hydroxyl group), and 1750 cm⁻¹ due to carbonyl group (Moqadam et al. 2018; Nikravan et al. 2018a, b). The spectra of semi-IPNs are a combination of PEGMA-PEGDA and SMC/OCM spectra and no new peaks are added or subtracted from, and this means the physical blending of PEGMA-PEGDA and CMS/OCMC together with no chemical bonding (Anjali et al. 2012; Brown et al. 2007; Lawal et al. 2007; Lin et al. 2006; Mauri et al. 2015; Pereira et al. 2011). To further prove the successful syntheses, ¹H NMR spectra of synthesized polymers are illustrated in Figure S2 and peaks are assigned in detail.

DSC and XRD are utilized to confirm that the synthesized semi-IPNs are amorphous (Fig. 1). According to results, there is no peak related to ordered and crystalline structure in diffraction patterns of PEGMA, natural polymers, and semi-IPNs (Fig. 1a). Additionally, from the DSC curves, synthesized polymers and semi-IPNS are utterly amorphous and there is no indication of melting phenomenon (Fig. 1b).

Scheme 1 Preparation of semi-IPN electrolyte films: a Molecular structure of PEGMA, PEGDA, OCMC, and CMS; b In-situ polymerization of semi-IPN-PEGMA/CMS and semi-IPN-PEGMA/OCMC; c Cell assembly of GPEs
Moreover, $T_g$ of semi-IPNs is increased with increasing CMS/OCMS content whereas it was between $T_g$ of PEGMA and CMS/OCMC. This increase in $T_g$ shows a positive deviation from Fox equation thanks to the strong interaction between these two phases (PEGMA-PEGDA network and CMS/OCMC) within the semi-IPNs. More deviation of semi-IPNs OCMC is due to the presence of carbonyl groups in the cellulose chain backbone and the possibility of creating more hydrogen interactions with P(PEGMA)-PEGDA network. This strong interaction between PEGMA and CMS/OCMC makes two components very compatible (Murthy et al. 1990; Prinos et al. 1995).

TGA is utilized to evaluate the thermal stability of the synthesized semi-IPNs (Fig. 2). TGA curves show

![Fig. 1](image1.png)  
**Fig. 1** a XRD patterns and b DSC curves of PEGMA, PEGMA-PEGDA, semi-IPNs of CMS and OCMC in various ratios

![Fig. 2](image2.png)  
**Fig. 2** TGA curves of a PEGMA, PEGMA-PEGDA, CMS, and OCMC, b semi-IPNS of CMS, and c, and semi-IPNs of OCMC
approximately same thermal stability for PEGMA and OCMC up to 200 °C, and high CMS thermal stability up to 345 °C. Therefore, by increasing the amount of CMS in PEGMA network, the thermal stability of the semi-IPNs is improved. However, by increment of OCMC in PEGMA-PEGDA, thermal stability is not changed remarkable. Also, in each case, residual char is increased with an increasing quantity of natural polymers (CMS/OCMC) inside the polymer network (Jagadish et al. 2011; Rajeh et al. 2019).

As known, the ionic conductivity of a polymer electrolyte depends on two important factors: (a) the quantity of polymeric host electron donor atoms, and (b) the $T_g$, which controls the mobility of the polymer chains. More electron donor atoms contribute to the dissociation of lithium salts and lower $T_g$ facilitates transfer of within the polymer host (Zhou et al. 2019a, b). PEO incorporates a low $T_g$; however, it has one electron donor atom in each repeating unit whereas CMS and OCMC have at least 14 electron donor atoms in their structures. However, because of

Fig. 3  Impedance plots of SS/GPEs/SS at room temperature. a semi-IPNs CMS and b semi-IPNs OCMC with various ratios. Temperature ionic conductivity of the c semi-IPNS of CMS and d semi-IPNs of OCMC with various ratios obtained from Figure S3
high $T_g$ and a small amount of solvent uptake, they may not be effective in the GPEs. Here, the semi-IPN structure is employed to maximum utilization of the high mobility of PEO chains and also the high ability of CMS and OCMC to establish coordination with $Li^+$. To verify this supposition, electrochemical tests are performed and the impact of adding natural polymers (CMS or OCMC) to PEGMA network on the electrochemical behavior of the resulting electrolytes are investigated. Nyquist curves for semi-IPN CMS and semi-IPN OCMC with different amounts of CMS and OCMC and their ionic conductivity at different temperatures (from 25 to 65 °C) are shown in Fig. 3 and Fig. S3. The results indicate a pointy decrease within the resistance of electrolytes by increasing the proportion of natural polymer. Semi-IPN CMS 50% and semi-IPN OCMC 50% show an ionic conductivity of 1.74*10$^{-2}$ and 1.92*10$^{-2}$ S cm$^{-1}$, respectively. The most GPEs show conductivity in the order of 10$^{-3}$ S cm$^{-1}$ and this is their main disadvantage compared to liquid electrolytes (Gou et al. 2020; Liu et al. 2020, 2021; Shen et al. 2020; Xue et al. 2021). However, here semi-IPN CMS and semi-IPN OCMC samples take the ionic conductivity of the GPEs one step further and makes them competitive with liquid electrolytes. The explanation for this high ionic conductivity is the presence of a large number of oxygen atoms within the CSM or OCMC in the electrolyte, that gives several sites prone to coordination with $Li^+$. Therefore, PEGMA chains permit lithium ions to move simply between these places due to their high mobility. As the amount of natural polymer in the network increases, the ionic conductivity becomes greater while $T_g$ increases. This means that the number of electron donor atoms is more controlling than $T_g$ of polymeric host in ionic conductivity. Due to the increase in $T_g$ and more importantly, reduced salt solution uptake of the semi-IPNs, it is expected that higher amount of natural polymer leads to difficulty in transfer of ions, Semi-IPN 50% of CMS and OCMC show the most increase of ionic conductivity. In this regard, PEGDA, as a long-chain crosslinker, plays a crucial role in these results, and provides a regular, free-volume network (Figs. S4 and S5) that is appropriate for placing CMS/OCMC chains next to PEGMA and great salt solution uptake (Fig. S6). Higher ionic conductivity of OCMC-based semi-IPNs than CMS-based ones despite its higher $T_g$ originates from greater importance of polar functional groups (carbonyl groups on OCMC backbone) on the ionic conductivity of the polymeric host.

![Fig. 4 Cyclic voltammetry curves of a semi-IPN CMS and b semi-IPN OCMC in various ratios for LiCoO$_2$/GPE/Li cell](image-url)
The Arrhenius ionic conductivity behavior with temperature and low activation energy ($E_a$) of semi-IPNs is well clear (Baskoro et al. 2019). Moreover, the decrease of the temperature affect conductivity by increasing the CMS/OCMC content due to rise in $T_g$ of semi-IPNs. The electrochemical stability window of GPEs based on semi-IPNs is critical for the practical application in LIBs. From cyclic voltammetry (CV) of semi-IPNs (Fig. 4), it is realized that there is no obvious oxidation current before 4.5 V for each semi-IPN CMS and semi-IPN OCMC, which is favorable for the feasible applications of semi-IPNs for high-potential electrolyte in LIBs (Shen et al. 2020). The stability window of both semi-IPNs is very close due to the similar structures. $Li^+$ transference number ($t^+$) as a vital parameter for evaluating the GPEs is the proportion of $Li^+$ transport to the total ions that transport within the polymer electrolyte. The low $t^+$ causes the maldistribution of ion concentration, polarization, and side reactions in GPEs (Lin et al. 2020). From the chronoamperometry and EIS tests in Fig. 5a–f, $t^+$ of semi-IPN CMS50% and semi-IPN OCMC 50% is 0.655 and 0.8, respectively, which is far above the liquid and ordinary polymer electrolytes. In addition, the increase in $t^+$ with an increase of CMS/OCMC is quite obvious. The very high value of $t^+$ for semi-IPNs is due to the high ionic conductivity and $Li$ electrode/electrolyte compatibility, which causes uniform solid electrolyte interface (SEI) (An et al. 2016). The oxygen
atoms in the structure of OCMC/CMS create more coordination sites for Li⁺, also are adapted to the volume expansion of lithium; and finally, the PEGMA chains accelerate the movement of Li⁺ ions in these pathways.

Figure 6 shows the initial charge–discharge curves of LiCoO₂/semi-IPN CMS50% and semi-IPN OCMC50%. Rate performance at various C rates, and charge capacities and Coulombic efficiency at 0.1 C-rate at a voltage range between 2.5 and 4.5 V of the semi-IPN CMS50% and semi-IPN OCMC50% for LiCoO₂/GPE/Li

Yue et al. 2016). Increasing the current density limits the Li⁺ kinetics and polarizes the battery, which results in reducing the battery capacity. This is why most batteries perform well at low currents, whereas it increases the power and charge rate of the battery (Vetter et al. 2005). The synthesized GPEs here show a high specific capacity even at high current densities, thanks to their unique structures. The most PEO-based GPEs do not show stable cyclic performance due to the incompatibility of the electrode/electrolyte interface, and as a result of the expansion of dendrites at the anode surface, the battery discharge capacity gradually decreases throughout the charge–discharge cycle (Zhao et al. 2020a, b). Figure 6c displays the rate performances of LIBs versus current density.
density from 0.2 to 2 C. The carbonyl and hydroxyl groups in CMS and OCMC increase the compatibility between the anode/electrolyte interfaces (Li et al. 2020), leading to a very stable charge–discharge cycle performance of the LIBs. The performance of charge–discharge cycles with 100 times at 0.2 C and

Fig. 7 FE-SEM results of a semi-IPN CMS50% and b semi-IPN OCMC50% before charge and discharge, and c semi-IPN CMS50% and d semi-IPN OCMC50% after 100 cycles
Coulombic efficiency (CE) of LIBs with semi-IPN CMS50% and semi-IPN OCMC50% are displayed in Fig. 6d. LiCoO₂/semi-IPN CMS50%/Li shows a CE ~ 88% at primary cycle with capacity retention of 85% after 100 cycles, and LIB based on semi-IPN-OCMC indicates CE ~ 92% and 88.5% capacity retention after 100 cycles. The interesting point is that the CE quickly reaches 100% and also the process of reducing the battery capacity is stopped in the same initial cycles. The prevalence of polymeric electrolyte over liquid one in addition to safety is the ability of the polymer to prevent dendritic growth because of its mechanical strength (Liu et al. 2018a, b; Wang et al. 2019). Adding CMS/OCMC to the PEGMA cross-linked network in addition to increase the strength of the ultimate semi-IPN structure (by increasing electrolyte Tg), can also form suitable interface (polar functional groups in CMS and OCMC, can introduce lithium ion uniform deposition); as a result the resistance of the GPEs against dendritic expansion is increased.

To further investigation the effect of natural polymers on the dendrite’s growth, electrolyte (anode-side) surface is studied by FE-SEM images (Fig. 7). The surface pictures of the gels before the charge–discharge test show the right dispersion of the two phases inside each other, and after 100 charge–discharge cycles, the dendrites are seen scattered without accumulation (due to sensible interaction at the electrolyte/electrode interface) and tiny in size (indicates that the electrolyte prevents the expansion of dendrites) on the electrolyte surface.

Conclusions

In a nutshell, unique semi-IPNs combination of CMS/OCMC and PEGMA-PEGDA was used to prepare gel polymer electrolytes for high performance LIBs. Ionic conductivity was increased sharply due to the addition of a large number of electron donor atoms (CMS/OCMC chains) to the PEGMA-PEGDA network, reaching 1.74 and 1.92 S cm⁻¹ for semi-IPN-CMS50% and semi-IPN-OCMC50%, respectively. The reason for the high conductivity of OCMC based electrolytes compared to CMS based is the presence of more electron donor atoms in OCMC chain, which creates more coordination centers for Li⁺. With the addition of modified natural polymers to the PEGMA-PEGDA network, the strength of the electrolyte and its compatibility with the electrolyte was increased with subsequent stopping the dendrites expansion. These properties together, provided stable charge–discharge behavior, high t⁺, and a supreme discharge capacity (195 and 184 mAh g⁻¹ for SIPN-CMS50% and SIPN-OCMC50%, respectively) for both Semi-IPNs after 100 cycles. The approach presented here for polymeric electrolyte synthesis has the potential to produce sustainable, economical, and safe LIBs.

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Data availability The raw/processed data required to reproduce these findings cannot be shared at this time as the data also form part of an ongoing study.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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