Life Cycle Assessment of Lithium Sulfur Battery for Electric Vehicles

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ABSTRACT Lithium-sulfur (Li-S) battery is widely recognized as the most promising battery technology for future electric vehicles (EV). To understand the environmental sustainability performance of Li-S battery on future EVs, here a novel life cycle assessment (LCA) model is developed for comprehensive environmental impact assessment of a Li-S battery pack using a graphene sulfur composite cathode and a lithium metal anode protected by a lithium-ion conductive layer, for actual EV applications. The Li-S battery pack is configured with a 61.3 kWh capacity to power a mid-size EV for 320km range. The life cycle inventory model is developed with a hybrid approach, based on our lab-scale synthesis of the graphene sulfur composite, our lab fabrication of Li-S battery cell, and our industrial partner's battery production processes. The impacts of the Li-S battery are assessed using the ReCiPe method and benchmarked with those of a conventional Nickel-Cobalt-Manganese (NCM)-Graphite battery pack under the same driving distance per charge. The environmental impact assessment results illustrate that Li-S battery is more environmentally friendly than conventional NCM-Graphite

battery, with 9%~90% lower impact. Finally, the improvement pathways for the Li-S battery to meet the USABC (U.S. Advanced Battery Consortium) targets are presented with the corresponding environmental impact changes.

Keyword: Lithium sulfur battery, graphene wrapped sulfur, lithium metal anode, life cycle assessment, environmental impact

1. Introduction

The ground transportation sector generates approximately 27% of the total greenhouse gas (GHG) emissions in the U.S [1]. To address global warming concerns, the U.S. EPA has set a regulatory standard to reduce the average GHG emissions of the U.S. light passenger vehicles from 225 g mile⁻¹ in 2016 to 143 g mile⁻¹ in 2025 [2], mainly to be achieved through adoption of electric vehicles (EVs) [3-5]. Current EVs are all powered by lithium ion batteries (LIBs) due to their high energy density and higher power density relative to other battery technologies. However, with 80-150 Wh kg⁻¹ energy density [6-8], current LIBs on board of EVs are not able to power the EVs for a comparable driving range with conventional vehicles. Meanwhile, current LIB technologies generate significant environmental impacts during their life cycle. For example, current LIBs consume 1141-1224 MJ-equivalent energy and generate 57-85 kg CO₂ equivalent emissions per kg battery during their life cycle [9,10]. Recent years have witnessed rapid progress on the research and development of next-generation battery technologies with higher energy density and better environmental performance.

Among various battery technologies under development, lithium-sulfur (Li-S) battery is widely recognized among the most promising battery technologies for next generation EVs [11-14]. Compared to the conventional Li-ion battery, Li-S battery offers a much higher energy

density, i.e., sulfur with a specific capacity of 1672 mAh g^{-1} [14], corresponding to a high theoretical energy density of $\sim 2600 \text{ Wh kg}^{-1}$. Besides, sulfur is abundantly available in nature and often considered as a more environmentally benign material than those heavy metals used in conventional lithium-ion batteries [15].

Li-S batteries have been facing some technical challenges, including rapid capacity fading due to the dissolution of sulfur active materials from the polysulfide shuttle effect, low ionic and electronic conductivity of the sulfur material, and low coulombic efficiency and dendrite growth of lithium metal anode, which all affect the battery life and cause safety hazard [12,14,16]. After recent years of intensive research and development, these technical challenges can now be effectively addressed. The dissolution of sulfur problem in Li-S batteries can be suppressed by confining the sulfur in thin film layered materials such as graphene [17-20]. Graphene including reduced graphene oxide has such functional groups as hydroxyl, carboxyl and ester groups which can effectively bind S_8 and polysulfide species, and hence to successfully trap polysulfide from dissolution [21]. It has been reported that the graphene-sulfur composite (GSC) with nitrogen-doping can achieve a stable cycling performance up to 1440 mAh g^{-1} with a decay rate as low as 0.028% over 2000 cycles [22]. Another study demonstrates that depositing nanosulfur on graphene layers can result in a low capacity fading of 0.039% per cycle over 1500 cycles in an ionic liquid electrolyte [23,24]. Recently, a water-based solution precipitation method has been developed for GSC production with a high yield rate, which eliminates the use of toxic solvents and is regarded as a low-cost and environmental-friendly process, with promising potential for future industrial-scale productions [20,22,25]. The low conductivity problem of sulfur can be resolved by adding such conductive additives as carbon black, carbon nanotubes, etc. in the active material [14].

The low coulombic efficiency and safety concerns of using a lithium metal anode in the Li-S battery can be addressed by the formation of a passivation layer on the lithium metal surface to isolate the anode from undesired side reactions to suppress dendrite growth and improving coulombic efficiency [16,26-28]. The passivation layer in nature is a lithium ion conducting ceramic membrane[29] that can be artificially produced by treating the lithium metal surface with such chemicals as tetraethoxysilane (TEOS) [30], chlorosilane [31], nitrogen [32], etc. In another way, a thin layer of materials including interconnected hollow carbon spheres [28], polymer nanofibres [33] and metal oxides [34] can also be coated onto the lithium metal surface prior to cell manufacturing to obtain the protective effect. Recently, the atomic layer deposition (ALD) technology has been applied for lithium metal anode protection through depositing a thin layer of Al_2O_3 [34]. In addition, LiNO_3 can be added into the lithium bistrifluoromethanesulfonimide (LiTFSI) electrolyte in the dimethyl glycol (DME) and Dioxolane (DOL) solution to enhance the formation of the protective layer by reacting with the polysulfide species and lithium metal material [16,35]. It is also reported that adding LiNO_3 into the LiTFSI electrolyte can greatly improve the safety performance of the lithium metal anode in Li-S batteries [23] and also can substantially reduce the self-discharging of Li-S batteries from over 10% per day to less than 2% per month [36-38]. All these technical advances have prepared the Li-S battery as a promising alternative to the conventional Li-ion battery for next generation EV applications.

Li-S batteries are ready to enter commercial production for next generation EV applications [39-41]. The European Union has launched an Advanced Lithium Sulphur battery for EV (ALISE) project to promote the applications of Li-S battery on EVs in future. Current industrial prototypes of Li-S battery have already achieved 300 Wh kg^{-1} at the cell level and 200

Wh kg^{-1} at the battery pack level, almost twice of conventional LIBs on EVs [40]. While Li-S battery is promising for next generation EV applications, the life cycle environmental impacts of Li-S batteries have never been studied and understood. The Li-S battery uses a wide variety of toxic chemicals in the electrode/electrolyte material synthesis and manufacturing processes, including hydrogen fluoride, sulfuric acid, hydrogen chloride, etc. Besides, the Li-S battery requires energy-intensive processes for the electrode materials and cell manufacturing. For instance, the synthesis of the GSC involves 1-2 hours of sonication of the GSC solution with an energy input of 140-300kW per cubic meter [42,43]; battery cell manufacturing requires a 100-150°C process heating to evaporate off the NMP solvent through around 8 hours of continuous operation [44], as well as dry room facility to maintain a moisture level less than 100 ppm. As the Li-S battery is rapidly moving toward commercial-scale production, it is important to perform a comprehensive life cycle assessment (LCA) of Li-S battery technology to quantify and understand its potential environmental impacts.

In this paper, we developed a hybrid LCA model for an Li-S battery pack for EV application, using a graphene-sulfur cathode, a lithium metal anode, and LiTFSI electrolyte. The graphene-sulfur synthesis is modelled from our lab-scale fabrication process, and the battery cell manufacturing processes are modelled with actual data collected from our industrial partner's pilot scale production facilities. The life cycle environmental impacts are assessed by the ReCiPe method [45]. To understand the relative significance of the impacts, the life cycle environmental impacts of the Li-S battery are benchmarked with those of a conventional LIB pack using a Lithium-Nickel-Cobalt-Manganese oxide cathode and a graphite anode (NCM-Graphite). The LCA results can be useful in sustainable design and manufacturing of Li-S battery packs for future EV applications.

2. Method

2.1 Li-S battery pack configuration for a mid-size EV

The Li-S battery pack in this study is configured to power a mid-size EV for a 320km driving distance (D) per charge with 120 kW power (Figure 1, Section 1 and calculations supplied in the electronic supporting information (ESI) for details) [46]. For the battery system configuration, first, the battery energy for traction at wheel ($E_{\text{traction}, i}$) is calculated for the EV at various speeds under both highway and local driving conditions, respectively, using the EPA Urban Dynamometer Driving Schedule (UDDS) and Highway Fuel Economy Test (HWFET) patterns (Section 1.1 in the ESI) [47]. The amount of energy discharged ($E_{\text{discharged}, i}$) from the Li-S battery pack is the sum of traction energy divided by the product of motor efficiency (η_{motor}) and the EV transmission efficiency ($\eta_{\text{transmission}}$), plus the energy consumed by the auxiliary system (P_{aux}). The specific energy consumption is the ratio of the discharged energy ($E_{\text{discharged}, i}$) over the distance of the driving schedule (s_i). Afterwards, the composite discharged energy ($E_{\text{discharged}}$) is the weighted-sum of specific energy consumptions. The weight factors ($a:b$) is set to be 45%:55%, which is the distance ratio of local and highway driving under the U.S. national average [48]. Finally, the nominal capacity of the Li-S battery pack, with 85% accessible fraction by user (UR), is calculated as the ratio between the amount of energy discharged from the battery pack and the battery discharging efficiency ($\eta_{\text{discharging}}$), while the total energy drawn from the wall outlet can be calculated as the ratio of the stored energy (E_{stored}) over the product of battery charging (η_{charging}) and charger efficiencies. The vehicle mass (M), as required for E_{traction} calculation, consists of glider, transmission, motor, and battery masses [49]. Transmission and motor masses are calculated according to mass-power coefficients, namely, 0.585 kg

transmission kW^{-1} and $0.9 \text{ kg motor kW}^{-1}$ [49]. Glider mass is derived based on a baseline electric vehicle and mass compounding coefficient of $0.57 \text{ kg change in glider mass per kg change in powertrain mass}$ [50]. Finally, the battery mass is calculated as the ratio between the nominal battery pack and energy density ($\sigma_{\text{Li-S}}$) of the Li-S battery.

Figure 1 Energy flows and efficiencies of EV powered by Li-S battery pack. Detailed information is provided in Section 1 in ESI. The entire calculation is presented in the excel spreadsheet.

The battery discharging and charging efficiencies are determined considering the heat loss induced by the battery resistance (Ω_{battery}), with Joule's law being used, considering the currents, I_d and I_c , and duration $t_{\text{discharging}}$ and t_{charging} , for discharging and charging, respectively. For the charging process, besides energy loss on battery resistance, hysteresis loss is also included. A range of 170mV-400mV open-circuit voltage (OCV) difference is recorded for the

Li-S battery cell [51-53]. Then, the hysteresis loss is calculated as the product of the overall battery voltage hysteresis ($U_{\text{hysteresis}}$) and the battery capacity (C_{battery}).

Determination of $\sigma_{\text{Li-S}}$ is based on the configuration of the Li-S battery. The Li-S battery pack is configured with stacked battery cells, a battery management system (BMS), a battery cooling system, and battery packaging. The BatPac, a battery design software developed by Argonne National Lab [46], is adapted to model the Li-S structure in this study (Section 1.2 and Section 1.3 in ESI) [25]. In the BatPac method, the area specific impedances (ASIs) of the electrode system at constant discharging for energy use and pulse power discharging for power use are two important parameters. The electrode ASI is calculated as a function of current density (i) from the polarization behavior [54]. A battery kinetic model is built to quantify the ASIs caused by charge transfer and conduction phenomenon in each step of the electrochemical cell under current densities at energy (i_E) and power (i_p) use. Other technical parameters of the Li-S chemistry in the BatPac modeling are based on current lab-scale experimental data. The cathode is porous structure composed of graphene-sulfur composite (GSC), carbon black, and PVDF binder at 7:2:1. The specific capacity of the sulfur (c_{sulfur}) is 1200 mAh g⁻¹ S with 56 wt% sulfur loading in the cathode ($S\%$) [54]. For the Li-S battery, a volume fraction range of 50%-90% of electrolyte over the total cathode is normally recommended [21]. In this study, 60% volume fraction of the electrolyte is used based on our experiments. The anode is made of a lithium metal with a surface protective layer. For the entire anode, we consider 50% access of the lithium metal ($NP=1.5$) with 3861 mAh g⁻¹ specific capacity (c_{Li}) compressed onto a 8 μm copper collector [28,55]. A conventional trilayer separator (polypropylene-polyethylene-polypropylene) with 20 μm thickness and 39% porosity is used. The cell container consists of a multilayer polymer pouch covering the cell layers, and two terminals made of aluminum and copper.

Through the BatPac calculation (Figure 1) a 61.3 kWh Li-S battery pack containing 12 modules each with 28 cells is configured. Each cell has 87.5 Ah capacity and is weighted at 547 g. The mass of the total battery pack is 279 kg, including 184 kg cells, 4 kg BMS, 27 kg cooling system, 23 kg module packaging, and 41 kg pack packaging. Meanwhile, the battery efficiency ($\eta_{battery}$) is calculated at 86% at a low 200 mV voltage hysteresis. This value is in line with the 78%-91% energy efficiency measured for the Li-S battery cell [56].

For the reference battery system, the NCM-Graphite battery pack is modelled at 120 Wh kg^{-1} gravimetric energy density, representing the average of the 105-140 Wh kg^{-1} range as reported in literature [7, 46]. Accordingly, this NCM-Graphite battery has a 63.8 kWh capacity to power the EV for 320 km per charge. This is in good agreement with previous industrial studies which states that a conventional LIB battery pack needs 56-75 kWh capacity to power an EV for 320 km driving distance per charge [57,58]. Table 1 summarizes the battery information and parameters for both the configured Li-S battery pack and the reference NCM-Graphite battery pack in this study. Li-S and NCM-graphite battery packs are estimated to represent 17% and 26% of the entire vehicle mass, respectively. The fractions are in line with the current EV design where battery consists of 15%~25% of total mass for a midsize vehicle [59].

Table 1 Comparison of technical parameters between the Li-S and reference battery pack

Parameters	Li-S	NCM-Graphite
Battery mass (kg)	279	531
Gravimetric energy density (Wh kg^{-1} battery)	220	120
Volumetric energy density (Wh L^{-1})	298	350
UR	85%	85%
Capacity (kWh)	61.3	63.8

Corresponding Vehicle mass (kg)	1625	2021
Driving distance per charge (km)	320	320

2.2 Life Cycle Assessment of the Li-S battery

A hybrid LCA model is developed in this study to analyze and understand the potential environmental impacts of Li-S battery technology for actual EV applications. An overview of the LCA system boundaries is illustrated in Figure 2. The life cycle of the Li-S battery pack is divided into five stages: raw materials extraction, materials processing, battery manufacturing, battery use, and end-of-life (EoL). The functional unit of the LCA is set per kilometer driving for a mid-sized EV powered by the Li-S battery pack. Based on the current lab-scale performance of the Li-S battery and the measured capacity fading rate, the overall driving distance of the EV is set at 200,000km during the life cycle of the Li-S battery. In this LCA study, the environmental impacts of the material and energy consumption, as well as waste and emissions directly associated with each life cycle stage of the Li-S battery are quantitatively evaluated (Figure 1). At the final EoL stage, battery recycling is modeled based on a hydrometallurgical process for material recovery, while recycling credit is not considered in this study because the recycled materials may not meet the high-quality standards of materials for battery manufacturing [10].

Figure 2 Scope and boundary of the LCA for the Li-S battery.

The ReCiPe method is adopted to derive both the midpoint environmental impacts and endpoint environmental impacts for the configured Li-S battery pack. With the ReCiPe method, the environmental impacts are quantified into 13 midpoint impact categories, including global warming (GWP), fossil depletion (FDP), ozone depletion (ODP), photochemical oxidant formation (POFP), particulate matter formation (PMFP), terrestrial acidification (TAP), freshwater eutrophication (FEP), marine eutrophication (MEP), freshwater ecotoxicity (FETP), marine ecotoxicity (METP), terrestrial ecotoxicity (TETP), human toxicity (HTP), metal depletion (MDP). Besides, in order to evaluate the environmental impacts of the novel GO nanomaterial, which cannot be assessed through the traditional ReCiPe method, we have developed a modified USEtox method to characterize the freshwater ecotoxicity of GO after it is released into the U.S. environment, based on recent toxicity studies of GO nanomaterials [60].

2.3 Inventory analysis for the Li-S battery

Table S5 and S6 in the ESI provide an overview of the materials and energy inputs for inventory of the Li-S battery pack. For the inventory analysis of such materials as current collector, multilayer pouch and terminals, cooling system, module and pack level packaging, inventories are constructed based on the outputs from the BatPac method (see Section 2 in the ESI). For inventory analysis of the GSC, lithium film, electrolyte (LiTFSI, DOL, LiNO₃) and Li-S cell manufacturing, we have developed process-based inventory models as presented below, with details provided in Section 2 of the ESI.

2.3.1 Inventory analysis for the Li-S battery

A hybrid inventory analysis model is developed in this study integrating our lab experimentation and theoretical modelling methods to compile the inventory data for Li-S

battery materials. Production of GSC and graphene oxide are modelled based on our lab scale experiments [25] and the Hummers' method [61], respectively (Section 2.2 and Section 2.3 in ESI). The material input inventories of the two materials production are linearly extrapolated from the lab scale data assuming a 98.5% efficiency from typical industrial tubular centrifuges [62]. The energy consumption of materials production are modelled according to the specific energy consumptions (SEC) of relevant unit processes (baseline consumption, stirring, reaction heating, centrifugation, and drying). The SECs of these basic unit processes are calculated based on conventional mechanical and thermal methods or directly used industrial data [63-66]. Finally, the absolute energy consumption of the unit processes is obtained by multiplying the SEC with the mass/volume of the materials being processed. No heat recovery is considered for the two materials production since both reactions are below 100°C [67].

Inventories of the lithium metal anode and the LiTFSI electrolyte were constructed by modelling their unit production processes and relevant data are compiled from literature and the Ecoinvent database (Section 2.5 and Section 2.6 of the ESI). The inventory of the lithium metal anode involves the unit processes of lithium film production and the following surface treatment for forming a protective layer (Section 2.5 in the ESI). Commercial production of lithium film is made by extruding lithium metal through a slit [67], followed by a sheet rolling process [68]. In this study, the extrusion process is modelled based on the mechanical model, and the cold sheet rolling of steel available in the Ecoinvent database was converted into lithium cold rolling based on the density ratio of the two materials. The inventory of the protective layer on the surface of the lithium metal anode was modelled as a surface treatment process using TEOS resulting in a 1000 nm lithium-ion conducting membrane formed at a density of 2.96 g cm^{-3} [28]. Production of LiTFSI was modelled according to the synthetic route from trifluoromethanesulfonyl fluoride

(CF₃SO₂F) [69], which is produced through electrochemical fluorination (ECF) of methanesulfonyl chloride (CH₃SO₂F) with liquid hydrofluoric acid (HF) [70].

2.3.2 Inventory analysis of battery pack production process.

After the electrode materials are fabricated, the Li-S battery cell is manufactured through similar processes as the conventional NCM-Graphite battery cell (Section 2.8 in the ESI). In this study, we have obtained the energy demand of the Li-S cell manufacturing through measuring and modelling the energy consumption of battery manufacturing equipment in a 93.2 m² pilot scale dry room facility of Johnson Controls Inc. (Figure S11 and Section 2.8 in the ESI). As calculated, the electricity consumption of a configured 87.5 Ah Li-S cell is 46.6 kWh kg⁻¹, including 27.2 kWh kg⁻¹ for the cell manufacturing processes and 19.4 kWh kg⁻¹ for the supporting dry room. The subsequent battery pack assembly is mainly performed manually with 3.9 Wh kg⁻¹ consumed during the battery pack assembly process [7].

As Li-S batteries are now at an early stage of commercialization, the pilot scale production can represent the near future situation of Li-S battery manufacturing. In regards to the future large-scale industrial production of Li-S batteries, the energy consumption will be even lower. To evaluate and benchmark the energy use of Li-S battery production at both pilot scale and industrial scale, here the Li-S battery manufacturing is divided into unit manufacturing processes, including active material mixing, slurry coating, drying, calendaring, notching, stacking, filling, welding, degassing, and packaging. The specific energy consumptions of each unit manufacturing process at an industrial scale are compiled based on corresponding industrial production data in literature (Table S20 in the ESI). Finally, the energy consumption of Li-S battery production at industrial scale is estimated in the range of 11.3-22.8 kWh kg⁻¹ Li-S cell.

The material inventory of the Li-S battery production is analyzed based on the mass compositions of the 87.5 Ah Li-S battery cell and the 61.3 kWh battery pack (Section 2.1 in the ESI). The material inputs are subsequently calculated based on the material efficiencies of the cell manufacturing process. It is expected that efficiencies of Li-S battery cell manufacturing resemble those in conventional LIB cell manufacturing, namely, 92% for the positive and negative electrodes, 98% for the separator, and 94% for the electrolyte [71]. In addition, the PVDF binder needs to be dissolved in NMP solvent at 8 wt% to produce the cathode slurry, with the NMP solvent recovered at a 98% efficiency. For the 61.3 kWh Li-S battery pack, 336 pouch cells are stacked and packaged in 12 modules with the BMS and battery cooling system. Finally, all of the modules are situated in the aluminium based pack housing and closed with a steel strap. Detailed inventory data for cell container (including pouch and terminals) are provided in ESI section 2.7, and inventory data for the module and pack packagings are provided in ESI section 2.9. Inventory data for BMS is based on the information in Ellingsen et al [7].

2.3.3 Inventory analysis of battery use.

The inventory for the Li-S battery use phase is analysed for actual EV operations under average U.S conditions, with the Li-S battery life considered first. With the Li-S battery degradation, the total driving distance, T_s , of the Li-S battery pack can be calculated through [7]

$$T_s = D_0 \left(c - \frac{rc^2}{2} \right) \quad (1)$$

where D_0 is the initial driving distance per charge (320km), c is the cycling number; and r is the capacity decay rate. Using an experimentally determined 0.028% capacity loss per cycle as the decay rate [22], and assuming a battery replacement needed when the capacity drops down to 70% of its original level, the T_s is calculated around 290,000 km using Equation (1). However, it is noted that in this calculation, calendar loss from Li-S battery aging is not considered, which in

fact causes additional capacity fading during the battery use phase and will shorten the total driving miles. As currently no study has been conducted on calendar loss of Li-S battery pack for EVs, here we assume the decay rate from Li-S calendar loss is at the same level with that of its cycling loss. Consequently, the actual drivable miles during the service life of the Li-S battery pack is set at 200,000 miles for about 10 years of service life under average U.S. driving conditions [72], according to equation (2). In this case, a single Li-S battery pack can be used to power the EV during the designed service life, with no battery replacement needed. The possible variations of battery decay rates and the resulting battery life are investigated in the later sensitivity analysis.

Then the inventory analysis for the Li-S battery use phase is based mainly on the electricity consumption during EV operations. In this study, the U.S. average electric grid is considered for electricity generation. The operation of the EV is 55% city and 45% highway driving, based on the U.S. national average data [48]. The electricity consumption of the Li-S battery during the use phase can be calculated through:

$$E_{use} = \frac{E_{disc\ charged}}{D\eta_{battery} \eta_{charger}} T \quad (2)$$

Calculation of the discharged energy ($E_{disc\ charged}$) is provided in Section 1 in the ESI. Charger efficiency ($\eta_{charger}$) is 0.90 [73]. Battery efficiency ($\eta_{battery}$) equals $\eta_{discharging} \times \eta_{charging}$, respectively. T is the total driving distance.

2.3.4 Inventory analysis of battery EoL.

Recycling of Li-S battery at the EoL of the EV is modelled from EV collection, battery removal, discharging, battery disassembly, materials shredding/sorting, until materials refining/disposal. The collection rate of EVs is taken at a generalized rate of 91% from literature

[74]. After that, the Li-S battery packs are removed from the vehicle and discharged in a salt solution to deplete the residual energy [71]. Since Li-S batteries do not contain precious transition metals (e.g. cobalt), a hydrometallurgical recycling process is adopted in this study [71]. Detailed information on the inventory of the Li-S battery hydrometallurgical recycling process is provided in Section 2.10 in the ESI.

2.3.5 Reference battery system.

In this study, a conventional 63.8 kWh NCM-Graphite battery is configured as a reference battery system for benchmarking and validating our results on the 61.3 kWh Li-S battery. The LCA data and results from Ellingsen et al. on the NCM-Graphite battery for EVs is adapted, using the same ReCiPe method [45]. In this study, the unit LCA results from Ellingsen's study are linearly scaled up to our configured NCM-Graphite battery (63.8 kWh), for comparison with our Li-S battery results.

3. Results and Discussion

3.1 Life Cycle Inventory of the Li-S battery pack

The life cycle inventory analysis results for the configured Li-S battery pack are compiled for both material and inventory data. The material inventory provides masses of all materials needed to produce the Li-S battery pack during its whole life cycle (Table 2). As calculated, a total of 471 kg of material inputs is required during the life cycle of the 279 kg Li-S battery pack. From the inventory analysis, the GSC based positive electrode is the most material demanding component in the Li-S battery pack, which requires 49.2% of total material inputs. Each gram of GSC synthesis requires 0.158 g GO, 4.00 g sodium thiosulfate, 0.063 g PVP, and 1.85g HCl acid (Table 2), from which the sodium thiosulfate and HCl acid combined together account for 41.3% of total material flow. Meanwhile, synthesis of GSC results in 0.266 liters of

wastewater flow for each gram of GSC synthesized. In comparison, production of the lithium foil anode and the passivation layer only accounts for 6.1% of the material flow due to the high efficiency of material utilization during the process, with 97.5% for extrusion and 99% for cold rolling.

The electrolyte requires 14.3% of total material inputs. The electrolyte includes 10.8 kg LiTFSI salt and 55.9 kg DOL/DME solvent. During the Li-S battery life cycle. The LiTFSI takes up only 2.3% of total battery material inputs, but it involves 0.57 g of HF toxic chemical and generates 3.57 g hazardous wastes per gram of LiTFSI production (Table S12 in ESI).

In the Li-S battery pack, common plastics including 3.6 kg PE (polyethylene) and 6.5 kg PP (polypropylene) are used, mainly for the separator in the Li-S cell as well as the trilayer pouch. The injection moulding and compression moulding processes are modelled for their production. In addition, a total amount of 86.6 kg aluminium (18% of total material inputs) is used for the Li-S battery with a distribution of produce pack housing (49%), inner and outer frames of cells in modules (16%), positive electrode current collector (16%), radiators in the cooling system (9%). The cooling system contains 20 kg ethylene glycol, determined through heat generation rate during battery operations. In the calculation, we set a criteria that the coolant amount should be sufficient to enable no more than 1°C increase of battery temperature when the EV is driving at a fast mode of 85 mph.

Copper use, as the main toxicity concerns for conventional LIB [7], is relatively limited in the Li-S battery. A total of 36.8 kg copper including the mass of copper wire, is used in the Li-S battery pack, representing a unit rate of 0.6 kg copper use per kWh Li-S battery capacity. When compared, the conventional LIB battery has a copper concentration of 1.33 kg per kWh capacity

[7]. In addition, a total of 2.5 kg steel is used in the battery pack, which are used to produce strap for pack packaging.

Table 2 Material inputs inventory for the 61.3 kWh Li-S battery pack production

	Quantity (kg)	Weight ratio (%)	Comment
Positive electrode			
Graphene oxide	5.3	1.12%	Input materials for GSC synthesis
Sodium thiosulfate	132.9	28.25%	Sulfur donor
PVP	2.1	0.45%	Additive, controlling sulfur size
HCl	61.4	13.06%	
Carbon black	9.5	2.02%	20 wt% of cathode
PVDF	4.7	1.01%	10 wt% of cathode, in 8 wt% NMP solution
Aluminium, ingot	14.2	3.02%	Current collector, 15 μ m thickness
NMP	1.1	0.23%	Solvent for PVDF binder.
Negative electrode			
lithium, billet, primary	13.5	2.87%	
TEOS	2.5	0.43%	20 wt% of TEOS are lost during surface treatment
Copper, billet	24.2	5.14%	Current collector, 8 μ m thickness
Separator			
PP	4.8	1.03%	20 μ m trilayer separator, 39 vt% porosity
PE	2.4	0.51%	
Electrolyte			
LiTFSI	10.8	2.29%	1M LiTFSI in DOL/DME solvent
DOL	19.5	4.15%	Organic solvent at 1:1 ratio by volume
DME	36.3	7.73%	
LiNO ₃	0.7	0.14%	Additive, at 1 wt% fraction of electrolyte system
Cell container			
Aluminium, ingot	5.7	1.21%	Production of the trilayer pouch
PP	1.7	0.37%	
PE	1.1	0.24%	
Aluminium, ingot	2.7	0.56%	Positive electrode terminal
Copper, billet	8.8	1.87%	Negative electrode terminal
Module packaging			
Aluminium, ingot	13.8	2.93%	Inner and outer frames of cells for heat conductance
Copper, wire	2.9	0.62%	Connection between modules
Integrated circuit	1.3	0.29%	Controller
ABS	6.1	1.30%	Module lid
Polymer	3.2	0.68%	Spacer between modules
BMS			
BMS	4.0	0.85%	
Cooling system			
Aluminium, ingot	7.8	1.65%	External heat radiator
ethylene glycol	20.0	4.26%	coolant
Pack packaging			
Aluminium, ingot	42.4	9.02%	Pack housing
Steel, billet	2.5	0.53%	Strap for battery pack
Copper wire	0.9	0.19%	
Total	471	100%	

The energy consumption throughout the life cycle of Li-S battery pack is another major component of the LCI results. Figure 3 (numerical results provided in Table S24 in ESI) presents detailed information on primary energy embodied in the main materials, components, and processes for the Li-S battery pack. Here the primary energy refers to the non-renewable energy extracted from nature that has not been refined into any form of secondary energy (e.g. electricity or steam). As calculated, the life cycle primary energy consumption is 2.36 MJ km^{-1} while the battery use phase takes a share of 71%. In this study, the primary energy consumption in the Li-S battery use phase is further broken-down into the electricity loss from the charger, during the battery charging and discharging (plug-to-battery output) process, and from the energy delivery process for driving the EV and supporting auxiliary systems (battery-to-wheel). In this study, it is found that the electricity loss accounts for 21% of total energy consumption during the use phase. Next to the battery use phase, battery manufacturing consumes 0.51 MJ km^{-1} of primary energy, in which dry room conditioning and electrode drying account for 38% and 13% of the total manufacturing energy, respectively. GSC manufacturing is found consuming 0.089 MJ km^{-1} , which can be traced mainly to the sonication process. The primary energy embedded in all Li-S materials is 0.16 MJ km^{-1} , less than half of the primary energy demand for battery manufacturing.

In this study, it is found that the Li-S battery is mainly constructed from such bulk materials as sulfur (thiosulfate form), hydrochloric acid, aluminium and DME, which can be obtained with moderate environmental burdens. For example, the sodium thiosulfate, the largest material flow in the Li-S battery production (see Table 2), is a by-product of sodium sulfide production. Therefore, production of sodium thiosulfate consumes a limited amount of primary

energy at 39.6 MJ kg^{-1} . In comparison, GO synthesis is highly energy-intensive at 448 MJ kg^{-1} , while the GO only takes 1.12 wt% share of the material flow in the Li-S cell.

Figure 3 Distribution and primary energy consumption of Li-S battery pack during its life cycle.

Numerical results are provided in Table S24

3.2 Life Cycle Impact Assessment Results

The life cycle environmental impacts of the Li-S battery are calculated using the ReCiPe method into 13 impact categories, and the hotspots are revealed by a contribution analysis in Figure 4. The pattern bars of Figure 4 represent the contributions of life cycle stages to the environmental impacts of the Li-S battery, including battery production (including all activities from raw material extraction to battery manufacturing), battery use (divided into plug-to-output

and output-to-wheel), and EoL; the colored bars illustrate the contributions of each component of the Li-S battery pack to the environmental impacts of the battery production stage.

3.2.1 Battery production.

As shown in Figure 4, within the production phase, the Li-S battery cell manufacturing produced around 60% of share in both GWP and FDP impact categories. This is mainly caused by the intensive electricity consumption in the amount of 46.6 kWh kg^{-1} during the Li-S cell manufacturing. Electrode drying, which is used to evaporate NMP solvent from the cathode slurry, has been identified as the primary contributor with 13% of share. Electrode drying requires 192 mins processing time per cell under 150°C temperature. For each 87.5 Ah Li-S cell manufacturing, drying consumes 8.2 kWh electricity, while other battery manufacturing steps, including mixing, coating, calendaring, notching, and stacking, only consume 0.10-1.77 kWh. Besides, energy demand from the dry room facility in cell manufacturing is substantial as well. The dry room of the pilot scale facility in this study is operating at 64.8 kW demand, in which 41% is required by the heating and dehumidification machines. The energy intensity of cell manufacturing is expected to be significantly reduced when large scale production of Li-S batteries is implemented in the future. Through modelling industrial-scale processes, our study estimates that an energy consumption in the range of $11.3\text{-}22.8 \text{ kWh kg}^{-1}$ cell can be achieved for the large scale Li-S cell production. In comparison, Ellingsen et al. estimated an energy consumption of $28\text{-}112 \text{ kWh kg}^{-1}$ cell for the conventional NCM-Graphite cell production [7]. However, some other studies reported substantially lower energy consumption data for conventional LIB pack production only in the range of $1\text{-}5 \text{ MJ kg}^{-1}$ pack (around $1.6\text{-}8 \text{ MJ kg}^{-1}$ cell assuming 60% mass fraction of cells) [9], mainly because of ignoring the dry room facility in their studies.

In this study, it is found that the positive electrode production takes a share of 7%-23% in most impact categories, which is mainly attributed to the considerable energy demand in GSC fabrication. Additionally, the positive electrode is the main impact source (48%) of the MDP impact category, confirming the fact that positive electrode fabrication involves the majority of mass inputs in battery production.

Figure 4 Contributions of Life cycle environmental impacts of the Li-S battery. Numerical results are provided in Table S25

The negative electrode, cell container, and module packaging are identified to be the main contributors to FETP, HTP, METP, and TETP impact categories. An in-depth analysis reveals that these toxicity impacts mainly stem from the copper uses as current collector and terminals, as well as the anodising process to produce the inner and outer aluminium frames in module packaging. This finding is largely consistent with the results of conventional NCM-Graphite LIB production in Ellingsen et al.[7]. They found that the copper current collector is the dominant source (>60%) for impacts in FETP, METP, TETP, and HTP.

To assess the impact of the novel GO nanomaterial used in the Li-S battery, we have developed an ecotoxicity model based on the modified USEtox methodology incorporating colloidal theory to reflect the planar structure of GO, and found that the ecotoxicity characterization factor for GO emission is only 7.77×10^2 PAF m^3 day kg^{-1} emitted [60]. In comparison, the ecotoxicity characterization factors of cobalt, copper, nickel, and manganese are several magnitudes higher, at 4.48×10^4 , 3.63×10^6 , 1.07×10^5 , and 6.32×10^3 PAF m^3 day kg^{-1} emitted, respectively [75]. With the derived characterization factor for GO, we employed the USEtox method to calculate the ecotoxicity impact of the Li-S battery. The release rate of GO during the production of the Li-S battery is assumed to be 0.2%, the same as the emission rate of carbon nanotubes (CNTs) [76]. It is found that the ecotoxicity impact of GO is 1306 PAF m^3 day, which accounts for only 2.9% of the ecotoxicity impact from the Li-S battery. For the 1306 PAF m^3 day impact, the GO production produces 1070 PAF m^3 day while the release of GO only incurs a small 8.2 PAF m^3 day impact on ecotoxicity. The low ecotoxicity of GO nanoparticles is from several aspects. First, GO is a photodegradable material [77]. Fragmented GO is highly immobile in water due to the formation of irreversible aggregates and can be removed from water quickly with sediments [78]. Furthermore, humic acid, a widely present environmental substance, is an effective natural antidote which can neutralize the toxicity of GO [79]. On the other hand, past studies show that GO concentration in water needs to reach 50 mg L^{-1} level to generate effective cytotoxicity on human cells, indicating a limited human health impact [80]. Moreover, the uptake of GO in a human cell is subtle due to its high aspect ratio, which also reduces the risk of human impact [81]. During the EoL treatment, the GO can be degraded during the high-temperature process. Therefore, the toxicity impact of GO is expected to be negligible.

Electrolyte contributes to about 21% of environmental impacts in Li-S battery pack production, but it accounts for a substantial environmental impact share over 85% in MEP and ODP categories. The significant contribution to the MEP impact category is found mainly from the synthesis of DME, with the associated ammonia and nitrate emissions. The significant impact share in ODP is mostly attributed to the large amount of methylchloride solvent used during the LiTFSI synthesis.

3.2.2 Battery life cycle impacts.

For the total life cycle impacts of the 61.3 kWh Li-S battery pack, it is found that the battery production phase contributes 28%-36% to such categories as GWP, FDP, PMFP, POFP, and TAP, while 67%-98% to such categories as FETP, FEP, HTP, METP, MEP, MDP, ODP, TETP. However, the battery use phase contributes 70% to both the GWP and FDP impacts (Figure 4). The battery use phase is also a major contributor to the PMFP, POFP, and TAP, sharing 61%-65% of their life cycle impacts. Since electricity use is the only considered impact source during the battery use phase, the environmental burdens from battery use are mainly associated with the U.S. grid power generation and distribution. When compared, battery recycling contributes about 4% in most impact categories. The only exception is the TETP impact where a considerable 21% impact share is observed, because the battery pack is assumed to be treated with hydrometallurgical recycling process involving a significant amount of liquid nitrogen which triggers large impact in TETP.

3.2.3 Comparison between Li-S and NCM-Graphite Battery Packs.

To understand the relative significance of the environmental impacts of the Li-S battery, here the life cycle environmental impacts of the 61.3 kWh Li-S battery pack is compared with

those of a conventional 63.8 kWh NCM-Graphite battery (Figure 5, Table S26 in the ESI for numerical results).

Figure 5 life cycle impact benchmarking between the Li-S and the NCM-Graphite battery packs.

As shown in Figure 5, the Li-S battery is more environmentally friendly than the conventional NCM-graphite battery technology. The calculated life cycle environmental impacts of the Li-S battery pack are 9%-90% lower than those corresponding impacts of the conventional NCM-Graphite battery, except for ODP where Li-S battery is 71% higher than the NCM-Graphite battery. It must be noted that the environmental impacts of the Li-S battery are evaluated here in a mixed lab-scale and pilot production scale, while the NCM-Graphite battery is assessed on a full industrial-scale production capacity with the optimized level of energy intensity for cell manufacturing. In a partial production capacity, the life cycle environmental impacts of the NCM-Graphite battery can be further increased by 12%-40% in the GWP and FDP categories. As a result, the Li-S battery will have significantly lower impacts than the conventional NCM-Graphite battery when it reaches the same large industrial production scale in future.

For GHG emission, the production of the Li-S battery generates $44.8 \text{ CO}_2 \text{ eq km}^{-1}$, 18.4% lower than the $54.9 \text{ CO}_2 \text{ eq km}^{-1}$ emission from the NCM-Graphite battery pack production. The lower impact of the Li-S battery in GWP can be mainly ascribed to those low-impact bulk materials such as sodium thiosulfate used in Li-S battery production. As calculated, the GHG emission from the battery use phase can be reduced from $117 \text{ g CO}_2 \text{ eq km}^{-1}$ from NCM-Graphite battery to $112 \text{ g CO}_2 \text{ eq km}^{-1}$ from the Li-S battery. Overall, a 9% of life cycle GHG emission reduction can be achieved from using the Li-S battery over the NCM-Graphite battery.

In addition, using a Li-S battery over a conventional NCM-Graphite battery can reduce 80-90% of impacts in such categories as FETP, METP, HTP, and TETP from the life cycle perspective, because the Li-S battery does not use heavy metals such as Nickel, Cobalt, and Manganese, and it uses much less copper than a conventional NCM-Graphite battery. As calculated, the 63.8 kWh NCM-Graphite battery contains 26.3 kg cobalt, 26.0 kg nickel, 24.1 kg manganese and 84.8 kg copper. Ellingsen et al.[7] reported that productions of these heavy metal based components contribute more than 80% shares to FETP, HTP, METP and TETP during the NCM-Graphite battery production phase. When compared, the 61.3 kWh Li-S battery contains only 36.8 kg copper. The substantial reductions of the toxic metals in the Li-S battery cell make it an environmentally sustainable energy storage technology over conventional lithium-ion battery technologies.

3.2.4 Sensitivity

To evaluate the reliability and viability of the LCA results, a sensitivity analysis is conducted in this study to check the influences of the intrinsic variabilities of six major LCA parameters by changing their baseline values across potential ranges, including: driving range per charge (D), battery accessible capacity ratio (UR), total mileage (T), battery efficiency

($\eta_{battery}$), energy consumption of cell manufacturing, and decay rates (r) of Li-S battery during actual EV operations. Detailed information is provided in Table 3.

Table 3 Parameter variations for sensitivity analysis

Parameter	Unit	Baseline	Variation	Comment
Driving range	km	320	250-400	a lower end value of 250km and a higher range of 400km are assumed for sensitivity analysis.
Accessible capacity	%	85	75-90	
Total mileage	km	200000	150000-300000	The boundary of the total mileage for EVs is between 150,000 km and 300,000 km, following the data reported in literature [82].
Battery efficiency	%	86	75-86	It is expected that battery degradation will induce a decrease in battery efficiency along time due to the rising of internal resistance and self-discharging.
Energy consumption of cell manufacturing	kWh	46.6	11.3-46.6	Industrial scale energy consumption of cell manufacturing is estimated to be 11.3-22.8 kWh kg ⁻¹ .
Battery decay rate	%	0.028	0.028-0.1	For the GSC structure, some other decay rates at 0.039% [21], 0.046% [83], and a higher estimate of 0.10%

were reported in the literature,

Detailed results of the sensitivity analysis are presented in Figure S14 and Table S27 in ESI. Summarily, the sensitivity analysis provides numerical evidence that the life cycle impact assessments conducted on the Li-S battery and the benchmarking made between the Li-S battery and the conventional NCM-Graphite battery are viable. Except for the battery decay parameter (Figure S14(f)), the influences of other parameters on the LCA results are moderate, within -24%-24% variations from the baseline level (Figure S14(a)-(e)). When compared, the life cycle impacts of the Li-S battery are 9%-90% lower than those of the conventional NCM-Graphite battery except ODP (Figure 5). On the other hand, the baseline energy density of the NCM-Graphite battery applied in the main text is 120 Wh kg^{-1} . The state-of-the-art NCM-Graphite, as applied in Tesla Model S, reaches 140 Wh kg^{-1} nowadays [85]. A sensitivity analysis has been conducted with the energy density of 140 Wh kg^{-1} resulting 6%-12% decreases among various impact categories (Figure S15). Hence, a conclusion can be reliably made that the Li-S battery is more environmental-friendly than the conventional NCM-Graphite battery.

From the sensitivity analysis, it is noted that increasing the driving range from 320 km to 400 km per charge will increase the life cycle impacts in GWP and FDP by 9% (Figure S14(a)). However, under such a case, the GWP and FDP of the conventional NCM-Graphite battery will be increased by 11% (Figure S16 in the ESI). Meanwhile, the scale-up of the Li-S production, with a 11.3 kWh kg^{-1} pouch cell assembly process, to the industrial scale will reduce the impacts in these two categories by 13% (Figure S14(e)). As a result, using a Li-S battery to replace the conventional NCM-Graphite battery will increase the driving range and reduce the life cycle impacts simultaneously in the future.

It must also be noted here that past LCA studies tend to select the same storage capacity among various batteries for benchmarking [10,84]. Following this protocol, the same 61.3 kWh NCM-Graphite battery pack will slightly lower the range to around 300 km per charge (Figure S17). Since previous studies show that the driving range of EVs is the major concern of consumers in market choice, and an acceptable driving range for an EV is expected to be 353 km and 437 km per charge, respectively, in Germany and the U.S.[86-88], the same driving range at 320 km is selected accordingly as the benchmarking basis in this study between the Li-S battery and the conventional NCM-Graphite battery.

3.3 Future Improvement Potentials

Current Li-S batteries are with a gravimetric energy density of 220 Wh kg⁻¹ and volumetric energy density of 298 Wh L⁻¹, which are still below the targets of U.S. Advanced Battery Consortium (USABC) set at 235 Wh kg⁻¹ and 500 Wh L⁻¹, respectively. In this study, we present a predictive study on the potential improvements of the Li-S battery performance via those key technical parameters including NP ratio, electrolyte fraction in the cathode, sulfur weight concentration in the cathode, and areal loading at three different production scales, as shown in Figure 6 [54]. The corresponding changes of the total environmental impacts along with these technical improvements are analysed, using the total ecopoints from the hierarchical perspective of the ReCiPe method. As predicted, the gravimetric energy density and volumetric energy density of the Li-S battery could be increased to 308 Wh kg⁻¹ and 415 Wh L⁻¹, respectively, with the NP ratio being reduced to 1.1, electrolyte fraction decreased to 50%, the sulfur weight concentration increased to 72%, and the areal loading increased to 10.6 mAh cm⁻¹. Corresponding, the total environmental impacts can be reduced by 20% in terms of the ecopoints. The pathway analysis indicates that a high areal loading is significant for the Li-S battery

to meet the USABC target while maintaining a lower environmental impact. However, a thick electrode, triggered by such a high areal loading, will intensify dendrite growth and sulfur shuttle effect in both anode and cathode. Therefore, further research on non-flammable electrolyte or solid electrolyte for the lithium sulfur battery are needed to solve the safety issue in future. For cathode, such approaches like constructing free-standing 3D electrodes and cross-linking nanostructured sulfur hosts are promising for developing high performance lithium sulfur batteries.

Figure 6 Pathways of the environmental impact changes of the Li-S battery in the production phase

Second, it is found in this study that the production of the nanostructured GSC cathode dominates the material flows during the life cycle of the Li-S battery. In particular, the sonication process used to create a homogenous dispersion of GO for sulfur precipitation is an energy intensive process. In the future, alternative energy-efficient technologies are needed to replace

the sonication process for dispersion of GO nanoparticles. Besides, the cathode structure is a crucial factor determining the decay rate of Li-S battery, which in turn has a substantial influence on the environmental impacts of the Li-S battery. Future investigations are needed on optimal control of the size and the sediment speed of sulfur particles during the precipitation process to ensure an improved binding and wettability between sulfur and graphene, and then, to alleviate the decay rate

Thirdly, the environmental impacts of the Li-S battery can be further reduced through an improved recycling process [6]. Currently, there is no established recycling system available for the conventional LIBs due to economic viability [83]. However, the economic potential of the Li-S battery recycling could be quite promising. Unlike conventional LIBs built on lithium oxides, pure lithium metal is used in the Li-S battery. Automated disassembly methods such as eddy current and density separators can be used to recover lithium metals by taking advantage of its substantially low density. Meanwhile, LiTFSI salt in the electrolyte can be another valuable substance for recovery because LiTFSI is a chemically and thermally stable compound with high economic value.

4. Conclusion

In this paper, a comprehensive LCA model is developed to assess and understand the life cycle environmental impacts of Li-S batteries for next generation EV applications, based on our lab experimentation, our industrial partner's battery manufacturing processes, and literature data. The Li-S battery is configured with a 61.3 kWh capacity capable of powering a mid-size EV for 320km per charge. From the LCA study, a total of 471 kg material inputs is needed to generate the 279 kg Li-S battery pack. Sodium thiosulfate and hydrogen chloride, which are used for GSC synthesis, are the two most significant material inputs, representing 28.0% and 13.0% of mass

flows during the life cycle of the Li-S battery, respectively. Moreover, this study obtained a 2.36 MJ km⁻¹ life cycle energy consumption for the configured 61.3 kWh Li-S battery. For the life cycle energy consumption, the battery use phase takes a share of 71%, followed by battery manufacturing at 22%, and battery materials processing at 7%. The intensive energy consumption in battery manufacturing is found mainly on the electrode drying process of NMP evaporation and dry room conditioning for cell manufacturing. The life cycle impact assessment reveals that battery use accounts for 70% of life cycle GWP and FDP impacts while battery production represents 28%.

The relative significances of the environmental impacts of the Li-S battery are compared with those of a conventional NCM-Graphite LIB at the same 320 km driving range. The results clearly show that the Li-S battery is a more environmentally friendly technology than the conventional NCM-Graphite battery, with 9%-90% lower impacts in most impact categories. Specifically, 158 g CO₂ eq km⁻¹ is generated from a Li-S battery during its life cycle, compared with 174 g CO₂ eq km⁻¹ from an NCM-Graphite LIB. The reliability of the LCA study is evaluated through a sensitivity analysis on six key parameters, including driving distance per charge, the accessible ratio of Li-S battery capacity, total mileage, Li-S battery efficiency, energy consumption of Li-S cell manufacturing, and Li-S battery decay rate.

Based on the findings from the LCA, the Li-S battery can be a more sustainable energy storage technology for next generation EV applications. Further reduction of the life cycle environmental impacts of the Li-S battery can be made through employing a binder-free electrode, developing an energy-efficient process for nanoparticle dispersion, improving the decay rate of the Li-S battery, and recycling Li-S batteries from retired EVs.

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Notes

The authors declare no competing financial interest.

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