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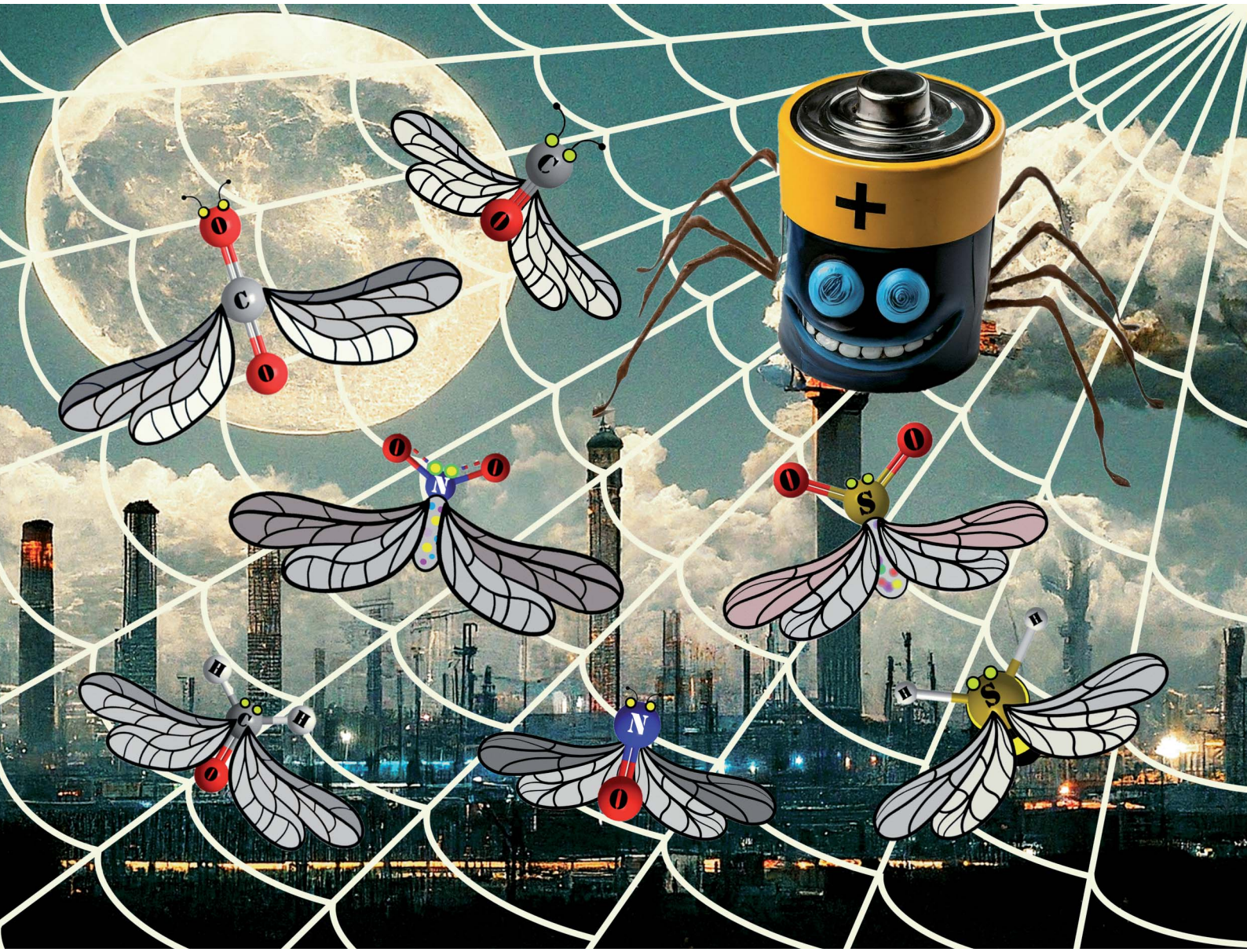

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TUTORIAL REVIEW
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Battery waste-derived functional materials for the capture and removal of harmful gases

Nishesh Kumar Gupta *

The persistent use of primary alkaline batteries in electronic gadgets and lithium-ion batteries in electric vehicles is creating a large volume of battery waste. Proper management and processing are necessary to prevent the dumping of used batteries in landfills. Valuable metals such as lithium, cobalt, nickel, and zinc can be extracted and purified from spent batteries. Alternatively, they can be used in synthesising functional materials. This review explores a promising solution for battery waste management by repurposing it to create materials capable of removing harmful gases. Reusing battery components such as electrodes, electrolytes, and polymer separators leads to the development of innovative strategies for creating adsorbents and catalysts. These materials are capable of efficiently capturing or catalysing harmful gases into harmless gases or ions. The review outlines various methods for converting battery waste into valuable materials, structural modifications, performance evaluations, and underlying mechanisms responsible for the removal of harmful gases. This review highlights the potential of battery waste as a sustainable resource for addressing rising air pollution and promoting a circular economy.

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Environmental significance

Repurposing battery waste for toxic gas removal minimizes environmental harm from electronic waste and mitigates air pollution. Transforming discarded battery components into functional materials reduces the reliance on raw materials and enhances air quality by efficiently neutralizing toxic gases. This innovative approach aligns well with the circular economy principles, promoting sustainable battery waste management while addressing severe environmental challenges.

Introduction

Given the increasing global demand for clean energy, managing waste from energy storage systems, particularly batteries, has become a major environmental concern. Primary alkaline batteries like Zn–MnO_2 batteries are extensively used to power portable electronic devices. However, post-exhaustion, billions of these single-use batteries end up in landfills, posing severe threats to the environment. Moreover, dumping these batteries in landfills leads to a significant loss of metal resources such as Zn and Mn.[1] Rechargeable batteries like lithium-ion batteries (LIBs) are considered the backbone of the electric vehicle (EV) industry. The need to transition from fossil fuel-powered vehicles to EVs is driving LIBs production at an unprecedented scale. It is projected that annual production will surpass the 'one million tons' mark by 2025.[2] The International Energy Agency estimated that EVs manufactured in 2019 alone generated 500 000 tons of LIBs waste. By 2040, this figure could escalate to a staggering 8 million tons of waste.[3] With improper disposal mechanisms, most spent LIBs are either temporarily stored or end up in landfills, causing severe contamination of the land and local ecosystem. These spent LIBs are valuable commodities, as the elements required for making the cathode of LIBs, including Li, Co, Ni, and Cu, hold significant market value.[4]

Recycling is considered the most sought-after method for extracting valuable metals from spent batteries.[5–8] However, battery recycling faces severe restrictions due to limited metal recovery, non-uniformity in cathode composition, overuse of acids, bases, and organic solvents, high energy costs, and the emission of toxic gases during processing.[9,10] Another approach to reducing battery waste is repurposing it into valuable functional materials, offering a promising avenue for upcycling. This could provide significant commercial value to battery waste before recycling, thereby reducing overall recycling costs. In the literature, numerous reports have demonstrated promising applications of battery waste-derived functional materials in heterogeneous catalysis,[11,12] energy storage devices,[13,14] and heavy metal sequestration.[15,16] Liu briefly reviewed these applications in 2018.[17] However, the review may be outdated, as battery-derived functional materials have since found new applications in gas capture and removal. Thus, there is a need for a review to highlight the diversified use of battery waste-derived functional materials for air decontamination applications.

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This review focuses on the emerging field of battery waste-derived functional materials, specifically highlighting their applications in capturing and removing harmful gases. Emissions from industrial facilities, thermal power plants, incineration sites, and vehicles contain a mixture of harmful gases, including sulphur oxides (SO_x), nitrogen oxides (NO_x), carbon oxides (CO_x), volatile organic compounds (VOCs), and hydrogen sulphide (H_2S). The complex interaction of these gases in the atmosphere, influenced by solar radiation and water vapour, leads to the formation of photochemical smog and acid rain, contributing to climate change and posing threats to both human health and the environment. Prolonged exposure to these airborne pollutants is associated with various adverse health outcomes, such as asthma, lung cancer, psychological disorders, autism, and low birth weight.[18,19] Addressing this urgent issue requires the development of effective and cost-efficient technologies for capturing and eliminating gaseous contaminants. By utilizing the inherent properties of battery waste constituents, including cathodes, polymers, anodes, and electrolytes, researchers are exploring novel opportunities to develop sustainable materials suitable for treating harmful neutral and acidic gases. This review analyses recent progress in the synthesis, characterization, and performance assessment of battery waste-derived functional materials for treating VOCs, toxic neutral gases (CO and NO), and acidic gases (CO_2, NO_2, SO_2, and H_2S). This review aims to highlight the concept of 'waste-to-wealth' in the context of battery waste, which could set a precedent for processing future battery wastes, including those from newly developed LIBs and sodium-ion batteries (NIBs).

Battery waste-derived functional materials

Batteries are typically divided into two categories, *i.e.*, primary and secondary batteries. The key difference lies in the nature of their chemical reactions. Primary batteries, such as Zn–MnO_2 and Zn–carbon batteries, are discarded once they can no longer provide sufficient electrical energy. In contrast, secondary batteries, like LIBs and NIBs, can convert chemical energy into electrical energy through reversible chemical reactions. This means the original chemical state can be restored by reversing the current flow, *i.e.*, by charging from an external source. However, with continuous use, even secondary batteries experience performance fading and are discarded when their performance reaches a minimum threshold. These LIBs are poorly collected and recycled, resulting in most of them being disposed of in landfills.

Alkaline Zn–MnO_2 batteries and LIBs are frequently used for synthesising functional materials. While multi-step synthetic approaches are commonly employed in developing these materials, some studies have reported the direct use of battery waste without significant pre-treatment. Here, a brief discussion has been included to inform readers about conventional approaches that have been adopted for developing functional materials derived from battery waste with some details about synthesis processes.

While discharging a Zn–MnO_2 alkaline battery, Zn oxidizes to produce ZnO, while MnO_2 undergoes reduction to form MnOOH and $Mn(OH)_2$. The MnOOH reacts with $Mn(OH)_2$ and $Zn(OH)_4^{2-}$ to yield Mn_3O_4 and $ZnMn_2O_4$, respectively.[20] Thus, the black mass derived from spent alkaline Zn–MnO_2 batteries is rich in ZnO and MnO_2 phases with minor presence of other metal and metal oxides, such as Zn, MnO, Mn_2O_3, Mn_3O_4, and $ZnMn_2O_4$, along with KOH electrolyte and graphitic carbon.[21] This black mass could be modified based on the requirements of the target gas molecule and the treatment process. For capturing highly acidic gases like H_2S, SO_2, and NO_2, the KOH electrolyte along with the ZnO–MnO_2 composite in the black mass is sufficient for gas oxidation, and thus, no pre-treatment is required.[21,22] However, for the thermal oxidation of gases like VOCs, researchers have treated the black mass with strong mineral/organic acids either to neutralize the KOH electrolyte[23–25] or to completely/selectively dissolve metals.[26,27] In some cases, a hydrometallurgical process like bioleaching is used to eliminate the use of strong mineral acids.[28,29] The leached metal solution was further processed to obtain the desired functional materials like $Zn_xMn_{3-x}O_4$,[30] MnO_2,[27] and Mn_2O_3.[26] Further modifications have been made to the black mass-derived materials to improve the catalytic properties, such as by adding photoactive TiO_2,[31] and catalytically active metals like Pd,[32–34] Cu,[27] and Ag.[35] Doping functional materials with active metals can improve physicochemical properties, such as surface area,[27] and lower the activation energy barrier associated with the catalytic elimination of gaseous pollutants.

The metal leachate obtained from the treated black mass of Zn–MnO_2 batteries could be used as a metal solution for developing new oxide materials, providing better control over the phase composition, morphology, and other desirable properties like surface area and porosity. In two such reports, Cu-loaded[27] and Ag-loaded MnO_2 catalysts[35] were prepared from the selective leaching of black mass obtained from discarded Zn–MnO_2 batteries. The black mass was treated with HCl (2 mol L^{-1}) at 80 °C for 4 h. The precipitate was filtered out and

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the filtrate (Mn-rich solution) was oxidised by NaClO solution at 45 °C for 6 h. The formed MnO_2 was phase-separated and washed several times with dilute HCl. While Cu loading over MnO_2 was performed by the wet impregnation method using copper nitrate salt, Ag was loaded by *in situ* reduction of Ag^+ ions (from the silver nitrate salt) using $NaBH_4$ as the reducing agent (Fig. 1). The formed catalysts possessed a higher surface area than the black mass, which is beneficial for the catalytic removal of gaseous pollutants.

LIBs consist of a cathode, an anode, an electrolyte, a separator, and current collectors, along with packaging components. There are five major types of cathodes used in LIBs, namely lithium cobalt oxide ($LiCoO_2$), lithium iron phosphate ($LiFePO_4$), lithium manganese oxide ($LiMn_2O_4$), lithium aluminium cobalt nickel oxide ($LiAl_xCo_yNi_{1-x-y}O_2$), and lithium cobalt manganese nickel oxide ($LiCo_xMn_yNi_{1-x-y}O_2$).[3] Since the cathodes of LIBs are composed of valuable metals, much research is focused on developing processes to leach out metals, extract Li as a soluble salt (with low Li purity), and synthesise transition metal-based functional materials.[36–38] In one such report, spent ternary LIBs were discharged in a 10% NaCl (aq.) solution for 24 h and manually disassembled to obtain the cathodes. The cathodes were calcined at 450 °C for 3 h to peel off active materials from the Al foils. The active cathode powder was treated with oxalic acid at 180 °C for 16 h in a Teflon-lined autoclave to extract Ni, Co, and Mn as insoluble oxalates. After phase separation and drying, the oxalate salt mixture was calcined at 550 °C for 3 h to yield $NiCoMnO_x$ catalysts (Fig. 2).[37] In another study, the active cathode powder was treated with an H_2SO_4–H_2O_2 solution to leach Co, Ni, Mn and Li. While the obtained leachate was treated with $KMnO_4$ solution or ozone to form Co/Ni-doped MnO_2, the majority of Li, Co, and Ni remained in the solution phase.[36]

While some researchers have developed novel processes to extract highly pure Li (as Li_2CO_3) along with transition metal oxides,[41,42] others have used the extracted Li_2CO_3 as a precursor for synthesising functional materials.[39,43,44] Qin and co-workers have extensively worked on extracting Li as pure Li_2CO_3 from LIBs' cathodes and subsequently using it as a precursor for synthesising Li_4SiO_4 sorbent for CO_2 capture. One such process involved discharging LIBs in a NaCl solution and manually disassembling them to obtain the cathodes. After treating the cathodes with NaOH solution to remove Al, the cathode material was placed in a leaching solution (H_2SO_4–H_2O_2, $Na_2S_2O_8$, or CH_3COOH–H_2O_2). The pH was adjusted with NaOH or NH_4OH to remove impurities and obtain a Li-rich solution. Na_2CO_3 was added to the solution phase at 95 °C to extract Li as a carbonate salt. The recovered Li_2CO_3, along with commercially available fumed silica, was mixed and calcined at 750 °C for 6 h to yield Li_4SiO_4 (Fig. 2).[39,44]

Apart from the cathode of LIBs, the anode (graphitic carbon) after proper chemical treatment has been upcycled to yield functionalized carbon adsorbents.[40,45] Aravindan and co-workers developed reduced graphene oxide (rGO) from the graphitic anode by first oxidising graphite using a modified Hummer's method and then reducing the GO with hydrochloric acid and the outer metallic Al casing of the battery. The group also reported the template-free synthesis of porous carbon hollow spheres by one-step carbonization of the recovered polymer separators (polypropylene (PP) and polyethene (PE)) at elevated temperatures (Fig. 2).[40] Many methods have been reported to modulate the physiochemical properties of LIBs waste-derived materials by metal doping,[46] integration with porous substrates,[47,48] and acid etching.[49,50] Although these methods have not been discussed in detail in this section, their role in the catalytic properties of materials will be discussed in subsequent sections.

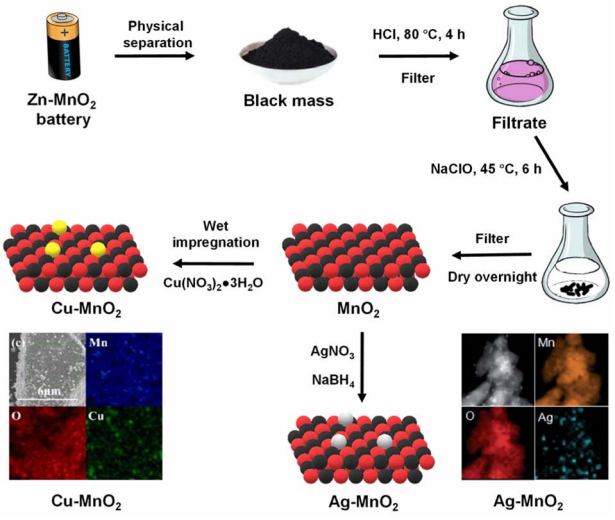

Fig. 1 Synthesis methodology for preparing Cu–MnO_2 (ref. 27) and Ag–MnO_2 catalysts.[35] EDX mapping of Cu–MnO_2 reproduced from ref. 27 with permission from Elsevier, copyright 2024. EDX mapping of Ag–MnO_2 reproduced with minor modification from ref. 35 with permission from The Royal Society of Chemistry, copyright 2024.

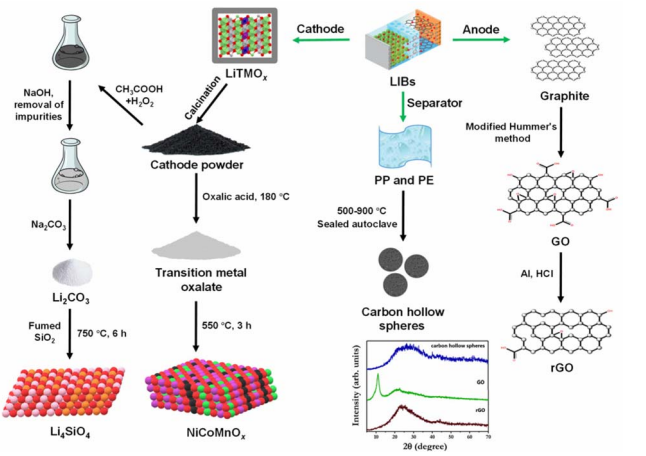

Fig. 2 A schematic illustration of synthesis methodologies adopted for processing LIB's components into functional materials.[37,39,40] The PXRD pattern of synthesised carbon materials reproduced with minor modification from ref. 40 with permission from The Royal Society of Chemistry, copyright 2024.

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Gas capture and decontamination

In the literature, battery waste-derived functional materials have been primarily used as catalysts for the thermal oxidation of gaseous pollutants such as VOCs, NO_x, and CO_x. However, some recent studies have demonstrated that these materials could also be used as room-temperature adsorbents/catalysts for treating harmful acidic gases. In the subsequent subsections, these functional materials will be discussed in the context of capturing and removing various neutral and acidic gaseous pollutants.

Removal of VOCs

Volatile organic compounds (VOCs) are a diverse group of carbon-based chemicals that evaporate easily at ambient temperatures. They are found in common household products, including paints, solvents, cleaning agents, building materials, and furnishings. While many VOCs are only mildly irritating at low levels, some can have toxic effects on human health and the environment. Some VOCs are known carcinogens, while many are considered precursors of ozone, photochemical smog, and secondary aerosols. Low-temperature catalytic oxidation is considered a suitable method for eliminating VOCs from the environment. Supported noble metals and transition metal oxides are promising catalysts for the total oxidation of VOCs at low temperatures.[51] Battery waste is rich in oxides of 3d-series transition metals and could be utilized for the purpose after suitable modification of the cathode material.

The black mass extracted from discarded Zn–MnO_2 alkaline batteries is rich in ZnO and MnO_x, which, after neutralization with mineral acids, was used for the thermal oxidation of VOCs at low-to-mid temperatures.[23,24,32] Black mass, after neutralization with H_2SO_4, catalysed the total oxidation of VOCs, including benzene, toluene, and *o*-xylene (collectively BTX) below 400 °C.[23] The type of acid used for neutralization played an important role in the catalytic activity. The catalytic activity followed this order: sulphuric acid > nitric acid > oxalic acid > hydrochloric acid > phosphoric acid > no acid, when these acids were used for neutralization. Neutralization with different acids yielded black mass with varying proportions of Mn and Fe (catalytically active metals) and surface area, where H_2SO_4-treated black mass possessed superior physicochemical properties.[24] The catalytic activity of acid-treated black mass was further improved by impregnating noble metals like Pd.[32] After Pd loading, the black mass effectively catalysed benzene (T_{90} ~ 298 °C), toluene (T_{90} ~ 253 °C), and *o*-xylene (T_{90} ~ 239 °C) (note: T_{90} is the temperature at which 90% conversion of VOC was observed). Without Pd, the T_{90} value was 385, 331, and 377 °C for benzene, toluene, and *o*-xylene, respectively. Increased Pd loading enhanced the lattice oxygen mobility available for effective oxidation of aromatic VOCs. ZnO, from the acid-treated zinc rod (from spent alkaline batteries), was used as a support over which catalytically active Mn[52] and Pd[33] sites were dispersed to oxidise VOCs. Increased MnO_x loading on ZnO improved the lattice oxygen mobility and strong acid-site density. BTX molecules adsorbed on the acidic sites reacted with the lattice oxygen to form CO_2 and H_2O. The formed O-vacancies were replenished by oxygen atoms formed by the dissociation of molecular oxygen (Fig. 3a).[52] MnO_x/ZnO with 30 wt% Mn loading had a T_{90} value of 411, 347, and 381 °C for benzene, toluene, and *o*-xylene, respectively. Contrarily, just 1.0 wt% of Pd loading over ZnO was sufficient for the total oxidation of BTX molecules at the same feed concentration, where the T_{90} for benzene, toluene, and *o*-xylene was 389, 325, and 318 °C, respectively.[33] Increased metallic Pd loading favoured the catalytic process by improving the lattice oxygen mobility. On the electron-rich Pd sites, BTX molecules were adsorbed and subsequently reacted with lattice oxygen near the Pd–ZnO interface to form CO_2 and H_2O (Fig. 3b). Though only a minuscule amount of Pd is sufficient for catalytic process, the high cost of Pd compared to MnO_x could offset the overall catalytic gain.

After comparing the T_{90} values, it is evident that the thermal oxidation of benzene is more difficult than that of toluene or *o*-xylene as the lower ionization potential of methylated benzene derivatives makes their oxidation much easier than benzene.[32] Another observation is that the oxidation of oxygenated VOCs like ethanol (T_{50} ~ 170 °C) over MnO_x catalyst is more favourable than that of aromatic VOCs like toluene (T_{50} ~ 280 °C). Ethanol is strongly chemisorbed on the MnO_x surface through the coordination of non-bonding oxygen electrons compared to the weak bonding observed for toluene through π-type C=C orbitals. Since strong chemisorption of ethanol lowers its activation energy, oxidation of ethanol occurs at a lower temperature than toluene.[29]

Cathodes of all different types of LIBs have been upcycled to transition metal oxides for the thermal oxidation of VOCs. Artificially created Li, Co, and O vacancies in $LiCoO_2$ through partial Co^{3+} leaching and de-intercalation of Li^+ ions by HNO_3-etching yielded catalysts possessing excellent oxidation efficiency for benzene. While pristine $LiCoO_2$ catalysed only 10% of

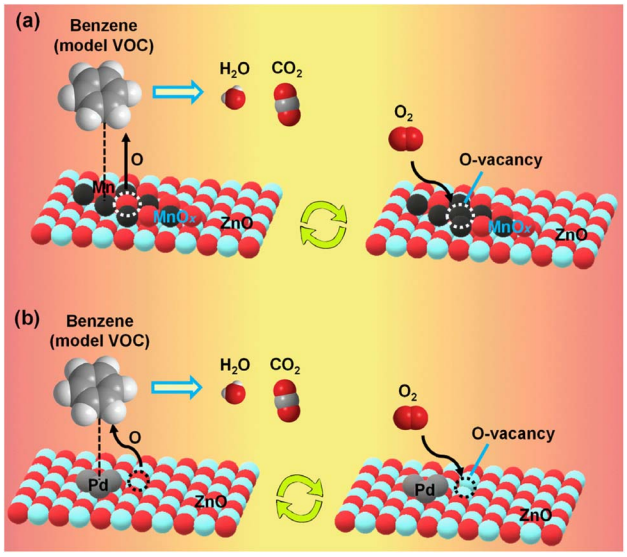

Fig. 3 Proposed reaction mechanism for complete oxidation of BTX molecules over (a) MnO_x–ZnO[52] (b) Pd–ZnO.[33]

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benzene at 300 °C, 100% oxidation was observed for the acid-treated $LiCoO_2$ from synthetic air. The Li and O vacancies in $LiCoO_2$ facilitated benzene adsorption and activation, while the Co and O vacancies induced the formation of active surface oxygen species. The number of vacancies and subsequently the catalytic activity was further improved by increasing the acid-etching time. Also, the acidic solution rich in Li and Co could be further processed to recover valuable metals.[50] Mixed metal oxides, such as $Co_{3-x}M_xO_4$ (M = Li, Ni, Cu, Al, Mn), synthesised from $LiCoO_2$, catalysed toluene ($T_{90} \sim 274$ °C) better than the Co_3O_4 synthesised from nitrate salt ($T_{90} \sim 282$ °C). The superior activity of $Co_{3-x}M_xO_4$ was related to a higher surface area, better low-temperature reactivity, a higher density of weak acid sites, and a higher proportion of high-valent cations and lattice oxygen. While impurities like Cu and Mn in the catalyst improved the activity, Li negatively affected it.[38] Several other mixed metal oxides like $CoMnNiO_x$ for the oxidation of propane,[53] MnO_x ($CoMn_2O_4$–$NiCo_2O_4$–$Cu_{1.2}Mn_{1.8}O_4$–Mn_2O_3) for the oxidation of 1-methoxy-2-propanol,[47] $CuNi_{0.5}Mn_{1.5}O_4$ for the oxidation of toluene, ethylbenzene, and formaldehyde,[54] and Mn_5O_8/CeO_2, $CuNi_{0.5}Mn_{1.5}O_4/CeO_2$, and Co_3O_4/CeO_2 for the oxidation of 2-ethoxy ethyl acetate,[55] have shown the potential of LIBs-derived catalysts in VOC elimination. In all these catalytic systems, a higher surface area, abundant high-valent transition metal sites, and a higher proportion of adsorbed oxygen species in catalysts determined their VOC oxidation activity.

On numerous occasions, LIBs-derived manganese oxides (MnO_x), especially MnO_2, have been reported for VOC oxidation. It is noteworthy that high-valent Mn-sites in MnO_x catalysts (in MnO_2) catalyse VOCs better than the low-valent Mn-sites (in Mn_2O_3 and Mn_3O_4).[28,56] Even the presence of different phases of MnO_2 and dopants could alter the catalytic activity of MnO_x. In one such study, Co/Ni-doped α-MnO_2 and β-MnO_2 catalysts were synthesised by the oxidative precipitation of Mn-rich leachate using $KMnO_4$ and ozone, respectively. While doped catalysts performed better than the pure MnO_2 catalysts, doped α-MnO_2 catalysed the oxidation of toluene and formaldehyde better than doped β-MnO_2.[36] α-MnO_2 with a [2 × 2] tunnel structure is more active than β-MnO_2 with a [1 × 1] tunnel structure, as the [2 × 2] tunnel structure could facilitate the absorption and diffusion of VOC molecules towards active sites.[57] An appropriate proportion of transition metal dopants like Co and Ni in MnO_2 could improve the catalytic activity by increasing the concentration and mobility of lattice oxygen. Similar observations have been made with Cu-doped α-MnO_2 during the oxidation of toluene and chlorobenzene. Cu-sites in α-MnO_2 favoured the catalytic process by increasing the surface oxygen species and active oxygen species through the Cu^{2+}/Cu^{+} redox cycle.[58] Even the morphologies of catalysts could influence their catalytic activity, as was the case with morphologically different MnO_2 catalysts, MnO_2-CM (microspheres), MnO_2-HM (stacked nanorods), and MnO_2/SBA-15 (microspheres), synthesised by hydrothermal, co-precipitation, and impregnation methods, respectively, for the oxidation of toluene. MnO_2-HM showed 100% conversion of toluene even with the lowest surface area due to its better redox ability and the large presence of adsorbed oxygen species at a low synthesis temperature of 140 °C.[48]

On rare occasions, spent ternary LIBs have been processed to synthesise perovskite catalysts, $LaMn_{1-x}B_xO_3$ (B = Co, Ni, Cu, Al) for the thermal oxidation of toluene[59] and $SmMnO_3$ and $SmCoO_3$ for propylene glycol methyl ether.[60] The LIBs-derived perovskites performed better than those synthesised from commercial salts, as the former has a higher surface area, Mn^{4+}/Mn^{3+} ratio (or Co^{3+}/Co^{2+} ratio for Co-perovskite), and lattice oxygen species. The partial substitution of Mn/Co sites with Ni, Co, Al, and Cu ions improved catalytic performance. However, the presence of Li as an impurity in the catalyst severely inhibited the activity.

Plasma-assisted catalytic oxidation of VOCs is another method that has been studied using battery waste-derived catalysts like Mn_2O_3 (ref. 26) and Mn_2O_3/Al_2O_3 (ref. 61) with BTX pollutants. Though the method effectively catalysed a quantitative amount of benzene and toluene, the oxidation of *o*-xylene was below 75% even under the best experimental conditions. The catalytic activity was significantly affected by synthesis conditions, including the type of acid, acid concentration, black mass-to-acid volume ratio, calcination temperature, and Mn content over the alumina substrate.[26,61] Other than thermal oxidation, photocatalytic oxidation of toluene (~50 ppm) has been performed over TiO_2-modified black mass (from Zn–MnO_2 alkaline battery).[31,62] The composite photo-oxidized 100% of toluene within 3 h of irradiation, better than TiO_2 alone, black mass alone, or even the TiO_2–ZnMn oxide composite synthesised from black mass leachate. The TiO_2–black mass composite, with higher photon absorption efficiency, better charge transfer properties, and low charge-recombination rate, effectively absorbed photons and generated superoxide and hydroxide radicals for rapid photo-oxidation of toluene.[62] Even the calcination temperature during the synthesis of TiO_2–black mass composite played a major role in the photocatalytic efficiency. The photo-catalyst synthesised at a lower calcination temperature (200 °C) showed the highest catalytic activity due to the highest surface area, highest photon absorption property, narrowest band gap, and lowest charge recombination efficiency.[31] Thus, low-concentration VOC sources are effectively treated by photo-oxidation using TiO_2–black mass composites.

Removal of CO and NO

Carbon monoxide (CO) is a highly poisonous gas produced from the incomplete combustion of organic matter. CO must be removed from tail gases, and for that, thermal oxidation of CO to CO_2 is a viable method. Battery waste-derived catalysts could efficiently oxidise CO to CO_2 at low-to-mid temperatures. Zn–MnO_2 battery-derived Cu–MnO_2 (ref. 63) and Ag–MnO_2 (ref. 35) completely oxidised CO at 120 and 150 °C, respectively, performing better than MnO_2 (240 °C). The inclusion of Ag and Cu in MnO_2 played a synergistic role and improved the catalytic activity. Importantly, MnO_2 with higher Cu loading performed better by providing a large surface area, more surface-active oxygen species and oxygen vacancies, and a higher proportion

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of Mn^{4+} and Cu^{2+} ions for catalysis.[63] $CoFe_2O_4$–LIB ($CoFe_2O_4$–Co_3O_4), derived from LIBs' cathode, has been used for CO oxidation. The composite oxidised 98% of CO at 300 °C, better than pure $CoFe_2O_4$ (60% CO oxidation at the same temperature). Detailed spectroscopic investigations suggested that both $CoFe_2O_4$ and Co_3O_4 were essential for CO oxidation, where CO was oxidised to CO_2 by interacting with the adsorbed oxygen species and lattice oxygen over $CoFe_2O_4$ and Co_3O_4, respectively (Fig. 4).[41]

Nitrogen oxides (NO_x), emitted from thermal power plants and incinerators, are some of the toxic gaseous pollutants responsible for acid rain and photochemical smog. Low-temperature NH_3-selective catalytic reduction (NH_3-SCR) technology is promising in reducing the NO_x concentration from stationary sources due to its high de-nitration efficiency. The process involves NH_3-driven reduction of NO to N_2 at low temperatures over a suitable catalyst. Though V_2O_5–WO_3/TiO_2 (an industrial catalyst) is used for the process, the high cost of V and W, V toxicity, low SO_2 resistance, and poor low-temperature activity make it essential to explore other economical and effective catalysts. Mn-based catalysts are inexpensive and perform well even at low temperatures.[64] Spent alkaline Zn–MnO_2 batteries are a good source for extracting necessary Mn for synthesising catalysts. Chang and co-workers estimated that CO_2 emission during carbothermal extraction of Mn from spent batteries was 1.0 kg per kg of black mass, which was ~15% of the CO_2 emitted during traditional Mn manufacturing (6.7 kg per kg Mn). Moreover, the recovered Mn cost is much lower than the commercial Mn salts. Thus, processing primary batteries for Mn seems to be an economical and environmentally benign approach. The battery-derived Mn/TiO_2 catalyst was found superior to commercial salt-based Mn/TiO_2. The superior catalytic activity and high N_2/N_2O selectivity of Mn/TiO_2 at 160–200 °C were ascribed to a higher Mn^{4+} proportion and favourable presence of Fe^{3+} impurity, which improved the oxidation ability of battery-derived Mn/TiO_2. However, certain impurities like carbon and Zn in treated black mass could reduce the activity of Mn/TiO_2 by decreasing the Mn^{4+} concentration and acidity of the catalytic surface. Thus, caution must be taken during the processing of black mass for Mn extraction using the carbothermal method.[65]

After Li recovery from LIBs cathode using oxalic acid, the residual precipitate was upcycled to yield $NiCoMnO_x$ catalyst for NO_x reduction. $NiCoMnO_x$ (Co_3O_4–$NiCo_2O_4$–$MnCo_2O_{4.5}$–NiO) catalysed 90% of NO_x in a broad temperature range of 110–230 °C, better than the catalyst synthesised with metal salts. The LIBs-derived catalyst possessed a higher surface area and abundant oxygen defects, which favoured the adsorption of reactant gases, *i.e.*, NO and NH_3 (Fig. 5). Though the LIBs-derived catalyst performed well in the presence of moisture, SO_2 in the feed gas severely hampered its catalytic activity by reacting with the adsorbed NH_3 to form ammonium sulphate and bisulphate species over the catalyst surface.[37] Polyethylene glycol (PEG), a water-soluble polymer, was used as a templating agent during the LIBs processing to synthesise $NiCoMnO_x$ catalysts with modulated physicochemical properties. The $NiCoMnO_x$–PEG catalyst possessed a higher surface area and a higher proportion of Co^{3+}, Mn^{4+}, and adsorbed oxygen species, which favoured the oxidation of NO to NO_2 (fast SCR reaction). Though $NiCoMnO_x$ catalysts synthesised with or without PEG catalysed 90% of NO in a similar temperature window of 80–230 °C, $NiCoMnO_x$–PEG performed better in the presence of H_2O and SO_2 in the feed gas. A higher SO_2 tolerance of $NiCoMnO_x$ catalyst was due to the presence of more acidic sites over the surface, which delayed SO_2 adsorption and subsequent conversion to sulphate species.[66] Zhang and co-workers modulated the physiochemical properties of $LiMn_2O_4$ (simulated cathode of LIBs) by exchanging some of the Li^+ ions with protons (acetic acid treatment) and/or by surface loading with a small amount of V_2O_5. While the inclusion of protons increased the surface acidity, V_2O_5 regulated the redox behaviour and increased the number of acidic sites. The Li_xH_{1-x}-Mn_2O_4–V_2O_5 (dual-modulated) catalyst showed the best

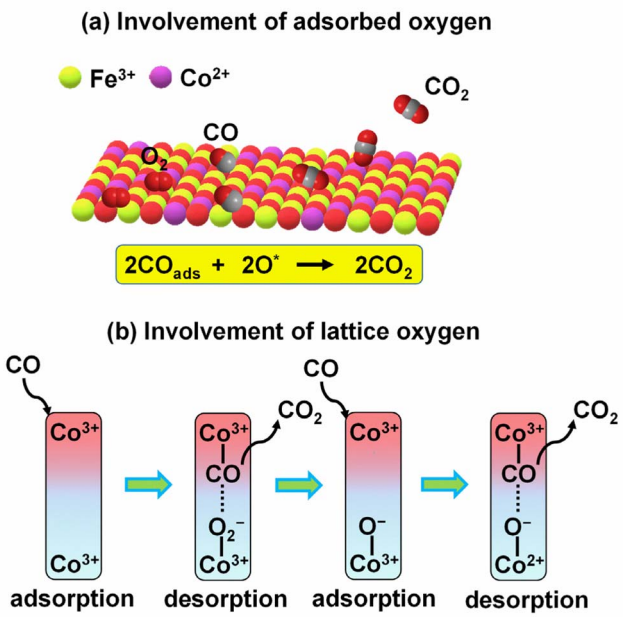

Fig. 4 The role of $CoFe_2O_4$–LIBs catalyst in CO oxidation involves the interaction of CO with (a) adsorbed oxygen species over $CoFe_2O_4$ and (b) lattice oxygen over Co_3O_4.[41]

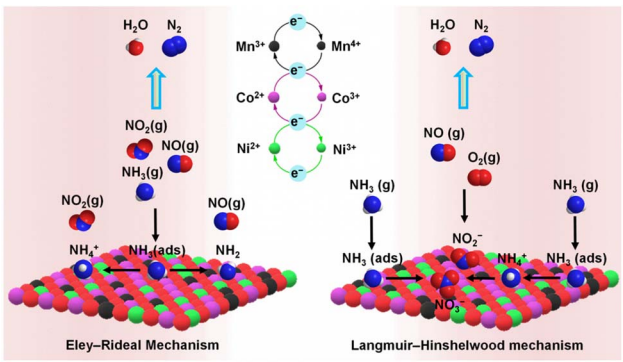

Fig. 5 Proposed NH_3-SCR mechanism for NO conversion to N_2 over waste LIBs-derived $NiCoMnO_x$ catalyst.[37]

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combination of NO reduction activity and N_2 selectivity than singly modulated catalysts due to improved NH_3 adsorption, superior nitrite decomposition, and reduced surface nitrate species formation.[49] These studies have highlighted that after suitable modifications, cathodes of waste LIBs could be upcycled as efficient NH_3-SCR catalysts.

Removal of acidic gases

Although carbon dioxide (CO_2) is a weakly acidic gas, it is considered an important greenhouse gas responsible for rising global temperatures and climate change. Carbon capture is a leading technology that relies on porous materials for preferential sequestration of CO_2 from flue gas or even air.[67] Carbon-based porous materials like reduced graphene oxide (rGO, surface area $\sim$ 374 m^2 g^{-1}) and porous carbon hollow spheres (surface area $\sim$ 402 m^2 g^{-1}) have been developed from LIBs' anodes (graphitic carbon) and polymer separators, respectively. These materials have shown potential in capturing CO_2 gas at 25 °C and 40 bar, with adsorption capacities reaching 61.2 and 170.3 cm^3 g^{-1} for rGO and carbon spheres, respectively.[40] Although these adsorbents store a large volume of CO_2 at 40 bar, for practical purposes, the material must be functional at low CO_2 pressures. A K_2CO_3-impregnated carbon residue has been demonstrated as a reusable adsorbent for capturing CO_2 from indoor air (1000–2000 ppm). In moist conditions, hydrated K_2CO_3 reacted with CO_2 to form bicarbonates. Through this reaction, the material adsorbed $\sim$9.7 wt% of CO_2 at 25 °C. Regeneration of the adsorbent requires heating to 150 °C and was regenerable for four cycles.[45]

High-temperature CO_2 chemisorption over alkali ceramics is a well-established approach where CO_2 is chemisorbed as a carbonate salt of an alkali metal. Lithium orthosilicate (Li_4SiO_4) is a lithium ceramic that has been explored as a CO_2 captor and possesses high capacity and regenerability.[68] More often, different types of cathodes from spent LIBs have been used to recover Li as Li_2CO_3, which was further utilized as a Li precursor for synthesising Li_4SiO_4. In one such strategy, CO_2 sequestration was done by using CO_2 as a leaching agent to extract Li out of the spent $LiFePO_4$ cathode as highly pure Li_2CO_3. Moreover, the $FePO_4$ residue was converted to $Na_4Fe_3(PO_4)_2P_2O_7$ (a cathode for NIBs). This approach effectively fixed $\sim$120 kg of CO_2 for every ton of recycled $LiFePO_4$.[42] A more direct approach involved using extracted Li_2CO_3 and a Si source (commercial silica or rice husk ash) to synthesise Li_4SiO_4 by a solid-state route. Through this, the cost of producing Li_4SiO_4 was reduced by 25–95% compared to the conventional route involving commercial precursors.[39,43,44,69] Different types of cathodes, carbon sources for pyrolysis of cathodes,[39] and leaching medium[43] affected the composition of Li_2CO_3, further influencing the physicochemical properties of Li_4SiO_4. The best CO_2 uptake was recorded for $LiFePO_4$ battery-derived Li_4SiO_4, where the material possessed a capacity of 270–280 mg g^{-1} for 80 cycles in a 15 vol% CO_2 feed.[43] Also, waste (battery and rice husk)-derived Li_4SiO_4 was found to be a better CO_2 captor than those synthesised with commercial precursors,[69] further highlighting the importance of battery waste-derived materials.

Fig. 6 An illustration showing energy-intensive and energy-efficient upcycling of battery waste for acidic gas removal.

Spent alkaline Zn–MnO_2 batteries have been upcycled as adsorbents/catalysts for treating highly acidic gases like H_2S, SO_2, and NO_2. $Zn_xMn_{3-x}O_4$ and ZnO synthesised from the leachate of Zn–MnO_2 batteries were used for treating H_2S gas at 400 °C. These transition metal oxides successfully removed H_2S from simplified gas mixtures and real syngas by reacting with H_2S to form α-MnS, γ-MnS, ZnS, elemental sulphur, polysulfide, and $MnSO_4$. The binary metal oxide with a high Mn/Zn ratio possessed superior catalytic activity and favoured the oxidation of sulphide to elemental sulphur and sulphate.[30] Since black mass derived from Zn–MnO_2 batteries is highly alkaline and has active ZnO, MnO_2, and $ZnMn_2O_4$ phases, it was possible to use the raw black mass directly for H_2S removal at 20 °C and high humidity. The black mass possessed an adsorption capacity of 60 mg g^{-1} for five cycles. Over the black mass, H_2S molecules dissociated to sulphide and further oxidised by H_2O and molecular O_2 to sulphur and sulphate. Theoretical calculations confirmed that ZnO was more reactive than MnO_2, and black mass derived from a fully discharged battery is expected to show even higher adsorption capacity.[22] In a separate study, untreated black mass from Zn–MnO_2 batteries of different brands was used as catalysts for treating 100 ppm of SO_2 and NO_2. These black mass samples have different phase composition, surface area, and alkalinity, which influenced their SO_2 uptake capacity. For three cycles, the best material exhibited an average SO_2 and NO_2 adsorption capacity of 30.2 and 13.8 mg g^{-1}, respectively, at 20 °C and high humidity. Further performance improvement was achieved by integrating black mass with calcium alginate to form hydrogel beads. The black mass catalysed SO_2 to sulphate and NO_2 to nitrite and nitrate ions.[21] These studies highlighted the potential of black mass in treating a wide range of acidic gases at room temperature. Unlike CO_2 captors like Li_4SiO_4, which require high energy input for both material synthesis and CO_2 chemisorption, direct use of black mass (ZnO–MnO_2–KOH) in treating acidic gases at low temperatures should be promoted for sustainable processing and upcycling of spent batteries (Fig. 6).

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Challenges and prospects

Waste LIBs and alkaline batteries are processed to develop functional materials for air decontamination applications. The synthesised materials serve as catalysts for the thermal oxidation of VOCs to CO_2 and H_2O, NH_3-SCR catalysts for reducing NO_x to N_2, and room-temperature adsorbents/catalysts for eliminating acidic gases like CO_2, SO_2, NO_2, and H_2S. Many of the battery-derived catalysts have shown higher catalytic performance than those synthesised with commercial salts. Methods have been developed to sequestrate CO_2 either by adsorbing or by converting it into carbonates. Additionally, CO_2 has been employed as a leaching agent to extract pure and high-valued Li_2CO_3 from waste $LiFePO_4$ batteries. To a greater extent, the main objectives of processing battery waste and developing functional materials for gas capture and removal applications have been fulfilled by the current literature. However, challenges persist for its translation from lab to industry. The biggest challenge in waste battery processing is the variation in the types of batteries available in the market. There is no one method which could be applied to all kinds of battery waste. This underscores the importance of consumer awareness in segregating battery waste at its source before collection by relevant authorities.

The second challenge associated with battery waste processing is the excessive consumption of concentrated mineral acids like sulphuric or nitric acid for the leaching of desired or undesired metals from the battery's cathodes. This practice must be discouraged as mineral acids are toxic, require large energy input during production, and upon unchecked disposal are catastrophic to the environment.[70] In such a scenario, the use of hydrometallurgical methods like bioleaching of metals using sulphuric acid-producing bacteria like *Acidithiobacillus thiooxidans* must be encouraged, which could reduce the volume of secondary waste generated from the cathode processing.[28,29] Another issue faced during the upcycling of battery waste to functional materials is excessive energy consumption during the calcination process. Some studies have highlighted that materials synthesised at lower temperatures are more efficient than those synthesised at higher temperatures. An energy optimization during the synthesis process could greatly reduce the overall cost of upcycling and CO_2 emissions associated with thermal energy consumption. Another approach is to upcycle battery waste with minimum steps to target a desired gas pollutant. It was observed that the black mass from alkaline batteries could be directly used for capturing H_2S at room temperature. Thus, the need to upcycle the black mass to metal oxide catalysts for mid-temperature removal of H_2S could be avoided. Moreover, many energy-intensive processes involved in gas treatment, like high-temperature CO_2 chemisorption over alkali ceramics, must be discouraged. Room-temperature sequestration of CO_2 over porous carbonaceous materials derived from polymer separators is a viable option for carbon capture, which should be explored more and extended to a larger scale after a systematic cost-to-performance evaluation. Though catalytic oxidation of aromatic VOCs is possible only at mid-temperatures, other VOCs like formaldehyde can be degraded even at room temperature.[71] Even photocatalytic oxidation using solar radiation is a feasible option for eliminating aromatic hydrocarbons like toluene over battery-derived catalysts. Implementing these energy-efficient strategies could reduce the generation of secondary waste, overconsumption of energy, and associated CO_2 emissions during the upcycling of battery waste. All these strategies are scarcely reported in the literature and need detailed investigation before their implementation in real conditions.

The urgent need to transition from fossil fuel to a renewable energy-driven economy is fuelling the growth of energy storage systems. Much of the research is concentrated on developing LIBs that could hold sufficiently large amounts of energy and are safe during operation. While research and development in battery manufacturing is a must to achieve the green economy targets, attention should also be given to the processing of battery waste. So far, a large volume of used batteries are either stored or disposed of in landfills. The situation for disposal of primary batteries is even worse as these batteries are consumed in billions with poor mechanisms for waste battery collection and processing in most of the countries. Though it is doubtful that the extraction of valuable metals like Li, Co, Ni, and Cu in LIBs could offset the entire cost of recycling, upcycling battery waste as functional materials and using them for gas pollutant removal could be an economical measure towards a cleaner environment. In the future, millions of tons of LIBs and Zn–MnO_2 batteries are expected to be available for processing. Public and private entities must act responsibly in tackling this environmental issue by educating the public about battery segregation and recycling. The government must incentivise the entities focused on recycling and repurposing of battery waste. "A better segregation strategy is the golden step towards processing any waste". Soon, more efficient and safer batteries like NIBs are expected to be rolled out in the market, which will further increase the volume of battery waste. Unlike LIBs, NIB's recycling cost will be even harder to offset as these are made with inexpensive metals like Na and Mn. Though some of the recent works have highlighted the potential of NIBs' cathode (Na–Mn oxides) in cleaning acidic gases in ambient conditions,[72–74] more efforts are needed in identifying and developing functional materials capable of degrading harmful organic/inorganic gaseous pollutants in ambient conditions. The future of upcycling battery waste is bright as the research is moving in the right direction and targeting the most important issues of rising battery waste and air pollution.

Conclusions

The upcycling of discarded primary alkaline batteries and rechargeable LIBs to functional materials for harmful gas removal represents a promising approach to addressing the rising concentration of gaseous pollutants in the atmosphere. Through innovative approaches, electrodes, electrolytes, and polymer separators of battery waste could be processed into various functional materials, including metal oxides, composites, and carbonaceous materials. The synthesised materials

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have been effectively utilized as catalysts for thermal oxidation of VOCs and CO, NH_3-SCR catalysts for NO_x reduction, and room-temperature adsorbents/catalysts for capturing and mineralizing acidic gases. In many cases, the battery waste-derived materials were found more efficient than those synthesised by metal salts for a desired application. Numerous strategies, like metal-doping, integration with porous substrates, and acid/base-etching have been implemented to further improve the performance of these materials. These research findings have shown immense potential in repurposing battery waste streams for creating high-performing materials capable of effectively removing harmful gases from various sources. As research in this field continues to advance, it holds the promise of not only improving air quality but also promoting the circular economy by transforming waste into valuable resources.

Author contributions

NKG is responsible for the literature survey and manuscript writing and reviewing.

Conflicts of interest

There are no conflicts to declare.

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