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Research Article

Spent Li-Ion Battery Electrode Material with Lithium Nickel Manganese Cobalt Oxide as a Reusable Catalyst for Oxidation of Biofurans

Ananda S. Amarasekara,* Sofia K. Pinzon, Tommy Rockward, and Hashini N. K. Herath

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ABSTRACT: The wide use of Li-ion batteries in energy storage has resulted in a new waste product stream rich in valuable metals Mn, Ni, and Co with well-known catalytic activities. In this work, a spent Li-ion battery electrode material with lithium nickel manganese cobalt oxide is shown as an excellent reusable catalyst for oxidation of biomass-derived furan aldehydes and alcohols to their value-added oxidation products with applications in the sustainable polymer industry. A mechanically separated, combined cathode and anode black material from a spent DELL 1525 laptop battery was pyrolyzed in air at 600 °C to remove binders and electrolytes to prepare the catalyst. The SEM, XRF, and X-ray crystallography analysis of the catalyst showed the presence of C, O, Li, Ni, Co, and Mn, indicating the presence of a lithium nickel manganese cobalt oxide ($LiNi_xMn_yCo_zO_2$)-type cathode material in the spent Li-ion battery employed in the study. This material was shown as an efficient catalyst for the oxidation of aldehyde and alcohol functional groups in biofurans, furan-2-aldehyde, 5-hydroxymethyl furfural, and 5,5′-[oxybis(methylene)]bis[2-furaldehyde], to their corresponding carboxylic acids in 82−97% yield, at 120−140 °C, under 1.24 MPa oxygen, and in 0.10 M aq. Na_2CO_3 medium.

KEYWORDS: *Li-ion batteries, lithium nickel manganese cobalt oxide, oxidation catalyst, furan-2-aldehyde, 5-hydroxymethylfurfural, 2,5-furandicarboxylic acid*

INTRODUCTION

The wide use of Li-ion batteries (LiBs) for energy storage in mobile electronic devices, electric tools, medical equipment, transportation, and home solar power system farms has caused a rapid rise in the ranking of spent LiBs as one of the fastest growing waste products. The valuable critical metals Li, Ni, Mn, and Co are major components in these batteries, and untreated disposal of these batteries can pose a substantial threat to the environment due to their high concentrations and the toxicity of Ni, Mn, and Co.[1,2] To minimize the adverse environmental impacts from the direct disposal of the spent LiBs, as well as to recover valuable critical materials from them, a number of end-of-life management approaches are currently in the development phase.[3−5] These technologies are based on pyrolysis, biochemical, or enzymatic methods as well as hydro-metallurgical process.[6−8] Among these recovery techniques, Badawy and Nayl proposed a 900 °C high-temperature pyrolysis method for the recovery of $LiCoO_2$ from spent mobile phone batteries.[9] In addition, Yang and co-workers reported the use of a LiOH-KOH (3:7 mole ratio) molten salt system at 300−500 °C for the recovery of $LiCoO_2$ from LiBs.[10] All these approaches are aimed at achieving high recovery efficiency and a lower environmental impact.[11,12]

Battery chemistry can vary across a wide range for this type of energy storage device. Polymer gel-type lithium-ion batteries are used in handheld and mobile electronic devices such as cell phones where weight is a critically important factor. These batteries are made with a polymer gel, instead of a liquid electrolyte, and generally use a lithium cobalt oxide ($LiCoO_2$) cathode material together with a graphite anode, offering a high energy density but a relatively shorter lifespan.[13,14] Lithium iron phosphate ($LiFePO_4$), lithium manganese oxides such as $LiMn_2O_4$ spinel or Li_2MnO_3-based lithium-rich layered materials, and lithium nickel manganese cobalt oxide ($LiNi_xMn_yCo_zO_2$) are known to offer longer battery lives and higher discharging rate capabilities. These batteries with liquid electrolytes are widely used in electric tools, medical equipment, and electric vehicles. In addition to a wide range of Li complexes, many Li, Ni, Mn, and Co complexes with composition variations are currently used as cathode materials. Elemental compositions and formulas of a selected set of common LiB cathode materials are shown in Table 1. Recycling of these elements from spent batteries is an essential step in the wider use of these batteries. However, the reuse of valuable elements in manufacturing of new batteries requires extraction of metals from carbon and binders, followed by a

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Table 1. Elemental Compositions and Formulas of Some Currently Used Common LiB Cathode Materials

	elemental composition (wt %)				
cathode material	Li	Co	Ni	Mn	reference
$LiCoO_2$	7.03	59.55			54
$LiMnO_4$	3.99			58.39	54
$LiNi_{0.3}Co_{0.3}Mn_{0.3}O_2$	2.52	7.01	6.76	6.81	55
$LiNi_{0.3}Co_{0.3}Mn_{0.3}O_2$	6.15	18.65	18.32	17.57	56
$LiNi_{0.5}Co_{0.2}$ $Mn_{0.3}O_2$	6.34	10.77	26.75	15.34	57
$LiNi_{0.6}Co_{0.2}$ $Mn_{0.2}O_2$	6.64	12.1	35.1	11.2	58
$LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$	7.36	6.28	46.01	5.40	59

challenging separation to pure compounds. Therefore, in addition to regeneration of pure compounds, repurposing in Li-ion battery black material (LiBBM) without separation of elements is a very attractive proposition. Co, Mn, and Ni oxides and sulfides are well known for their catalytic properties; especially, these compounds are excellent catalysts for oxidation reactions.[15,16] However, there are only limited attempts to use this waste material as catalysts, where it was used as a reduction catalyst for electrochemical oxygen reduction and carbonyl group reduction.[17−19] In addition, LiBBM presents a no-cost or minimal-cost prefabricated catalyst material where these metals are immobilized on a graphite carbon support.

Biofurans are a small class of furan aldehydes and alcohols derived from a cellulosic fraction of biomass, which is the most widely distributed natural polymeric material on earth.[20] In recent times, an increased effort has been made to utilize this cellulosic fraction of biomass and derived biofurans for the production of fuels and chemicals as renewable polymer industry feedstocks as alternatives to petroleum-based resources.[21−25] Acid-catalyzed depolymerization and dehydration of the cellulosic fraction are an extensively explored industrial route for the biofurans. Furfural or furan-2-aldehyde (FA) and 5-hydroxymethylfurfural (HMF) are the most common biofurans formed in the dehydration of pentoses and hexoses, respectively. The main drawback of these important furan aldehydes is their instability as these compounds polymerize to humins during storage as well as darken due to air oxidations. The widely adopted method to get around these problems is conversion of furan aldehydes to their more stable derivatives or other stable value-added chemicals.[26] As a promising biobased platform chemical, furfural can be further converted into a variety of C4 and C5 chemicals such as furfuryl alcohol, cyclopentanol, cyclopentanone, levulinic acid, γ-valerolactone, tetrahydrofuran, and succinic acid.[27] Similarly, C6 aldehyde HMF can be upgraded to value-added chemicals such as 2,5-furandicarboxylic acid (FDCA), 2,5-dimethylfuran, levulinic acid, formic acid, 5,5′-[oxybis(methylene)]bis[2-furaldehyde] (OBMF), and 2,5-diformyl furan (DFF).[28] These building block chemicals play important roles in multiple industries.

We have been studying the depolymerization of polysaccharides for renewable fuel applications and processing of biofurans to value-added feedstock chemicals for over a decade.[29−33] Our interest in the development of industrially feasible catalytic methods for processing renewable biomass feedstocks for sustainable polymer applications has led to the current work on the development of biofuran oxidation methods using a waste product, spent Li-ion battery black material, as a minimal-cost, reusable catalyst.[29,33−35]

EXPERIMENTAL SECTION

Materials and Instrumentation. Furan-2-aldehyde (FA), 5-hydroxymethylfurfural (HMF), 2,5-furandicarboxylic acid (FDCA), and 2,5-dimethylfuran (DMF) were purchased from Aldrich Chemical Co. 5,5′-[Oxybis(methylene)]bis[2-furaldehyde] (OBMF) and 5,5′-[oxybis(methylene)]bis[2-furancarboxylic acid] (OBFCA) were prepared using our previously described methods.[36,37] Thermogravimetric analysis (TGA) in air was carried out using a PerkinElmer Diamond High Temp 115 instrument (temperature: 25−800 °C; scanning rate: 20 °C/min). LiBBM samples were pyrolyzed in air by placing inside a 12 mm × 200 mm quartz tube horizontally inserted to a Lindberg Blue M Mini-Mite tube furnace (Thermo Scientific). LiBBM was powdered using a Bel-Art SP Scienceware Micro-Mill II Grinder. A Scios 2 Duel Beam by Thermo Fisher Scientific and FEI Quanta 400 ESEM instrument were used for scanning electron microscopy (SEM). X-ray photoelectron spectroscopy (XPS) was performed using a PerkinElmer PHI 5600 XPS instrument with excitation by Al-Kα (1586.6 eV) or Mg-Kα (1253.6 eV) X-rays. All high-pressure reactions under oxygen atmospheres were carried out using a Parr Instrument Co. reactor with a 50 mL 4720 stainless-steel pressure vessel, 4838 reactor temperature controller, and pressure gauge and without stirring. Reaction products were analyzed using an Agilent Technologies 1220 Infinity II series HPLC with a C-18 column (4.6 × 150 mm, Luna 5 micron, C18-2,100A) and a UV detector at 275 nm and 35 °C with a flow rate of 0.8 mL/min. Furfural and 5-hydroxymethylfurfural oxidation products were analyzed using isocratic elution with a mobile phase of 20 mM KH_2PO_4 buffer:acetonitrile (95:5) mixture. 5,5′-[Oxybis(methylene)]bis[2-furaldehyde] (OBMF) oxidation products were analyzed using isocratic elution with a mobile phase of 20 mM KH_2PO_4 buffer:acetonitrile (80:20) mixture.

Figure 1. Preparation of the LiBBM-600 catalyst from a spent DELL 1525 laptop battery (87 Wh, 11.1 V).

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Preparation of the LiBBM-600 Catalyst. A spent DELL 1525 laptop battery (87 Wh, 11.1 V) was discharged by complete immersion in a 10% aqueous sodium chloride solution at room temperature for 5 days. The casing was opened to collect nine 18,650 Li-ion cells, these cells were dismantled, and the black anode coating on copper foil and the black cathode coating on aluminum foil were collected and air-dried for 2 days to give 45.67 g of combined Li-ion battery black electrode (LiBBM) material (Figure 1). TGA of LiBBM showed that the complete removal of binders and residual electrolytes is possible by heating above 600 °C in air (Figure S1). Therefore, a 10.00 g sample of LiBBM was pyrolyzed at 600 °C in two batches using a 12 mm × 200 mm quartz tube horizontally inserted to a Lindberg Blue M Mini-Mite tube furnace for 30 min in air. Then, this sample was cooled to room temperature, ground in a laboratory mill, sieved through mesh size 25 to give a fine black powder, stored in an air-tight bottle until use, and named as LiBBM-600 (8.34 g). The LiBBM-600 catalyst was characterized using SEM, XPS, and powder X-ray analysis, and these spectrographs are shown in Figures 2–4.

General Procedure for Oxidation of Biofurans Using the LiBBM-600 Catalyst under an Oxygen Atmosphere. Three biofurans, furan-2-aldehyde (FA), 5-hydroxymethyl furfural (HMF), and 5,5′-[oxybis(methylene)]bis[2-furaldehyde] (OBMF), were tested in the oxidation experiments. A mixture of biofuran (0.50 mmol), LiBBM-600 catalyst (5–10% w/w), and 3.00 mL of 0.10 M aqueous sodium carbonate was prepared in the 50 mL Parr reactor. The reactor was closed and flushed with oxygen three times to remove air, pressurized to 1.24 MPa (180 psi), heated to the desired temperature, and maintained at this temperature using a 4838 reactor temperature controller. Then, the reactor was cooled to room temperature and diluted to 10.00 mL with deionized water. The contents were transferred into a centrifuge tube and centrifuged at 1700*g* for 15 min to remove the catalyst. The clear supernatant was analyzed using HPLC after filtering through a 0.22 μm hydrophobic microfilter, and products were identified by comparison of retention times with authentic samples. The amount of product was determined by a standard addition method. The reaction conditions, catalyst loading, conversion (%), and product yield (%) in LiBBM-600-catalyzed oxidation of furan-2-aldehyde (FA), 5-hydroxymethyl furfural (HMF), and 5,5′-[oxybis(methylene)]bis[2-furaldehyde] (OBMF) are shown in Tables 2–4, respectively. Conversion (%) and product yield (%) were calculated using eqs 1 and 2:

$$\text{conversion}(\%) = \frac{\text{mol of biofuran used} - \text{mol of biofuran unreacted}}{\text{mol of biofuran used}} \times 100\% \quad (1)$$

$$\text{product yield}(\%) = \frac{\text{mol of product detected}}{\text{mol of biofuran used}} \times 100\% \quad (2)$$

Recovery and Reuse of the LiBBM-600 Catalyst in the Oxidation of Furan-2-aldehyde (FA) to Furan-2-carboxylic Acid (FCA). Recovery and reuse of the LiBBM-600 catalyst in the oxidation of furan-2-aldehyde (FA) to furan-2-carboxylic acid (FCA) were tested for four catalytic cycles. A mixture of furan-2-aldehyde (0.50 mmol), LiBBM-600 catalyst (5% w/w), and 3.00 mL of 0.10 M aqueous sodium carbonate was prepared in the 50 mL Parr reactor. The reactor was closed and flushed with oxygen three times to remove air, pressurized to 1.24 MPa (180 psi), and heated to 140 °C for 5 h. Then, the reactor was cooled to room temperature and diluted to 10.00 mL with deionized water. The contents were processed as in previous experiment. The recovered catalyst was transferred back to the Parr reactor and used for the next cycle using the same procedure. The reuse of the catalyst was tested for four catalytic cycles, and the furan-2-carboxylic acid (FCA) yield in the reuse of the catalyst is shown in Figure 8.

RESULTS AND DISCUSSION

Preparation of the LiBBM-600 Catalyst and Characterization. The LiBBM-600 catalyst was prepared by pyrolysis of combined black anode and cathode coatings on copper and aluminum foils collected from 18,650 cells from a spent DELL 1525 laptop battery. A sample of LiBBM was first subjected to

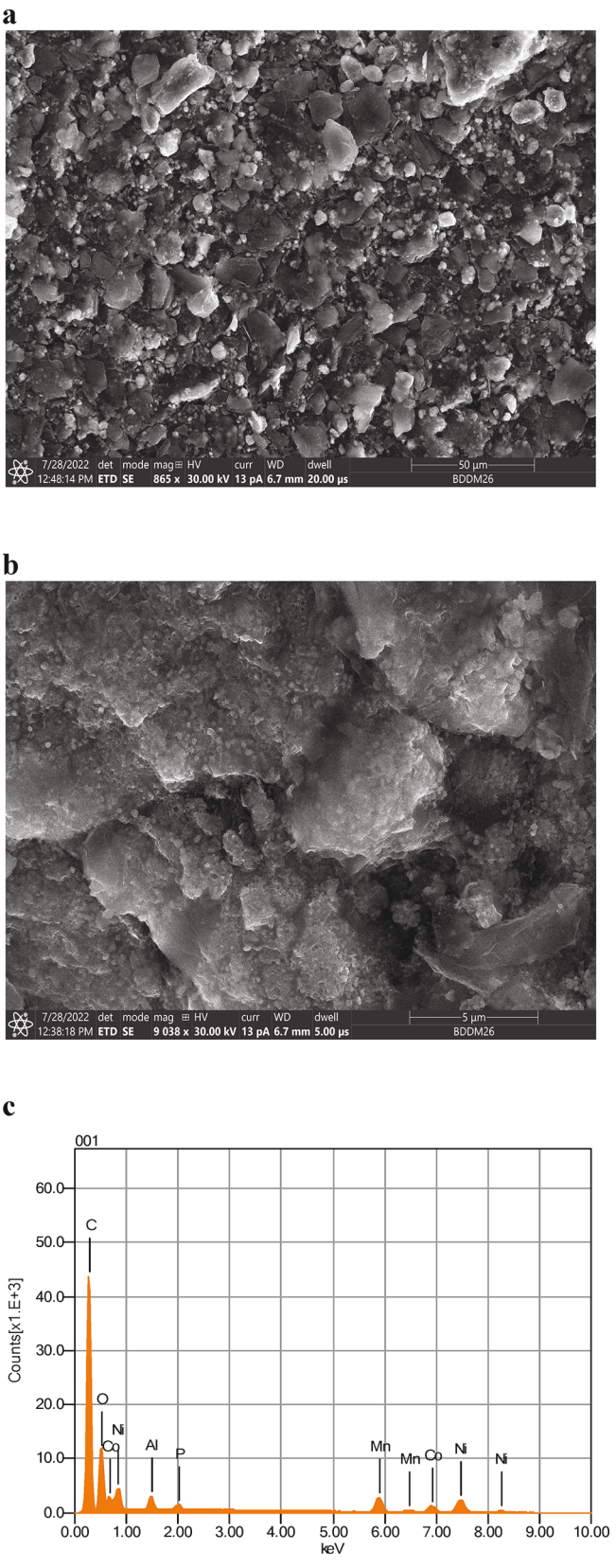

Figure 2. High-resolution scanning electron microscopy (SEM) images, with magnifications of (a) ×865 and (b) ×9038, and (c) energy-dispersive X-ray spectroscopy (EDX) spectra of LiBBM-600.

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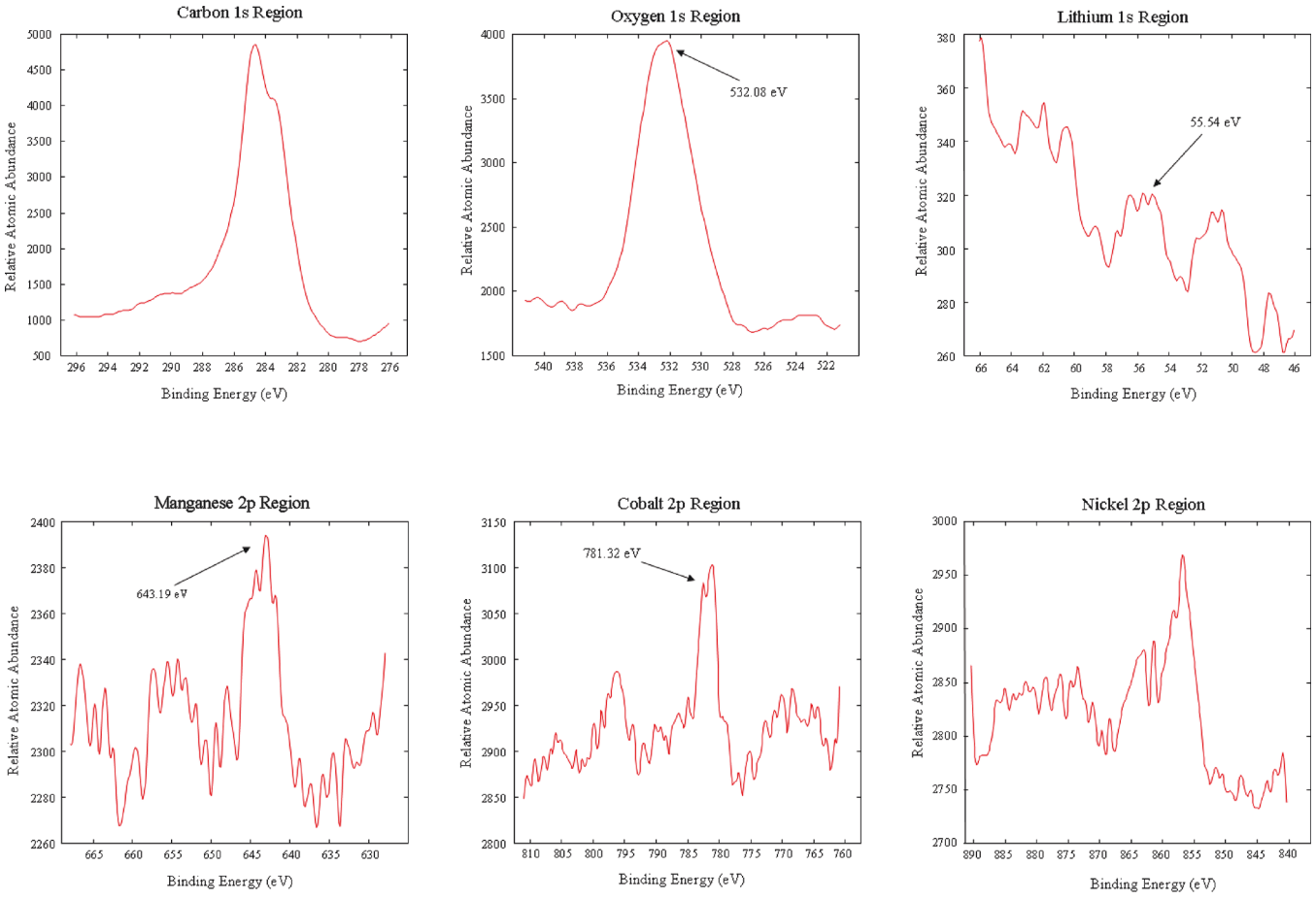

Element	Atomic Concentration (%)
C	70.98
O	21.10
Li	6.14
Mn	0.35
Co	0.99
Ni	0.45

Figure 3. X-ray photoelectron spectroscopy (XPS) analysis of LiBBM-600.

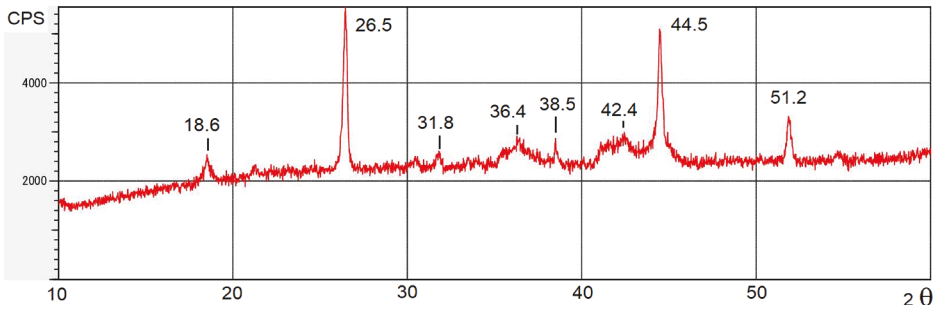

Figure 4. Powder X-ray analysis of LiBBM-600.

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Table 2. Reaction Conditions, Catalyst Loading, Conversion (%), and FCA Yield (%) in LiBBM-600-Catalyzed Oxidation of Furan-2-Aldehyde (FA) to Furan-2-Carboxylic Acid (FCA)

entry	reaction conditions and catalyst	conversion (%)	FCA yield (%)
1	120 °C, 2 h, 1.24 MPa O_2, 10% (w/w)	42	25
2	140 °C, 14 h, 1.24 MPa O_2, 10% (w/w)	100	45
3	140 °C, 5 h, 1.24 MPa O_2, 5% (w/w)	100	97

Table 3. Reaction Conditions, Catalyst Loading, Conversion (%), and Yield (%) in LiBBM-600-Catalyzed Oxidation of 5-Hydroxymethyl Furfural (HMF) to 2,5-Diformyl Furan (DFF), 5-Hydroxymethyl Furan-2-carboxylic Acid (HMFCA), 5-Formyl Furan-2-carboxylic Acid (FFCA), and 2,5-Furan Dicarboxylic Acid (FDCA)

			yield (%)			
entry	reaction conditions and catalyst	conversion (%)	DFF	HMFCA	FFCA	FDCA
1	120 °C, 2 h, 1.24 MPa O_2, 10% (w/w)	42	2	3	28	5
2	120 °C, 24 h, 1.24 MPa O_2, 10% (w/w)	100		25	19	51
3	140 °C, 4 h, 1.24 MPa O_2, 10% (w/w)	100		7	1	87

Table 4. Reaction Conditions, Catalyst Loading, Conversion (%), and Yield (%) in LiBBM-600-Catalyzed Oxidation of 5,5′-[Oxybis(methylene)]bis[2-furaldehyde] (OBMF) to 5,5′-[Oxybis(methylene)]-2-formyl-2′-furancarboxylic acid] (OBFFC) and 5,5′-[Oxybis(methylene)]bis[2-furancarboxylic acid] (OBFCA)

			yield (%)	
entry	reaction conditions and catalyst	conversion (%)	OBFFC	OBFCA
1	120 °C, 5 h, 1.24 MPa O_2, 10% (w/w)	100	41	47
2	140 °C, 15 h, 1.24 MPa O_2, 10% (w/w)	100	10	82

thermogravimetric analysis to determine the pyrolysis temperature, and this TGA profile is included in the Supporting Information (Figure S1). The TGA curve shows an approximately 24% weight loss at 600 °C, and the weight remains practically constant beyond 600 °C. This result was interpreted as the loss of binders like carboxymethyl cellulose and styrene butadiene copolymer as well as residual liquid electrolytes from LiBBM at ∼600 °C in air. Therefore, 600 °C was selected as the optimum pyrolysis temperature for preparative scale experiments. During the catalyst preparation, pyrolysis of 10.00 g of LiBBM at 600 °C for 30 min resulted in 8.34 g of LiBBM-600 due to loss of binders and residual electrolytes.

Two high-resolution scanning electron microscopy (SEM) images with magnifications of (a) ×865 and (b) ×9038 are shown in Figure 2. The magnification ×865 image shows 5−10 μm-sized, irregularly shaped, mixed graphite carbon particles with heterogeneous dispersion of metallic and/or metal oxide particles. This is likely due to the fact that we have collected and combined black electrode coatings from the cathode and anode of the spent battery. The higher-magnification ×9038 image in Figure 2b shows fine details of <1 μm-sized metallic and/or metal oxide catalyst clusters dispersed over the graphite carbon particles. The energy-dispersive X-ray spectroscopy (EDX) analyses show peaks for elements C, O, Ni, Mn, Co, Al, and P. The expected Li is not detected as EDX is not sensitive to Li. The Al present may be due to a contamination from aluminum foil used in the cathode, and P is likely from the residual electrolyte. Surface concentrations of active elements in LIBBM-600 were determined using X-ray photoelectron spectroscopy (XPS) as this material is used as a heterogeneous catalyst, and this result is shown in Figure 3. The peaks expected for C, O, Li, Ni, Mn, and Co were detected with XPS.[38] Elemental analysis shows a significantly high Li atom concentration of 6.14% and a Ni:Co:Mn ratio of 0.45:0.99:0.35; confirming the presence of a lithium nickel manganese cobalt oxide ($LiNi_xMn_yCo_zO_2$)-type cathode material in 18,650 cells of the spent DELL 1525 laptop battery. Powder X-ray analysis of LiBBM-600 is shown in Figure 4. This X-ray diffraction pattern is comparable to other typical LiB cathode material X-ray chromatograms reported in the literature.[39] The strong peaks at 2θ = 26.5° and 44.5° are due to graphite carbon.[19] The smaller peaks at 2θ = 18.6°, 31.8°, 36.4°, and 38.5° are assigned to $LiMO_2$-type oxides where M = Co, Ni, or Mn.[19,40,41] In addition, the peaks in the region of 42.4° are assigned to MnO.[19]

Oxidation of Biofurans Using the LiBBM-600 Catalyst under an Oxygen Atmosphere. Three biomass-derived furan aldehydes, furan-2-aldehyde (FA), 5-hydroxymethyl furfural (HMF), and 5,5′-[oxybis(methylene)]bis[2-furaldehyde] (OBMF), were tested to evaluate the activity of the LiBBM-600 catalyst as in Figures 5−7. The reaction

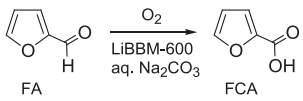

Figure 5. LiBBM-600-catalyzed oxidation of furan-2-aldehyde (FA) to furan-2-carboxylic acid (FCA).

conditions, catalyst loading, conversion (%), and product yield (%) in these experiments are shown in Tables 2−4, respectively. Oxidation of furan-2-aldehyde (FA) produced furan-2-carboxylic acid (FCA) as the only product as in Figure 5, and the reaction carried out with 10% (w/w) catalyst loading at 120 °C for 2 h under 1.2 MPa O_2 showed only a 42% conversion and a 25% yield of furan-2-carboxylic acid (FCA) (Table 2, entry 1). Increasing the reaction time to 14 h improved conversion to 100%; however, it only produced 45% yield of the desired carboxylic acid product, most probably due to polymerization or degradation of the product under 120 °C and 14 h reaction conditions as shown in entry 2 in Table 2. Next, the catalyst loading was reduced to 5% (w/w), although the temperature was increased to 140 °C. Under these conditions, the highest FCA yield of 97% could be achieved after 5 h with complete conversion of starting aldehyde as shown in entry 3 in Table 2.

The bifunctional 5-hydroxymethyl furfural (HMF) can result in four products, 2,5-diformyl furan (DFF), 5-hydroxymethyl furan-2-carboxylic acid (HMFCA), 5-formyl furan-2-carboxylic acid (FFCA), and 2,5-furan dicarboxylic acid (FDCA), as shown in Figure 6. Initial experiments with reaction conditions

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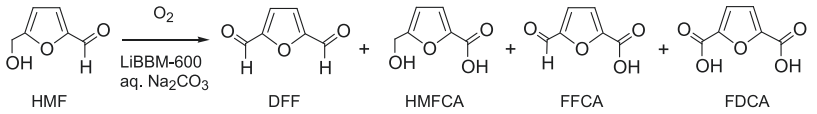

Figure 6. LiBBM-600-catalyzed oxidation of 5-hydroxymethyl furfural (HMF) to 2,5-diformyl furan (DFF), 5-hydroxymethyl furan-2-carboxylic acid (HMFCA), 5-formyl furan-2-carboxylic acid (FFCA), and 2,5-furan dicarboxylic acid (FDCA).

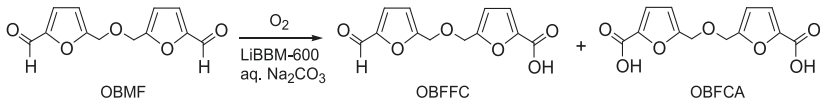

Figure 7. LiBBM-600-catalyzed oxidation of 5,5′-[oxybis(methylene)]bis[2-furaldehyde] (OBMF) to 5,5′-[oxybis(methylene)]-2-formyl-2′-furancarboxylic acid] (OBFFC) and 5,5′-[oxybis(methylene)]bis[2-furancarboxylic acid] (OBFCA).

of 10% (w/w) catalyst loading, 120 °C, 2 h, and 1.24 MPa O_2 resulted in poor 42% conversion of 5-hydroxymethyl furfural (HMF), yielding all four possible products and only 5% yield of the most desired FDCA (Table 3). Controlled oxidation of HMF has received considerable attention in recent years as its oxidation products are key new generation feedstocks. A variety of oxidants are effective in controlled oxidation of HMF to DFF including NaOCl when used with Mn-salen catalysts and Ru/γ-alumina with O_2 as the oxidant.[42,43] DFF and FDCA are attractive monomers for the synthesis of renewable polymeric materials.[42,44] The dialdehyde DFF has been used in the preparation of resins with urea as well as Schiff base polymers with diamines.[45,46] However, the diacid is probably the most important derivative of HMF and, in recent years, FDCA has been used as a monomer in the preparation of polyesters using a range of polymerization techniques including the use of dicarboxylic acid dichloride-diol method, trans-esterification, and interfacial polycondensation.[47−50] In addition, FDCA is listed in a 2004 US Department of Energy National Renewable Energy Laboratory (NREL) report as one of the 12 building blocks that can be subsequently converted to a variety of high-value biobased chemicals and polymeric materials.[51] The reaction conditions of 140 °C, 4 h, 1.24 MPa O_2, and 10% (w/w) catalyst loading produced the highest yield of FDCA of 87% (entry 3, Table 3), and this yield is comparable to the best yields reported for the oxidation of HMF to FDCA using Ni-, Co-, or Mn-based catalysts using air or oxygen as the primary oxidant.[52,53]

As the third biofuran, we have tested the oxidation of 5,5′-[oxybis(methylene)]bis[2-furaldehyde] (OBMF) and this HMF dimer can result in two products, 5,5′-[oxybis-(methylene)]-2-formyl-2′-furancarboxylic acid] (OBFFC) and 5,5′-[oxybis(methylene)]bis[2-furancarboxylic acid] (OBFCA), under oxidation as shown in Figure 7. In our earlier work, we have prepared the starting material 5,5′-[oxybis(methylene)]bis[2-furaldehyde] (OBMF) directly from D-fructose using Dowex 50 W X8 as the catalyst. The experiment with reaction conditions of 10% catalyst, 120 °C, 5 h, and 1.2 MPa O_2 resulted in a mixture of diacid (OBFFC) and aldehyde acid (OBFFC) in 47 and 41% yields, respectively, as shown in entry 1 in Table 4. Nevertheless, a longer reaction time of 15 h at 140 °C improved the diacid yield, producing OBFCA in 87% yield.

Furthermore, previously, we have shown that OBFCA can be oxidized to 5,5′-[oxybis(methylene)]bis[2-furancarboxylic acid] (OBFCA) in excellent 98% yield using a PtO_2/C catalyst and oxygen gas at 1.0 atm. as the oxidant, where the diacid was used to prepare renewable carbon-based polyesters. However, the use of LiB waste material as a replacement for expensive catalysts like PtO_2 in the preparation of stable value-added products with many applications is a significant cost reduction in industrial production.

Recovery and Reuse of the LiBBM-600 Catalyst in the Oxidation of Furan-2-aldehyde (FA) to Furan-2-carboxylic Acid (FCA). The recyclability of the LiBBM-600 catalyst was studied by reusing the catalyst in four cycles, where the catalyst was separated and recovered by centrifugation. Furan-2-carboxylic acid (FCA) yields during the reuse of the LiBBM-600 catalyst for the oxidation of furan-2-aldehyde (FA) and in four reaction cycles are shown in Figure 8. The FA conversion

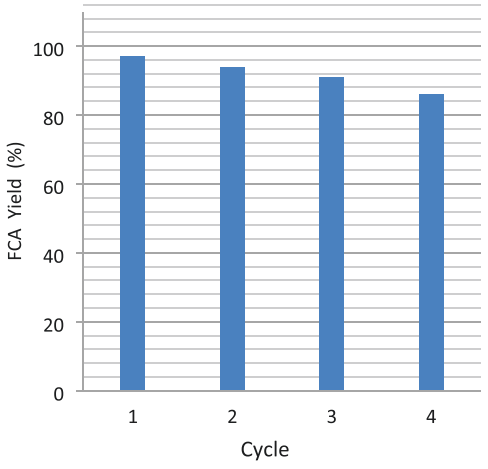

Figure 8. Furan-2-carboxylic acid (FCA) yields during the reuse of the LiBBM-600 catalyst for the oxidation of furan-2-aldehyde in four reaction cycles.

to FCA remained 100% throughout the recycling experiment; however, FCA yields showed small and gradual decreases while using up to four cycles. Reuse experiments carried out in a larger scale (×6) also showed similar results.

The catalyst weight remains practically the same in reuse experiments. Furthermore, the recycling experiment was repeated under the experimental conditions in entry 1 in Table 2 (120 °C, 2 h, 1.24 MPa O_2, and 10% (w/w)) as well using furan-2-aldehyde as the substrate. In this reuse experiment, conversion remained at 42% in all reuse cycles; however, the furan-2-carboxylic acid (FCA) yield decreased as follows: 25, 22, 22, and 20% in four cycles. This steady decrease in FCA yields may be due to declining catalytic activity as a result of an accumulation of the oxidation products on the catalytic surface; therefore, the loss in catalytic activity may be restored after pyrolyzing the catalyst again after a number of cycles. In addition, we have investigated the

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leaching of metal ions to the aqueous phase by evaporation of the aqueous phase and then thermogravimetric analysis of the residue obtained in the experiment described under entry 3 in Table 2. The white residue from evaporation completely burned at temperatures above 600 °C, leaving no metal oxide residues, indicating that no metal leaching occurs during the LiBBM-600-catalyzed oxidation of biofurans and the catalyst is stable under the reaction conditions used.

CONCLUSIONS

We have shown that an excellent biofuran oxidation catalyst can be prepared by pyrolysis of the DELL 1525 laptop Li-ion battery combined cathode and anode black material in air at 600 °C. The new catalyst was shown to contain lithium nickel manganese cobalt oxide ($LiNi_xMn_yCo_zO_2$) on carbon and with a Ni:Co:Mn ratio of 0.45:0.99:0.35 by SEM, XRF, and X-ray crystallography analysis. The activity of the new catalytic material was evaluated by oxidation of three biomass-derived furan aldehydes, furan-2-aldehyde (FA), 5-hydroxymethyl furfural (HMF), and 5,5′-[oxybis(methylene)]bis[2-furaldehyde] (OBMF), under a 1.24 MPa oxygen atmosphere, in 0.10 M aqueous sodium carbonate medium at 120−140 °C, and by using 5−10% (w/w) catalyst loading. In the oxidation of furan-2-aldehyde (FA) to furan-2-carboxylic acid (FCA), the highest yield (97%) was obtained with 5% (w/w) catalyst loading, 140 °C, 5 h, and 1.24 MPa O_2 reaction. The oxidation of 5-hydroxymethyl furfural at lower temperature and under the reaction conditions of a shorter reaction time of 120 °C, 2 h, 1.24 MPa O_2, and 10% (w/w) catalyst resulted in a poor conversion of 42%, yielding a mixture of four oxidation products, 2,5-diformyl furan (DFF), 5-hydroxymethyl furan-2-carboxylic acid (HMFCA), 5-formyl furan-2-carboxylic acid (FFCA), and 2,5-furan dicarboxylic acid (FDCA). However, increasing the temperature to 140 °C and a longer reaction time of 4 h resulted in the most valued dicarboxylic acid product 2,5-furan dicarboxylic acid (FDCA) in 87% yield. Furthermore, the catalyst is shown to be effective in oxidation of the HMF dimer: 5,5′-[oxybis(methylene)]bis[2-furaldehyde] (OBMF) to the corresponding dicarboxylic acid 5,5′-[oxybis(methylene)]bis[2-furancarboxylic acid] (OBFCA) in 82% yield as well. The new catalyst showed only a small loss of the catalytic activity after four cycles, and this used catalyst may be rejuvenated by repyrolysis at 600 °C after several cycles. In conclusion, we have presented a new use for the spent Li-ion battery waste electrode material rich in Li, Ni, Co, and Mn as a prefabricated catalyst for the preparation of value-added feedstock chemicals and sustainable monomers from biofurans.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.2c03346.

Figure S1: thermogravimetric analysis of LiBBM (PDF)

AUTHOR INFORMATION

Corresponding Author

Ananda S. Amarasekara − *Department of Chemistry and Center for Energy and Environmental Sustainability, Prairie View A&M University, Prairie View, Texas 77446, United States;* orcid.org/0000-0002-2052-3947; Phone: +1 936 261 3107; Email: asamarasekara@pvamu.edu; Fax: +1 936 261 3117

Authors

Sofia K. Pinzon − *Department of Electrical and Computer Engineering, Florida International University, Miami, Florida 33174, United States*

Tommy Rockward − *Los Alamos National Laboratory, Los Alamos, New Mexico 87544, United States*

Hashini N. K. Herath − *Department of Chemistry, Prairie View A&M University, Prairie View, Texas 77446, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acssuschemeng.2c03346

Notes

The authors declare no competing financial interest.

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