The synthesis of $\text{Li}(\text{Co-Mn-Ni})\text{O}_2$ cathode material from spent-Li ion batteries and the proof of its functionality in aqueous lithium and sodium electrolytic solutions

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HIGHLIGHTS

- $\text{Li}(\text{Co-Mn-Ni})\text{O}_2$ cathode material was recycled from spent Li-ion batteries.
- Better sodium than lithium cycling stability was evidenced in an aqueous solution.
- A high Na-storage capacity of 93 mA h g^{-1} was achieved at a scan rate of 0.8 C .
- Differences between lithium and sodium charge storage capability were discussed.

GRAPHICAL ABSTRACT

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ABSTRACT

Several spent Li-ion batteries were manually dismantled and their components were uncurled and separated. The chemical composition of each battery's component was determined by atomic absorption spectroscopy. Among several ways to separate cathode material from the collector, the alkali dissolution treatment was selected as the most effective one. After both complete separation and acid leaching steps, the co-precipitation method, followed by a thermal treatment (700°C or 850°C), was used to resynthesize cathode material $\text{LiCo}_{0.415}\text{Mn}_{0.435}\text{Ni}_{0.15}\text{O}_2$. Its structure and morphology were characterized by XRD, Raman spectroscopy and SEM-EDS methods. The electrochemical behavior of recycled cathode materials was examined by cyclic voltammetry and chronopotentiometry in both LiNO_3 and NaNO_3 aqueous solutions. High sodium storage capacity, amounting to 93 mAh g^{-1} , was measured galvanostatically at a relatively high current of $\sim 100 \text{ mA g}^{-1}$. Initial lithium intercalation capacity of $\sim 64 \text{ mAh g}^{-1}$, was determined potentiodynamically at very high scan rate of 20 mV s^{-1} ($\sim 40 \text{ C}$). Somewhat lower initial capacity of $\sim 30 \text{ mAh g}^{-1}$, but much lower capacity fade on cycling, was found for sodium intercalation at the same scan rate. The differences in the Li and Na charge storage capability were explained in terms of ion rearrangement during charging/discharging processes.

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1. Introduction

In a Li-ion battery, the anode is lithiated graphitic carbon bonded to the Cu current collector, while the cathode is typically a transition metal oxide usually of layered structure, able to intercalate lithium ions, attached to the Al current collector. The electrolyte is lithium salt dissolved in an organic solvent (LiPF₆ in ethylene carbonate-dimethyl carbonate is usually used). LiCoO₂ is the first used cathodic material in commercial Li-ion batteries. Due to the toxicity and high cost of cobalt, LiCoO₂ has been replaced, firstly, by LiMn₂O₄ and then by the layered LiNi_xCo_yMn_{1-x-y}O₂ ($x > 0$, $y < 1$) which now dominates in almost all commercial Li-ion batteries. Olivine LiFePO₄ is also developed as a cathodic material [1].

Since the lithium-ion batteries contain metals (Cu, Al...) and metal oxides (Li, Co, Mn, Ni oxide) as well as organic solvents, they can be harmful if their components are released into environment. Therefore, the development of recycling technology is very important in order to avoid the environmental contamination [2,3]. The need for the progress of the recycling technology resulted in a strong international regulations including EU Directive 2006/66/EC [4]. Numerous studies have aimed at recycling the spent Li ion batteries in order to recover the valuable metals (Co, Li, Cu, Mn, Ni...) as much as possible, trying to find the fast, economical and simple approach. The various recycling methods have been developed and proposed. Their review can be found in several papers [5–8]. Besides, there are also studies on recycling the spent materials of Li-batteries (usually cathodic material) with the purpose of their renewal.

The first question in the recovering of cathode material is how to separate it from the Al current collector. Several ways were proposed: burning of carbon and binder in the temperature range 500–900 °C [9], dissolving the poly(vinylidene fluoride) (PVDF) binder in the N-methyl-pyrrolidone (NMP) or dimethylformamide (DMF) [10,11] and dissolving the Al current collector in the alkaline solution [12,13]. The efficiency of these processes ranged from 80% to 100%, depending on the process applied and operating conditions [11]. The next step is the leaching of the metallic species from the separated cathode material. The acid leaching step is common for all recycling processes. Namely, metal species are usually leached by HCl, HNO₃ or H₂SO₄ with the addition of H₂O₂ as reducing agent. After both separation and acid leaching steps, the conventional processes including solvent extraction, chemical precipitation, ion exchange, crystallization or electrocatalysis process are usually performed to recover the valuable metals in a form of various compounds [5–7].

The recovery of active cathode material, and its re-functionalization have been intensified in recent years. The re-synthesis of cathode materials including LiCoO₂ [9,13–17], LiCo_{1-x}Mn_xO₂ [18], Li(Co–Mn–Ni)O₂ [10,19–22] and even LiFePO₄ [23], were reported. Lee et al. [9] used the recycling process involving mechanical, thermal, hydrometallurgical and sol-gel route (amorphous citrate precursor process), to recover Co and Li and synthesize LiCoO₂ from leach liquor. The obtained material displayed a good initial charge and discharge capacities (165 mAh g⁻¹ and 154 mAh g⁻¹) which, after 30 cycles, kept 90% of initial capacity. The separation and renovation of LiCoO₂ cathode material from spent cathode can be carried out simultaneously, avoiding striping procedure, by a hydrothermal method [14]. The specific capacity of the recovered material amounted to 144 mAh g⁻¹, with the capacity retention of 92% after 40 charging/discharging cycles. By using the recovered compounds of Li and Co, Nan et al. [13] also obtained the LiCoO₂ with a high specific capacity of 136 mAh g⁻¹ at 0.2 C. Recently, Nie et al. [17] developed a green and efficient recycling process of batteries with LiCoO₂ cathode. They regenerated LiCoO₂

by solid state synthesis with Li₂CO₃ whereas obtained electrochemical properties of LiCoO₂, regenerated at 900 °C, are close to those of commercial LiCoO₂. Namely, the discharge capacity amounted to 152 mAh g⁻¹, with a very high capacity retention during 80 cycles.

The re-synthesis of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ from spent Li-ion batteries has also been reported [10,19–23]. Li et al. [19] described a recycling process including separation of electrode materials by ultrasonic treatment, acid leaching, iron removal, and precipitation of Co, Ni Mn and Li, to re-synthesize LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ which displayed specific capacity of 161.2 mAh g⁻¹ (0.3 C) and a fair cyclic stability during 20 cycles. By a combination of dismantling, ball milling, leaching and impurities removal [20], LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ powder was prepared from purified leaching liquor, via coprecipitation followed by heat treatment. The regenerated material displayed an excellent charge (175.4 mAh g⁻¹) and discharge (152.7 mAh g⁻¹) capacity at rate of 0.2 C, with fair capacity retention (94% after 50 cycles). Recently, Zhang et al. [10] also synthesized LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂, from the separated cathodic material, by solid state reaction method. The capacity of the obtained material was also high, amounting to 201 mAh g⁻¹ on charging and 155 mAh g⁻¹ on discharging.

The recovery of LiPF₆ from organic electrolyte solution is rarely considered [24]. Aqueous rechargeable Li-ion batteries are intensely investigated in order to replace organic electrolytes with the low-cost and environmental friendly aqueous electrolytes. Therefore, the use of recycled material obtained from classic Li-ion batteries in aqueous ones provide an excellent close-loop procedure interesting from the environmental and economical viewpoint.

This study relates to the investigation of recycled cathode material of spent Li-ion batteries in aqueous solutions. To the best of our knowledge, the evaluation of the re-synthesized cathode material in aqueous electrolytes has not been reported till now. The research proceeded in two stages. The first stage was focused on the detailed analysis of the chemical composition of battery components and separating the cathodic material by using the economic payable recycling procedure. The producers do not provide the detailed chemical content of the batteries, so the analysis of the batteries is desirable in order to perform properly the recycling processes. Although it reveals the manufacturers' secrets, the analysis is justified by the need to protect the environment from the pollution caused by exponentially growing production of Li-ion batteries. The second part is related to the structural testing of recovered material and its electrochemical examination in aqueous electrolyte solutions. The cyclic stability was examined in both LiNO₃aq and NaNO₃aq and correlated to the structural parameters of the layered oxide.

2. Experimental part

The spent batteries of the same brand, capacity and voltage (900 mAh, 3.7 V), were subjected to the recycling procedure as shown in Fig. 1. The details of each step were described separately.

2.1. The dismantling of the spent Li-ion batteries

After removing the plastic parts, the five spent Li-ion batteries were cut on the lathe and the metal containers were removed with pliers. Then the cathode, anode and separator were separated. The mass of each component was measured. The difference of the masses of unopened batteries and the mass of the components was attributed to the loss of the electrolyte solvent. The mass of the separator was measured after the residue of cathode and anode materials were removed by soaking into the NMP.

Fig. 1. Schematic presentation of the recycling procedure.

2.2. Procedures of separating the current collectors from the electrode materials

2.2.1. The separation of the cathode material from the Al collector

The separation of the cathode material from the Al collector was performed in three ways (the following paragraphs a–c), with the purpose of finding the procedure providing the minimum loss of cathode material.

- The removal of Al by alkali dissolution was performed by boiling in 5 M NaOH for 30 min. The residue was filtered, washed with hot water till pH = 7 was reached, dried at 110 °C and then annealed at 600 °C in air. The annealing served to remove carbon and PVDF binder by combustion. The filtrate containing NaAlO₂ can be used repeatedly until saturation, and can be used in zeolite or aluminium production.
- The separation of the cathode material from the Al collector by NMP is based on the dissolution of the PVDF binder in this organic solvent. This procedure is performed in an ultrasonic bath for 60 min. The obtained suspension of cathode material, carbon and Al scraps was filtered. The surplus of NMP was removed by vaporization at 250 °C for 3 h. Carbon was burned by heating at 600 °C in air. The Al scraps were separated by sieving through a set of 120–45 µm sieves.
- The separation of the cathode material from the Al collector by annealing at 600 °C in air atmosphere, is based on the combustion of both binder and carbon additive, making the cathode material eligible for mechanical stripping from the Al collector. It should be noted that this method of separation suffers from the fact that the material agglutinates to the current collector.

2.2.2. The separation of the anode material from the Cu collector

The Cu collector was separated from the anode material by immersion into water under ultrasonification. The residue of Li in anode material was negligible, and thus it was not recycled. The mass of copper was measured after washing and drying.

2.3. The chemical analysis of cathode material and battery crust

Since the efficiency of the separation of cathode material from the current collector was the highest in the case of alkali

dissolution, the cathode material obtained by this procedure was selected for the determination of its chemical composition. For its dissolution, 3 mL 30% H₂O₂ in 100 ml of 2 M HNO₃ heated at 70 °C was found to be optimal. 6.262 g of the cathodic material was dissolved in 250 ml of acidic solvent. The 0.0478 g of crust was dissolved in 28 ml of HCl/HNO₃ v/v 3:1, for 60 min. After complete dissolution, the solution was transferred to a volumetric flask of 100 ml volume and bidistilled water was added to the mark.

The determination of the chemical composition of the container, Al and Cu collectors and cathode material, using these acidic solutions, was performed by the FAAS GBC SensaAA DUAL A and GFAAS GBC SensaAA DUAL G.

2.4. The resynthesis of cathode material and its characterization

70 ml 10 M NaOH was added to the 250 ml of 2 M HNO₃ solution in which 6.262 g of cathode material was dissolved till pH = 14 was attained. During precipitate formation under magnetic stirring, the color of the solution changed from red to dark blue one. The precipitate was separated by centrifugation, when the solution was discolored. After washing with the alcohol, the precipitate was mixed with 2.37 g Li₂CO₃. Upon thorough grinding the mixture was divided in two parts, one was annealed at 700 °C and the other one at 850 °C. The obtained products were labeled as re-LiCMNO@700 and re-LiCMNO@850. For comparison, the pristine LiCo_{0.415}Mn_{0.435}Ni_{0.15}O₂ was prepared with the same co-precipitation method, starting from the pure Co(NO₃)₂ × 6H₂O, Mn(NO₃)₂ × 6H₂O, Ni(NO₃)₂ × 6H₂O and Li₂CO₃, followed by heating treatment at 700 °C. The pristine NaCo_{0.415}Mn_{0.435}Ni_{0.15}O₂ was obtained by Li–Na electrochemical exchange of the pristine LiCo_{0.415}Mn_{0.435}Ni_{0.15}O₂ in 6 M NaNO₃. These samples were labeled as LiCMNO@700 and NaCMNO@700.

The characterization of the cathode material obtained by recycling was performed by X-ray diffractometry (XRD) of powder, Raman spectrometry, SEM/TEM and electrochemical methods. The diffractograms were recorded using Philips 1050 diffractometer with CuKα_{1,2} radiation in a 2θ range 10–80°, in steps 0.02°, and counting time of 14 s per step. The Raman spectra were obtained on the Thermo Scientific DXR Raman Microscope (λ = 532 nm, 9.4 mW). After the potentiodynamic cycling up to different potentials, the electrodes were placed on an X-Y motorized sample stage and the laser beam was focused on the sample at 50× objective magnification. The morphology was observed by SEM Model JSM-6610LV. For TEM analyses, a probe aberration-corrected JEM-ARM200CF equipped with the JEOL Centurio 100 mm² EDXS detectors was employed. The electrochemical characteristics were examined by cyclic voltammetry (CV), chronopotentiometry (CP) and Electrochemical Impedance using Gamry PCI4/300 Potentiostat/Galvanostat. The three-electrode cell was used, with the Pt electrode as the counter and the saturated calomel electrode as the reference electrode. The working electrode prepared by mixing the recycled cathode material, carbon black (Vulcan) and PVDF in a 85:10:5 weight ratio homogenized in NMP in an ultrasonic bath. A droplet of the homogenized slurry was transferred to the glassy carbon support and heated at 120 °C under vacuum. The electrolytes were 6 M LiNO_{3aq} and 6 M NaNO_{3aq}. The impedance diagrams were measured in the 100 kHz to 0.01 Hz range (5 mV AC amplitude), after different charge/discharge cycles, at potentials of cathodic and anodic maxima of CVs.

3. Results and discussion

3.1. The mass fraction of individual components upon battery dismantling

The average mass of components of the spent lithium-ion battery is shown in Table 1. On the average, 30.46% of battery mass belongs to cathode material, 19.3% to anode material, 19% to container and 10.12% to separator and other components. Having in mind that container, current collectors and cathode material bear ~62% of total battery mass, these components are selected to be worthy of recycling.

3.2. The yield of cathode material separation by various methods

The fast and effective separation of cathode material from the Al current collector is a very hard task due to the strong adhesion and small Al thickness. The percent of the active cathode material lost in various separation ways is presented in Table 2.

If we compare the presented results, we can conclude that the separation by alkali dissolution procedure is mostly effective (100%). The effectivity of this process was confirmed by both chemical analysis and EDS of cathodic powder, as we show later below. Although the NMP was reported as very effective [11,25], especially under strongly controlled ultrasonic treatment [11], in our study only 68% of cathode material was successfully separated by this method. This procedure needs expensive solvent and power consumption which makes it uneconomic. Further to this, this procedure is difficult feasible. It is difficult to observe the separation of phases during filtration, and the sieve set is necessary to separate cathode powder from Al collector scraps. The simplest procedure is that consisting in annealing at 600 °C in air, but the obtained results show the lowest yield caused by cathode material agglutination.

3.3. The analysis of chemical composition of individual components of spent batteries

3.3.1. The container and the cathode current collector

The results of chemical analysis of the container and cathode current collector are presented in Table 3. The targeting of alloying elements for chemical analysis is based on the commercial alloys data [26,27]. One can see that both the container and the current collector are dominantly Al alloys in which Fe and Mn present the dominating alloying elements. By varying the content of alloying elements, it is possible to achieve better tensile strength, plasticity, ability of multiple bending and higher melting point.

3.3.2. The anode current collector

The chemical analysis of the anode collector confirmed that it is dominantly composed of copper, and contains the traces of Al (0.09%), Mn (0.05%) and Zn (0.02%) as the alloying elements. The choice of targeted elements is incited by the literature data [28,29].

Table 1
Chemical composition of lithium-ion battery.

Component	Mass (g)
Battery	20.16 ± 0.65
Container	3.85 ± 0.12
Copper	1.55 ± 0.05
Aluminium	0.97 ± 0.03
Carbon (total)	4.86 ± 0.16
Cathode material	6.14 ± 0.20
Loss (PEC/DEC)	0.73 ± 0.02
separator + plastics	2.04 ± 0.07

Table 2

Efficiency of the separation of cathode material from the current collector.

Procedure	Cathode material loss (%)
Alkali dissolution with NaOH	~0,00
Separation with NMP	32,46
Separation by annealing at 600 °C	43,21

Table 3

The chemical composition of crust and cathode current collector.

Element	Container, %	Cathode current collector, %
Al	Up to 100	Up to 100
Cr	0.003	<0.001
Cu	0.155	0.101
Mn	1.010	0.031
Zn	0.030	0.010
Fe	0.900	1.000
Ti	0.170	0.160
Mo	0.040	<0.001

3.3.3. The cathode material

The results of chemical analysis of cathode material dissolved in acidic solution (upon its separation from the current collector, carbon black additive and polymeric glue, as described in Experimental section) is shown in Table 4. The main metals in the cathodic material were Li, Co, Mn and Ni. Aluminium was not detected, which confirms a high efficiency of the alkaline dissolution separation technique.

3.4. The behavior of recycled cathodic material

3.4.1. The chemical composition of recycled cathodic material

The chemical composition of the recovered cathodic material is shown in Table 4. The molar atomic ratio of Li, Co, Mn, and Ni is 1:0.415:0.435:0.15 and it differs somewhat from the conventional $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ composition. The obtained composition is similar to that reported in Ref. [30] ($\text{LiNi}_{0.1}\text{Co}_{0.4}\text{Mn}_{0.5}\text{O}_2$) and in Ref. [31] ($\text{Li}_{1.049}\text{Ni}_{0.161}\text{Mn}_{0.466}\text{Co}_{0.325}\text{O}_2$). Assuming that Ni, Mn and Co are in the 2+, 3+ and 4+ oxidation states, respectively, the experimentally determined composition does not look to be charge balanced between cations and anions. The explanation can be found in the existence of metal site vacancies [31]. By calculating the vacancy content in the way applied in Ref. [31], the formula unit of recycled sample can be expressed as $\text{Li}_{0.935\pm0.13}\text{Ni}_{0.140}\text{Mn}_{0.406}\text{Co}_{0.388}\text{O}_2$.

3.4.2. Structural characterization of resynthesized cathodic material

The structure of resynthesized cathodic materials re-LiCMNO@700 and re-LiCMNO@850 was determined by XRD (Fig. 2a). The position of the well-defined reflections, corresponding to (003), (101), (102), (104), (105) and (110), shows that recovered materials belong to the layered structure type α -NaFeO₂ with the space group of R-3m [32]. The split of the (006)/(102) and (108)/(110) pairs, which is characteristic of the highly ordered

Table 4

Chemical composition of the leach solution of cathode material.

M	C, mol/l	Molar fraction in the cathode material
Li	—	1
Co	0.0053	0.415
Mn	0.0056	0.435
Ni	0.0019	0.150

Fig. 2. XRD patterns (a) and deconvoluted Raman spectra (b, c) of resynthesized $\text{Li}(\text{Co-Mn-Ni})\text{O}_2$ cathode materials.

hexagonal structure, is not pronounced in the re-LiCMNO@700 due to the small size of crystallite at low temperature, which causes the broadening of diffraction lines. The increase of the temperature to 850 °C resulted in the splitting of the mentioned doublet (Fig. 2a) indicating a better crystallization of the sample. On the other hand, a rather high value of $R = (I_{006} + I_{102})/I_{101}$ [33] was found, indicating a low ordering degree of the hexagonal structure developed at 850 °C. Additionally, the low $I(003)/I(104)$ intensity for both samples, amounting to 0.99 for LCMNO@700 and 0.85 for LCMNO@850, was found. Both are lower than 1.2 which reveals the position exchange between lithium and transition metal ions known as “cation mixing” [33,34].

The Li–Ni mixing is usually observed for these structure [34] due to the smaller difference between the radius of Li^+ ion (0.690 Å) and radius of Ni^{2+} ion (0.76 Å) than the one between radii of ions Li^+ and Co^{3+} (0.545 Å) or Li^+ and Mn^{4+} (0.530). Although the Li–Ni mixing is generally observed for the high amount of the Ni in the $\text{Li}(\text{Co-Ni-Mn})\text{O}_2$ material, it can also occur in the composition with the low Ni content. The sample calcined at lower temperature exhibits a lower degree of Li–Ni mixing which, as an indicator of the layered structural arrangement, is contradictory to the splitting of diffraction doublets. Still, it can be concluded that the highly ordered layered structure cannot be obtained or recovered through the presented pathway of recycling. One may conclude that the level of impurity, being negligible one, cannot influence the electrochemical properties of the observed samples.

The structure of the recycled materials was further examined by Raman Spectroscopy (Fig. 2b, c). The Raman bands positioned at $\sim 490\text{ cm}^{-1}$ and $\sim 587\text{ cm}^{-1}$ can be assigned to the M–O stretching (A_{1g} mode) and O–M–O bending modes (E_{1g} mode) within MO_2 layers, respectively. Actually, these bands comprise from the bands

of Ni–O (at $442\text{--}449\text{ cm}^{-1}$, 554 cm^{-1}), Mn–O (594 cm^{-1}) and Co–O (486 and 596 cm^{-1}) vibrations within a hexagonal lattice that belongs to the same space symmetry group (R-3m) [35]. The additional band, positioned at $\sim 650\text{ cm}^{-1}$, can also be deconvoluted in Raman spectra of both samples, which can be attributed to the local distortion caused by structural symmetry decreasing [36]. The difference in the E_{1g}/A_{1g} intensity ratio may be due to different degree in the Li–Ni mixing. The E_{1g}/A_{1g} intensity ratio decreases with the increase of temperature. This is the result of the E_{1g} intensity decrease (Fig. 2b, c) upon heating. Since the degree of Li–Ni mixing is higher in re-LiCMNO@850 than in re-LiCMNO@700, the lower fraction of Ni^{2+} ions can be found in the intra slab layers of re-LiCMNO@850. This can cause the lower intensity of E_{1g} band in Raman spectrum of re-LiCMNO@850 compared to the one measured for re-LiCMNO@700.

3.4.3. Morphological properties

Figs. 3 and 4 illustrate representative SEM and TEM micrographs of re-LiCMNO@700 (Fig. 3) and re-LiCMNO@850 (Fig. 4) samples. One can see that the morphology changes with the increase of the temperature. At lower temperature (Fig. 3a), the particles have rice shape. Interestingly, with the temperature rise, they changed in shape from rice to belt one. Actually, the morphology of re-LiCMNO@850 includes both agglomerated rice-shaped particles, with the average diameter of 150 nm and belt-like particles, with the average thickness of 300 nm (Fig. 4a–c).

In addition to the results of AAS analysis (section 3.4.1), chemical composition of the samples was checked by the EDS (Figs. 3b and 4d). The presence of Al is not detected in the examined samples, which confirms the successful separation of the spent cathodic material from the current collector. This shows clearly the

Fig. 3. SEM micrographs (a), EDS spectrum (b) and TEM (c, d) of re-LiCMNO@700.

advantage of the alkaline dissolution technique in comparison to the NMP dissolution performed by Yang et al. [25]. Besides Ni, Co and Mn, Na atom is also detected in the examined samples. Sodium originates from the re-synthesis route. The characteristic reflections of standard $\text{Na}[\text{Co}-\text{Mn}-\text{Ni}]\text{O}_2$ (ICSD#184734) are different from those presented for recycled samples in Fig. 2a. Therefore, sodium atoms are probably adsorbed at the oxide surface. When temperature increased to 850 °C, the amount of sodium was reduced (liberating in the form of Na_2O), with the preservation of the layered structure.

A closer insight into the morphology of both samples was achieved by means of TEM. The re-LiCMNO@700 specimen revealed slightly lower crystallinity and smaller crystallite's size (Fig. 3c and d) compared to that of re-LiCMNO@850 specimen (Fig. 4e and f), which is well seen in the SAED patterns shown in the insets. In the re-LiCMNO@700 specimen, additional fractions that were not stable under the electron beam were observed. In the re-LiCMNO@850 specimen, the belt-like crystallites observed in the SEM images were not present due to their large sizes.

3.4.4. Electrochemical behavior of recycled cathode material in aqueous electrolytic solutions

The electrochemical behavior of the recovered material was examined in the $\text{LiNO}_{3\text{aq}}$ and $\text{NaNO}_{3\text{aq}}$ in order to find out its functionality as the cathode material in aqueous rechargeable batteries.

3.4.4.1. Lithium storage behavior. The lithium intercalation behavior of the obtained powdered samples was examined in $\text{LiNO}_{3\text{aq}}$ using CV as the fast method. The redox peaks of the first

cyclic voltammogram, which are positioned at $\sim 0.69/0.75$ V (vs. SCE) for re-LiCMNO@700 (Fig. 5a) and $\sim 0.68/0.9$ V vs. SCE for re-LiCMNO@850 (Fig. 5b), correspond to the lithium deintercalation/intercalation reactions. These typical pair of redox peaks is well-documented in the literature for $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, in both aqueous [37] and organic electrolytes [38–44]. It was ascribed to the $\text{Ni}^{2+}/\text{Ni}^{4+}$ redox process occurring via Ni^{3+} intermediate. The redox peaks which originate from the $\text{Co}^{3+}/\text{Co}^{4+}$ redox couple [43] can be identified close to the cut-off voltage (Fig. 5a). However, the potential was cut at 1.3 V vs. SCE to avoid the parallel reactions of water electrolysis.

The peak-to-peak potential separation, as the main parameter of electrochemical reversibility, is lower for re-LiCMNO@700 (~ 56 mV at 20 mV s^{-1}) than that for re-LiCMNO@850 (220 mV at 20 mV s^{-1}). It indicated a faster charge transfer of the material annealed at 700 °C, which may be the consequence of the lower degree of cation mixing in the re-LiCMNO@700 structure. Additionally, rice-shaped particles have shorter path for Li^+ ions and electrons than the belt-like particles, which enables better lithiation/delithiation kinetics of re-LiCMNO@700. Furthermore, the peak potential separation of re-LiCMNO@700 is very small for such high applied currents. It is much lower than that measured for the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ in both aqueous [37] and organic electrolytes [42–44], which suggests smaller polarization effects in re-synthesized electrode in comparison to the reported materials.

The coulombic capacity was measured in this study from the potentiodynamic data, when the charging rate is commensurable to the sweep rate. In the literature, capacity was determined often from galvanostatic curves, where the charging rate was reported as the fraction of C units (1C = current strength needed to charge one

Fig. 4. SEM micrographs (a–c), EDS spectrum (d) and TEM (e, f) of re-LiCMNO@850.

gram of electrode material within 3600 s). For a rough comparison of the capacities obtained by these two methods, the conversion of sweep rate to the galvanostatic charging rate is required, however, due to the differences in working principles, this conversion may be only tentative. To calculate which galvanostatic charging rate corresponds most closely to the potentiodynamic sweep rate, the following formula was used: (galvanostatic charging rate) $\approx$ (potentiodynamic sweep rate) $\times$ (3600/ ΔV), where ΔV is relatively invariant potential window required for either complete charging of discharged material, or for complete discharging of charged material [45].

By integrating the area under CV curves shown in Fig. 5a and b, the coulombic capacitance of recycled materials, expressed in mAh g⁻¹, can be evaluated (Fig. 5c). The initial discharge (lithiation) capacity was found to be 64.7 mAh g⁻¹ and 52.7 mAh g⁻¹ for re-LNCMO@700 and re-LNCMO@850, respectively. The full utilization of capacity is not possible due to the avoiding of water

decomposition. Nevertheless, the measured values are pretty high for aqueous electrolytes, especially if it is taken into account that the polarization rate of 20 mV s⁻¹ corresponds to a very high galvanostatic rate of ~ 40 C. However, the capacity decreases during cycling which is a common property of the layered structure, particularly in aqueous solutions. The increase of the potential distance between redox peaks, during consecutive cycling, indicates the gradual decrease of Li intercalation/deintercalation reactions reversibility. The capacity remains only $\sim 26\%$ of its initial value at the end of 50th cycle (Fig. S1).

A complete deintercalation of lithium from Li(Ni–Co–Mn)O₂ structure corresponds to the phase change from the “O₃” phase (comprised of three MO₂ sheets in the unit cell along c-axis) to “O₁” phase (including one MO₂ layer in the unit cell along c-axis) [34,46]. Since this phase transformation starts when more than 0.7 Li is extracted (approximately at the potential of 4.6 V vs. Li⁺/Li) [46], the difficulty of conversion of O₁ to O₃ phase, during the reverse

Fig. 5. Cyclic voltammograms of re-LiCMNO@700 (a) and re-LiCMNO@850 (b) during initial ten cycles, measured in an aqueous solution of LiNO₃, at scanning rate of 20 mV s⁻¹; The corresponding lithiation and delithiation specific capacity (c).

(lithiation) process cannot be regarded as responsible for the capacity fade. Various factors, including transition metal ion dissolution, phase transformation of electrode material, water decomposition etc., have been reported as responsible for capacity fade [37]. Since the trend of change of CV's during the cycling is similar for both samples, it can be concluded that the capacity fade originates exclusively from the irreversible structural changes caused by oxidation/reduction processes. The factors affecting the capacity fade of recovered samples, upon cycling in aqueous electrolytes, are discussed below more thoroughly. A possibility that the capacity decreases due to the intercalation of water, or some reactions with water, may be discarded. Namely, the similar capacity decrease of re-LCMNO materials has also been obtained in organic Li-salt solution confirming that the irreversible capacity loss may be the consequence of the structural changes during lithiation/delithiation. A doping of these recycled structures with foreign ions [20] can be a good strategy in preventing structural changes and consequential capacity fade.

3.4.4.2. Sodium storage behavior. The re-LiCMNO@700 was also examined in NaNO₃aq. The electrochemical Li–Na exchange in the obtained layered structure was successfully achieved (Fig. 6a). Such obtained NaCMNO@700 was found to be capable of intercalating/deintercalating Na⁺ ions without loss in the charge storage capacity (Fig. 6b), as evidenced by the overlapping of CV curves during consecutive cycling. The CV curve of re-NaCMNO@700, consists of main cathodic peak, which originates from the insertion of Na⁺ ions, and three anodic peaks, which correspond to sodium ion deinsertion. Still, redox peaks at 5 mV s⁻¹ (Fig. 6c) indicate that both redox processes occur via several steps. The redox pairs are not well defined probably due to the faster sodiation than

desodiation process. Interestingly, CVs of some other intercalate structures such as Na_{1.2}V₃O₈ [47], NaFePO₄/C [48], NaFe_{0.95}V_{0.05}PO₄/C [49], measured in NaNO₃aq, also show faster sodiation than desodiation. Anodic redox peaks of re-NaCMNO@700 are positioned at -0.027, 0.198 and 1.078 V (vs. SCE) while the cathodic peaks of re-NaCMNO@700 are positioned at -0.719, -0.323 and 0.858 V (vs. SCE), at a scan rate of 5 mV s⁻¹. Having in mind the CVs of pristine NaCMNO@700 measured in the NaNO₃ (Supp. data), one can conclude that two anodic peaks positioned at -0.027 and 0.198 V vs. SCE correspond to the main cathodic peak positioned at -0.323 V vs. SCE. The splitting of the anodic peak, matching to one cathodic peak, is the typical behavior of olivine NaFePO₄ [48,49] and is also recognized in the sodiated layered oxide. The small desodiation peak which corresponds to the first cathodic peak at -0.719 V vs. SCE (Fig. 6c) is not clearly visible, as in the pristine NaCMNO@700, due to the capacitive response and the prevailing cathodic current in this potential region.

The redox peaks of re-NaCMNO@700 are generally in accordance with those of NaNi_{0.33}Mn_{0.33}Co_{0.33}O₂ layered phase [50], measured in organic electrolyte, and are attributed to the Ni⁴⁺/Ni²⁺ redox couple. Additional redox peaks, which may be observed in Fig. 3 of ref [50] at the potentials of 3.19/3.09 V vs. Na⁺/Na (~0.70/0.55 V) and 3.46/3.37 V vs. Na⁺/Na (~0.97/0.88 V vs. SCE), with the scan rate of 1 mV s⁻¹, cannot be seen in Fig. 6, due to their overlapping by a high capacitance baseline current.

Tarascon et al. [50] suggested that deintercalation of sodium from NaNi_{0.33}Mn_{0.33}Co_{0.33}O₂ occurs through the sequence phases O₃ → O₁ → P₃ → P₁ (O₃ stands for Na in octahedral geometry with three MO₂ layers per unit cell, O₁-Na in octahedral geometry with one single MO₂ layer, P₃-Na in prismatic geometry with three MO₂ layers, P₁-Na in prismatic geometry with one single MO₂ layer)

Fig. 6. CVs of re-LiCo_{0.415}Mn_{0.435}Ni_{0.15}O₂, measured in an aqueous solution of NaNO₃ at scan rate of 20 mV s⁻¹ from 1st–10th (a) and 10th–20th cycles (b), demonstrating the transition to NaCo_{0.415}Mn_{0.435}Ni_{0.15}O₂; CV of re-NaCo_{0.415}Mn_{0.435}Ni_{0.15}O₂, measured in an aqueous NaNO₃ solution at 5 mV s⁻¹ (c); The cyclic stability of re-NaCMNO@700 in NaNO₃ at 20 mV s⁻¹ (d).

which differ by a specific gliding of the oxide layers. Following this study, the first two peaks visible in the anodic sweep (Fig. 6c) correspond to the O₃ → O₁ phase transition where the second peak indicates the presence of only O₁ phase. The third anodic peak represents the formation of P1 phase. Although the NaCMNO@700 undergoes various structural transformations upon reversible sodium cycling, there happens no change in the capacity during cycling (Fig. 6d), which indicates a good structural stability of the sodiated layered structure. Unlike the corresponding lithiation/delithiation process, the above mentioned phase transformations are completely reversible.

The capacity of re-NaCMNO@700, obtained by the integration of CVs shown in Fig. 7a, in function of the scan rate, is presented in Fig. 7b. At the first glance, the capacitance is very small amounting to ~30 mAh g⁻¹. Still, it was measured at a very high scan rate of 20 mV s⁻¹ which corresponds to the very high galvanostatic rate of approximately ~30 C. The initial sodium storage capacity is approximately two times lower than the lithium one. Such results were expected since NaNi_{1/3}Co_{1/3}Mn_{1/3}O₂ is capable to intercalate 0.5 mol of sodium [50] (120 mAh g⁻¹), while LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ can intercalate 1 mol of lithium (278 mAh g⁻¹) [51]. However, the stability of the sodiation capacity in comparison to the lithiation one, during cycling, was significantly better. The capacity of re-NaCMNO@700 remains almost constant over 50 cycles.

In order to find out the sodium storage capacity at lower currents, the chronopotentiometric curves (Fig. 7c) were measured. The value of charge (desodiation) capacity amounted to

78.5 mAh g⁻¹ and 93.02 mAh g⁻¹ while the discharge (sodiation) capacity was found to be 100.6 mAh g⁻¹ and 120.6 mAh g⁻¹ at 1 C and 0.8 C, respectively (1C = 120 mA g⁻¹). The differences between the charge and discharge capacity do not originate from the low coulombic efficiency of material but from the small hydrogen participation, caused by the decomposition of water at the vertex cathodic potential. One can say that the sodium storage capacity of NaCo_{0.415}Mn_{0.435}Ni_{0.15}O₂ is close to the maximum value of NaNi_{1/3}Co_{1/3}Mn_{1/3}O₂, at the current density of 100 mA g⁻¹.

The resynthesized layered oxide has a lower initial capacity for sodiation than for lithiation. However, as shown, the charge storage stability is much better during cycling in sodium than in lithium salt solution. It makes the recycled material more promising for sodium than for lithium aqueous rechargeable batteries. Therefore, the low-ordered hexagonal layered structure can be very important in developing sodium aqueous rechargeable batteries. The possibility that such promising materials can be obtained from the spent Li-ion batteries presents an additional advantage. This study opens directions towards development of novel host layered structural compounds, as cathodic Na-storage materials, as well as challenges for promoting recycling processes with the aim of improving electrochemical performances.

In order to understand more thoroughly the charge storage behavior during stable reversible cycling in sodium salt solution, the kinetic analysis of CV's measured at various scan rates, was performed (Supplementary data). By plotting the logI–logv dependence (Fig. S2a), the exponent b is determined at various

Fig. 7. Cyclic voltammograms at various scan rates (a), corresponding specific capacities (b) and charge/discharge curves (c) of re-NaCMNO@700, measured in the aqueous NaNO₃ solution.

fixed potentials (Fig. S2b). These values were found to be in the range 0.7–0.9 indicating the domination of surface-controlled redox process over the diffusion-controlled process. It is caused by the nanoparticulate nature of the NaCMNO@700 electrode material which provides the occurring of redox reactions at or near the surface (extrinsic pseudocapacity [49,52,53]). The diffusion of Na⁺ ions during intercalation/deintercalation into/from crystallographic sites of oxide is a fast process which is probably facilitated by the open layered structure [54]. The pseudocapacitance behavior [49,55] is favorable for high current capability of some electrode materials making these structures attractive as well.

Different potential positions, between Na and Li redox peaks, indicate that intercalated Na⁺ and Li⁺ ions occupy different crystallographic positions, which can cause different cation order in re-LiCMNO and re-NaCMNO. In order to get better insight into local structural surrounding of oxygen atoms, the Raman spectra of cycled electrodes were measured. The corresponding changes in the Raman active modes are shown and discussed in Supplementary data. Since they are in a good agreement with the literature [56–61], these published data helped to deduce the conclusions. The different cation redistribution in Li and Na-layered oxides was evidenced. It may be a key factor for differences in the cyclic stability of these two materials in corresponding aqueous solutions. According to the XRD, small fraction of lithium occupies nickel positions due to the fact that Ni²⁺ (0.69 Å) and Li⁺

(0.76 Å) have closer ionic radii. However, the mixing of Na⁺ ion (1.02 Å) with Ni⁺ ion is probably avoided due to the big difference in their radii. Accordingly, different Na⁺ structural sites from the Li⁺ ones during the Li–Na exchange of re-LiCMNO can be expected. The absence of the cation mixing in re-NaCMNO structure could be the reason of significantly better stability during the sodium than during the lithium cycling. Nickel atoms, which occupy the Li⁺ sites in the layered structure, don't block the sodium insertion. This will be discussed in detail below, in order to shed the light on the lithium and sodium storage mechanism in layered structures.

For comparison, fast CV measurements of the pure LiCMNO@700 are performed in both LiNO₃aq and NaNO₃aq. The shape of the LiCMNO@700 and NaCMNO@700 voltammetric response (Fig. S3) is the same as the one measured for corresponding recycled samples. The lithium discharge capacity was found to be ~82 mAh g⁻¹ (1st cycle) and ~58 mAh g⁻¹ (10th cycle) at 20 mV s⁻¹ while the corresponding sodium capacity amounted to ~30 mAh g⁻¹. Therefore, the capacity of re-LiCMNO@700 sample in LiNO₃ is somewhat lower than the one obtained from the pristine LiCMNO@700, while the capacity of re-NaCMNO is comparable with the pristine NaCMNO@700 one.

The electrochemical behavior of Li(Co–Mn–Ni)O₂ has been widely examined in the Li-containing organic electrolyte over the last 15 years which resulted in its commercialization, while the electrochemical behavior in an aqueous electrolytic solution is

studied to a lesser extent [37,62–69]. Table S1 (Supp. data) summarizes the comparative electrochemical characteristics of examined recycled and directly synthesized reported samples [37,63–68], in an aqueous solution. The corresponding discussion is also provided in Supp. data.

3.4.4.3. Impedance analysis. The Nyquist diagrams of re-LiCMNO@700 and re-NaCMNO@700 in LiNO_3 and NaNO_3 aqueous solutions, respectively, measured after different charge/discharge cycles, are shown in Fig. 8. High frequency intercept on the real axis in Nyquist plots (R_s), which is controlled by the ohmic electrolyte resistance, amounted to $\sim 1.9 \Omega$ and $\sim 1.5 \Omega$ in LiNO_3 and NaNO_3 , respectively. This is the consequence of the somewhat lower radius of hydrated ionic radius Na^+ (3.58 Å) than Li^+ (3.82 Å) [70] which results in the better mobility of hydrated Na^+ ions versus Li^+ ones.

The Nyquist plots of re-LiCMNO@700 in LiNO_3 , measured after the first cycle, for both anodic and cathodic maximum, consist of depressed high frequency semicircle related to the charge-transfer process and straight line, in the low frequency region, which refers to the Li^+ diffusion through the bulk of the material. Although the semicircle is depressed, its radius, corresponding to the charge-transfer resistance (R_{ct}), can be estimated to the value of $\sim 1.8 \Omega$. It indicates a very fast charge transfer of lithium redox reactions of recycled $\text{Li}(\text{Co-Mn-Ni})\text{O}_2$ which corresponds to a high degree of reversibility based on the small peak potential separation. The R_{ct} is much lower than those measured for $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ in an organic electrolyte [22,38,39,43,44] due to a lower activation

energy for the interfacial lithium-ion transfer [71] and the absence of the solid electrolyte interface resistance in the aqueous electrolyte [38,72]. However, the impedance diagrams of re-LiCMNO@700 in LiNO_3 are changing with the cycling (Fig. 8a and b) which is in accordance with the CV measurements. After the 10th cycle, the R_{ct} increased up to $\sim 45 \Omega$ for anodic and $\sim 55 \Omega$ for cathodic scan. The low frequency resistances also increased. After the 30th and especially the 50th cycle, the large change in the impedance diagram can be seen, at both potentials. Namely, the charge transfer semicircle spreads over the whole measured frequency region indicating very sluggish kinetics of lithiation/delithiation reactions. This is in agreement with the decrease of CV redox response and the increase of the peak potential separation during cycling. Accordingly, a very small lithium storage capacity was measured after 50 cycles.

The Nyquist diagrams of re-NaCMNO@700 in NaNO_3 , measured after the first cycle of sodiation/desodiation at the potentials of maxima of CVs, exhibit higher resistances than those corresponding to the lithiation/delithiation reactions. As a result, the lower sodium than lithium storage capacity was found. However, these Nyquist plots remain almost unchanged during 50 cycles (Fig. 8c), thus confirming the stable reversible behavior of sodiation/desodiation reactions of layered structure in an aqueous electrolytic solution.

3.4.4.4. Factor affecting the cycling stability of re-cathode material in aqueous solutions. The $\text{Li}(\text{Co-Ni-Mn})\text{O}_2$ layered oxides are made

Fig. 8. The Nyquist plots of re-LiCMNO@700 (a, b) and re-NaCMNO@700 (c) in aerated LiNO_3 and NaNO_3 aqueous electrolyte, respectively, at the potentials of cathodic and anodic maxima of CVs. Insets show the enlarged high-frequency regions.

up of alternating $[\text{MO}_2]^-$ ($M = \text{Co}, \text{Ni}, \text{Mn}$) close-packed oxygen and lithium layers. Li^+ ions occupy 3a sites, the transition metal ions ($M = \text{Mn}, \text{Co}$ and Ni) are randomly placed on 3b sites and O ions are on 6c sites. The predominant oxidation states of Ni, Co and Mn in the compound are 2+, 3+ and 4+, respectively [42,43,73]. The redox processes of Co, Mn and Ni-containing layered structure, which occur during charging/discharging processes, within the potential interval of water stability, correspond to the $\text{Ni}^{2+} \leftrightarrow \text{Ni}^{4+}$ couple. Mn^{4+} ions do not participate in those redox processes [74] while the redox pair of $\text{Co}^{3+}/\text{Co}^{4+}$ in the $\text{Li}(\text{Co}-\text{Ni}-\text{Mn})\text{O}_2$ structure is active at higher potentials (~ 1.55 – 1.65 V vs. NHE) [42]. The cation mixing, involving Li–Ni exchange is encountered in these layered structures and is known to degrade the electrochemical performances [42,75]. As shown by X-ray diffraction, the re-LiCMNO possesses a certain fraction of cation disorder involving the presence of nickel in the 3a Li sites as well as the existence of the fraction of lithium in the 3b Ni sites. It can be concluded that the Li–Ni mixing in the recycled sample controls the coulombic capacity of material and its stability during cycling. Namely, when the re-LiCMNO was subjected to the anodic polarization in LiNO_3 , Li^+ ions, in both the transition metals and lithium planes, were deintercalated from the Li-rich solid phase. This process is accompanied by oxidation of Ni^{2+} to Ni^{4+} . The changes in the oxygen vibrational modes, caused by anodic polarization (Supp. data), indicate that the Li^+ ions can be deintercalated from both TM and lithium layers. As also shown by Raman Spectroscopy, supported by the literature data [56–61], the migrations of the nickel metal ions to octahedral sites vacated by Li^+ ions, can occur upon anodic polarization, which is kinetically allowed [76,77]. In this way, the nickel ions occupy the original MO_6 octahedral sites. Therefore, the returning of the Li^+ ions, upon cathodic polarization, to their emptied sites can be blocked by the nickel ions. This impedance can cause the capacity fade during cycling. Further, the migration of Li^+ ions from the inter- to the intra-slab positions during anodic polarization [78] cannot be excluded, which also disturbs the kinetics of lithiation/delithiation reactions.

In the case of sodiation, the cation mixing doesn't present the problem since there is no tendency of sodium and nickel ions to be replaced, due to their high difference in the radii. Therefore, the stable capacity of the $\text{Na}(\text{Co}-\text{Mn}-\text{Ni})\text{O}_2$ structure during cycling in sodium salt solutions was measured. Actually, during initial cycling of re-LiCMNO in $\text{NaNO}_{3\text{aq}}$, Li^+ ions leave the structure while the Na^+ ions enter into it. By observing the changes in Raman spectra of both Li and Na cycled electrodes (Fig. S4), we can conclude that some nickel ions can occupy the positions emptied from the Li^+ ions during the initial exchange of Li–Na in LiCMNO. However, the occupancy of these sites by nickel ions, doesn't present the problem for the insertion of sodium ions since they have no tendency to occupy the positions of Ni ions. The discharging induced changes in the Raman modes indicate the different Li and Na ordering in the structure. Different positions of Li and Na ions in the structure were confirmed by different potentials of their redox peaks. Since the nickel metal ions don't disturb the kinetic of sodiation/desodiation reactions and lithium is emptied, the stability in the charge storage of re-NaCMNO during potential cycling was observed. It can be said that re-NaCMNO, obtained by electrochemical Li–Na exchange of re-LiCMNO, has a more ordered structure than its Li analogue. This is shown by the narrowing of the main A1g mode, sensitive to Na ordering [61], during the Na deintercalation. It is also confirmed by the similarity of measured CVs, for re-NaCMNO material (Fig. 6c), with those shown in Ref. [50], related to the well-defined hexagonal layered structure.

The differences in the structural behavior between re-LiCMNO and re-NaCMNO, during their cycling in $\text{LiNO}_{3\text{aq}}$ and $\text{NaNO}_{3\text{aq}}$, respectively, can be explained from another structural aspect. As

suggested by the literature data, the main problem for the instability of the layered structure during charging batteries (cathode delithiation) is the oxygen loss from the material at vertex voltage [76,34]. Here, the applied voltage is low to cause a significant release of oxygen [34,76,79]. However, some distortions in the oxygen bonding can occur at high applied potentials. It can be suggested that the charge compensation, caused by deintercalation of Li^+ ions, originates not only from the removal of electrons from nickel ions, but also from the O^{2-} species [74]. A deficit in Ni ions in the recovered material contributes to it. From the aspect of the capacity utilization, oxygen involved in the charge transfer can be desirable for materials with low amount of Ni, since low Ni content limits the charge storage. On the other hand, it can result in structural instability of material during cycling. The removal of electrons from oxygen atoms of re-LiCMNO, during delithiation in the potential of water stability, can make the oxygen-containing bonds in the MO_6 octahedral weaker and cause the structure instability. We believe that these effects reduce the blue-shift of the main M–O mode [80] during anodic polarization of oxide in LiNO_3 which can occur due to repulsion of oxygen layers upon removal of the intercalated ions. The presence of lithium ions or their vacancies in the MO_6 planes, instead of nickel ions, facilitates this structural collapse due to the lower charge density of lithium than one of oxidized nickel ion. Namely, the greater effective charge of nickel metal ions, especially in the delithiated state of oxide, in comparison to those for both lithium and sodium metal ions, prevents the structure from the collapse. This can be confirmed by the larger blue-shift of the main A1g mode during sodium against lithium discharging, which reveals the stronger M–O bonds in the desodiated oxide.

4. Conclusions

Several spent Li-ions batteries of the same type and capacity were subjected to the relatively simple, fast and environmental friendly process of recycling. It was shown that Al and Cu current collectors, together with cathodic material, bear $\sim 62\%$ of battery mass. Therefore, these components are selected as worthy of recycling. The chemical analysis reveals that both crust and Al-collector are, in fact, Al–Fe–Mn alloy while the Cu foil also contains the traces of other metals such as Al, Mn and Zn. The complete separation of spent cathodic material from the current collector was achieved by dissolving Al foil in an aqueous NaOH solution. This procedure provides i) the precipitate including the cathodic material which can be further subjected to various technological processes in recovering of individual precious metals ii) filtrate containing Al, in the form of Na-aluminate, which can serve for various applications. The co-precipitation method of dissolved metallic species, followed by both lithiation and thermal treatment, was used to renew the cathodic material $\text{LiCo}_{0.415}\text{Mn}_{0.435}\text{Ni}_{0.15}\text{O}_2$, from spent Li-ion batteries. The capacity of recovered (Co–Mn–Ni)-bearing oxide and its stability during cycling strongly depends on whether the Li or Na present in the material. In comparison to the initial lithium capacity (~ 64 mAh g^{-1}), a lower sodium capacity of layered oxide (~ 30 mAh g^{-1}) was measured. However, the cyclic stability was much better in $\text{NaNO}_{3\text{aq}}$ than in $\text{LiNO}_{3\text{aq}}$. The differences in capacity stability between the lithiated and the sodiated cathode material originate from the ion rearrangements during cycling process. On Li^+ extraction, nickel ions, in Li-layers positions, migrate into vacated Li^+ octahedral sites, in transition metal ion positions, thus blocking the return of deintercalated ions. On Na extraction, nickel ions don't have tendency to occupy emptied sodium ion sites which provides the undisturbed sodiation/desodiation process on repeated cycling.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2016.12.115>.

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