Generating Lithium Vacancies through Delithiation of $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ towards Bifunctional Electrocatalysts for Rechargeable Zinc-air Batteries

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ABSTRACT

Defects in the catalyst are considered to be important for generating the active sites for electrocatalytic reactions, due to the changed distribution of the charge density. In this work, Li vacancy defects are purposely created in a series of one-dimensional (1D) porous multi-shell $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ hollow fibers by a facile electrochemical lithium ion (Li^+) intercalation and extraction. The total Li vacancy concentrations are 0.52, 0.49, and 0.53 in one unit of delithiated $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ hollow fibers (De- $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$) for De- $\text{Li}(\text{Ni}_{0.20}\text{Co}_{0.60}\text{Mn}_{0.20})\text{O}_2$, De- $\text{Li}(\text{Ni}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33})\text{O}_2$, De- $\text{Li}(\text{Ni}_{0.65}\text{Co}_{0.25}\text{Mn}_{0.10})\text{O}_2$, respectively. When evaluated as oxygen electrocatalysts, the De- $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ shows the best performance with onset potential of ~ 1.46 V *vs.* reversible hydrogen electrode (RHE) outperforming IrO_2/C at 1 M KOH in OER and much improved onset potential of ~ 0.85 V *vs.* RHE than that of $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ (~ 0.71 V *vs.* RHE) at 0.1 M KOH in ORR. Density functional theory (DFT) calculations for the sample before and after delithiation certified that the delithiated samples have a significantly improved carrier concentration and electronic conductivity in the Co-*d* orbitals near the sites of Li vacancies. This results in enhanced H_2O (3.34 eV) and O_2 (2.75 eV) adsorption energies and thus greatly reduces the OER-ORR potential difference (ΔE) (0.17 V). A ZAB with the De- $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ as the air cathode was also assembled, which shows high efficiency and long-term stability. At a constant current rate of 5 mA cm^{-2} , the final charge and discharge potential is ~ 1.97 V and ~ 1.23 V after 441 h.

KEYWORDS: lithium vacancy; bifunctional oxygen electrocatalysts; delithiation; $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ hollow fiber; metal-air battery.

1. Introduction

Zn-air batteries (ZABs) with high theoretical energy density, low cost and high safety have been under intense scrutiny currently to meet demands for future electric vehicles and other energy-demanding devices. The electrocatalytic oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) are the heart of electrochemical energy conversion processes in ZABs. Due to their multi step proton-coupled electron transfer reaction pathways, those two oxygen

electrode reactions exhibit sluggish kinetics and require intensive energy to overcome the overpotential than their counter hydrogen electrode reactions in respective devices [1]. Accordingly, catalysts are necessary to lower the overpotentials for facilitating the reactions. However, the current active OER catalysts such as ruthenium (Ru) and iridium (Ir) oxides, and the ORR catalysts such as platinum (Pt) and its alloys are suffering from high cost and limited reserve to sustain large-scale commercial applications. More importantly, Ru and Ir oxides have low activity for the ORR, and Pt has only moderate activity for the OER [2]. Therefore, tremendous efforts have been devoted to developing alternative catalysts with low cost, superior durability and efficient bifunctional electrocatalytic activity for both OER and ORR. The bifunctional of OER and ORR is very important for metal-air batteries because only two electrodes (the metal is for anode and the bifunctional one is for air cathode) are required. Recently, binary and ternary transition-metal oxides, such as $\text{CoMn}_2\text{O}_4/\text{N-rGO}$ [3], (Ni, Co)/CNT nanoaerogels [4], and NCNT/CoO-NiO-NiCo [5], have been investigated and developed intensely as promising candidates because of their bifunctional catalytic activity for both OER and ORR. However, the catalytic performances of these compounds are still unsatisfactory due to low current density for OER and negative onset potential as well as weak stability for ORR.

Defects in acatalyst can change the distribution of the charge density and are instrumental in forming the active sites for electrocatalytic reactions [6], such as intrinsic defects of the carbon support and point defects of ion vacancies in metal compounds [7-12]. Among them, point defects of anion vacancies in transition-metal oxides have shown significant positive effects on OER and ORR, which has been becoming the current research focus. Oxygen vacancy, which is the most studied anion vacancies, can effectively adjust the band gap and d band center of the metal cations in single-crystal cobalt oxides. So the OER and ORR activities can be enhanced significantly [13,14]. However, the oxygen vacancies could lead to serious lattice distortion due to the large ion radius of O^{2-} (0.14 nm), which is not favorable for the catalytic stability [15,16]. Theoretically, point defects of cation vacancies have a smaller ion radius and minor lattice distortion than that of oxygen vacancies [17]. They can be structurally stable and also delocalize electrons around the adjacent transition-metal atoms and the O atoms [18,19]. Such tailored electron distribution and orbital variation are favorable for fast charge transfer and can achieve optimal adsorption of reaction intermediates. Therefore, generation of cation vacancies is

beneficial to create active and stable catalytic centers for oxygen catalysis. However, due to the larger formation energy of metal-cation vacancies than those of anion vacancies [20,21], creation of cation vacancy point defects in the ternary transition-metal oxides used for oxygen electrocatalysts is difficult and rarely reported.

In this communication, a series of one-dimensional (1D) porous multi-shell $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ hollow fibers were treated by the process of electrochemical lithium ion (Li^+) insertion and extraction to generate Li vacancy defects. When evaluated as oxygen electrocatalysts, the delithiated $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ hollow fibers ($\text{De-Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$) can offer high-performance toward bifunctional OER and ORR, due to the modification of Li vacancies on carrier concentration and electrical conductivity. By comparing density functional theory (DFT) calculations for the sample before and after delithiation, it is found that the delithiated samples have a significantly improved carrier concentration and higher electronic conductivity in the Co-*d* orbitals near the sites of Li vacancies. This results in enhanced O_2 (2.75 eV) and H_2O (3.34 eV) adsorption energies and thus greatly reduce overpotentials in the whole OER (0.31V) and the whole ORR (0.48V). In addition, the grain boundaries and dislocations resulting from delithiation are helpful to increase the electrochemically active site density and 1D porous multi-shell structure can effectively shorten the electron transfer length thus increase the electron diffusion [22-24]. The high bifunctional OER and ORR activities of $\text{De-Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ offered us opportunity to assemble rechargeable ZABs. For instance, using $\text{De-Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ as air cathode, a ZAB exhibited a high round-trip efficiency evidenced by a narrow discharge-charge voltage gap of 0.74 V and a stable voltage plateau up to 441 h at a constant current rate of 5 mA cm^{-2} .

2. Results and discussion

The multi-shelled $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ ($x = 0.2, 0.333, 0.65, y = 0.6, 0.333, 0.25, z = 0.2, 0.333, 0.1$) hollow fibers were fabricated using sustainable alginate fiber (AF) as precursor [25,26]. The detailed description of the experimental method is presented in the Supporting Information (SI). Specifically, as shown in **Figure 1a**, Li-M-AF ($M = \text{Ni, Co, Mn}$), which was obtained by ion-exchange, converted to multi-shelled $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ hollow fibers after pyrolysis in air. Then the $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ hollow fibers were assembled into a 2016-type coin cell configuration acting as the cathode and combined with Li metal as the anode. 1 M LiPF_6 in 1:1:1 w/w/w

ethylene carbonate/dimethyl carbonate/diethyl carbonate was used as the electrolyte. The electrochemical tuning was carried out by charging the materials to 4.9 V following the reaction $\text{LiMO}_2 \rightarrow \text{Li}_{1-x}\text{MO}_2 + x\text{Li}^+ + xe^-$ [18]. The extraction and intercalation of Li^+ from and into the lithium ion battery spanning a wide potential range is considered to be an efficient method to tune the electronic structure and increase the electrocatalytic active surface area of the electrocatalyst. The chemical composition was determined by using inductive coupled plasma atomic emission spectrometry (ICP-AES). The specific compositions of the three De-Li($\text{Ni}_x\text{Co}_y\text{Mn}_z$) O_2 samples are $\text{Li}_{0.48}(\text{Ni}_{0.20}\text{Co}_{0.60}\text{Mn}_{0.20})\text{O}_2$, $\text{Li}_{0.51}(\text{Ni}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33})\text{O}_2$, $\text{Li}_{0.47}(\text{Ni}_{0.65}\text{Co}_{0.25}\text{Mn}_{0.10})\text{O}_2$, respectively (**Table S1**). This means that the corresponding total Li vacancy concentrations are 0.52, 0.49, and 0.53 in one unit of De-Li($\text{Ni}_x\text{Co}_y\text{Mn}_z$) O_2 , respectively.

Fig 1. (a) Schematic illustration of the morphology and structure evolution process. Cross-section SEM images of (b) Li-M-AF, (c) Multi-shelled $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ hollow fibers, (d) multi-shelled $\text{De-Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ hollow fibers. (e) SEM image of $\text{De-Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ and the corresponding EDS mapping for Ni, Co, Mn elements. (f) XRD

patterns of $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ and $\text{De-Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ ($x = 0.2, 0.333, 0.65$). (g) Selected area of XRD patterns of $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ and $\text{De-Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ ($x = 0.2, 0.333, 0.65$).

The morphology and structure evolution were characterized by use of field emission scanning electron microscopy (FESEM). The Li-M-AFs are about 10-15 μm in diameter with smooth surfaces (**Figure 1b**). However, the morphology changes significantly after pyrolysis treatment. As shown in **Figure 1c** and **Figure S1a,b**, the three $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ samples exhibit a typical 1D fibrous morphology and multi-shelled hollow structure. After the electrochemical tuning process, the three $\text{De-Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ samples inherit the 1D multi-shelled hollow fibrous morphology (**Figure 1d** and **Figure S1c,d**). The diameter of these fibers is ~ 10 μm . The thickness of the shell layer can reach several hundred nanometers, and a typical porous network can be observed in the shell. The wide space between the shells and the porous network with the shell can effectively shorten average path length for mass transport in aqueous electrolytes. The elemental mapping by energy dispersive X-ray spectroscopy (EDS) was further used to analyze the composition of $\text{De-Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$. As shown in **Figure 1e**, Ni, Co and Mn elements are homogeneously distributed along a single fiber.

The powder x-ray diffraction (PXRD) patterns of the pristine $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ and $\text{De-Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ are displayed in **Figure 1f,g**. The intensities of all these six patterns are normalized. The pristine $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ fibers exhibit a well-defined layered structure based on a hexagonal $\alpha\text{-NaFeO}_2$ structure with a R-3m space group. We refined the XRD patterns based on the Rietveld method using General Structure Analysis System (GSAS) software. **Figure S2a-c** shows the fitting results of the XRD profiles of LNCMO with $x = 0.2, 0.33$, and $x = 0.65$, respectively. Based on the fitting results (**Figure S2d**), the initial structural models of $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ (PDF#97-015-3446), $\text{Li}(\text{Ni}_{0.333}\text{Co}_{0.333}\text{Mn}_{0.333})\text{O}_2$ (PDF#97-017-1750), and $\text{Li}(\text{Ni}_{0.65}\text{Co}_{0.25}\text{Mn}_{0.1})\text{O}_2$ (PDF#97-010-9319) approximate the actual structures. The clear peak splits in (108)/(110) and (006)/(102) doublets were observed for all samples, indicating the formation of well-crystallized $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ [25]. After 5-cycle electrochemical tuning of the Li^+ extraction and insertion, the peak splits in (108)/(110) and (006)/(102) doublets became unclear and the intensity of the main peak became weak. This means that the degree of the crystallinity has decreased since the cycling process may destroy the crystalline structure to some extent (**Figure 1f**). **Figure 1g** shows that the (003) peak shifts to lower angles for De-

$\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$, thus implying that the c axis is expanding as Li^+ is deintercalated in the charging of the $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ electrode [26]. During the same charge process, the (101) peak shifts continuously to higher angles, indicating that a parameter contracts during the Li^+ extraction process [27-29].

Fig 2. (a) TEM image of pristine $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ with the schematic illustration of the single-crystal NPs (inset). (b) TEM image of $\text{De-Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ with the schematic illustration of the ultra-small interconnected grains (inset). (c) HRTEM image of the square area in (a) with the corresponding FFT pattern (inset). (d) HRTEM image of the square area in (b) with the corresponding FFT pattern (inset). The white lines represent the created boundaries in the whole particle. (e) HAADF-STEM image of $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$. (f) HAADF-STEM image of $\text{De-Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$. The yellow circle represents the Li vacancies in the crystals.

Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) were performed to further study the evolution of the crystalline structure. As shown in **Figure 2a**, the whole lattice of $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ is clear and regular. However, the $\text{De-Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ exhibits interconnected smaller grains with sufficient grain boundaries (**Figure 2b**). This indicates that the complete $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ NPs (inset in **Figure 2a**) can transform into much smaller grains (inset in **Figure 2b**) once the Li^+ extracted from $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$. The HRTEM image shows d -spacings of 0.19 and 0.24 nm, corresponding

to (10-5) and (01-1) lattice fringes of hexagonal $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ (space group $R\text{-}3m$, $a = b = 0.2841$, and $c = 1.4168$ nm), respectively. The lattice structure and the corresponding fast Fourier transform (FFT) pattern (inset in **Figure 2c**) indicate the single-crystalline nature of the pristine NPs. After Li^+ extraction and insertion, the HRTEM images show that the monocrystalline $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ converted into interconnected smaller grains, with ultra-small size of ~2-6 nm (**Figure 2d**). Compared with the pristine $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$, more diffraction spot patterns were observed from the FFT image of $\text{De-Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$. This suggests that single-crystal NPs in $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ have transformed into poly-crystalline grains in $\text{De-Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$. The ultra-small grains create many grain boundaries and dislocations, which are considered to be active centers and help to maintain good mechanical and electrical contacts. To further depict the defects in the $\text{De-Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$, high-angle annular dark-field scanning TEM (HAADF-STEM) images are performed as shown in **Figure 2e** and **2f**. $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ exhibits a uniform lattice of bright dots without indication of defects (**Figure 2e**). However, the bright dots turned to weak and even disappeared in $\text{De-Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ (**Figure 2f**), since the atomic density reduced in the corresponding columns. This resulted from the formation of Li vacancies during the Li^+ extraction process. These Li vacancies can result in modification of carrier concentration and electrical conductivity, which is helpful to improve the bifunctional catalytic activities toward OER and ORR.

The electrochemical water oxidation activities of the multi-shelled $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ hollow fibers before and after electrochemical tuning were investigated in 1 M KOH on a rotating disk electrode (RDE), at a scan rate of 10 mVs^{-1} and a rotation rate of 1600 rpm (**Figure 3**, and **Figure S3,S4**). As shown in **Figure 3a** and **Figure S3**, large overpotentials of 1.64, 1.67, and 1.72 V were needed to reach the current density of 10 mA cm^{-2} for $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$, $\text{Li}(\text{Ni}_{0.333}\text{Co}_{0.333}\text{Mn}_{0.333})\text{O}_2$, and $\text{Li}(\text{Ni}_{0.65}\text{Co}_{0.25}\text{Mn}_{0.1})\text{O}_2$, respectively. This indicates the less active OER of the pristine $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ fibers. However, the linear sweep voltammetry (LSV) curves of the delithiated samples shift negatively clearly. Specifically, the $\text{De-Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ fiber showed the best performance with onset potentials of ~1.46 V vs. RHE and ~1.53 V at 10 mA cm^{-2} . For $\text{De-Li}(\text{Ni}_{0.333}\text{Co}_{0.333}\text{Mn}_{0.333})\text{O}_2$ and $\text{De-Li}(\text{Ni}_{0.65}\text{Co}_{0.25}\text{Mn}_{0.1})\text{O}_2$, the onset potentials were ~1.48 V and ~1.49 V vs. RHE and ~1.54 V and ~1.57 V at 10 mA cm^{-2} , respectively. Their OER performances were superior to that of IrO_2/C . The improved OER activity mainly arises from the introduction of Li vacancies.

Fig 3. (a) LSV plots of multi-shelled $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ hollow fibers before and after delithiation and commercial IrO_2/C catalysts at 10 mV s^{-1} in 1 M KOH . (b) Tafel slopes of multi-shelled $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ hollow fibers before and after delithiation in 1 M KOH . (c) The 1st and 500th LSV curves of $\text{De-Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ catalyst in 1 M KOH at 1600 rpm with a scan rate of 10 mV s^{-1} . The inset is the corresponding repeated CV cycling for 500 times. (d) LSV curve comparison of multi-shelled $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ hollow fibers before and after delithiation at 1600 rpm . (e) LSV curves of multi-shelled $\text{De-Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ hollow fibers at various rotation speeds. The inset shows the K-L plots from LSV curves at 0.35 V , 0.40 V , 0.45 V , 0.50 V . (f) Long-term stability comparison of multi-shelled $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ hollow fibers before and after delithiation.

To gain further insight into the OER activities influenced by the electrochemical tuning, Tafel plots were recorded with the linear regions fitted to the Tafel equation, $\eta = b \log(j/j_0)$, where η is the overpotential, j is the current density, b is the Tafel slope, and j_0 denotes the exchange current density (**Figure 3b** and **S4**) [30–32]. The $\text{De-Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ hollow fibers exhibit a Tafel slope of 36 mV dec^{-1} , which is better than that of pristine $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ (50 mV dec^{-1}). The other delithiated samples also display lower Tafel slopes than the pristine ones (**Figure S4**). Apparently, the electrochemical tuning could efficiently improve the OER kinetics *via* the

generation of Li vacancies. As shown in **Figure S5** and **Figure S6**, the electrochemically active surface areas (ECSA) of the catalysts were estimated from measurements of the electrochemical double-layer capacitance (EDLC). The EDLC of $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ is only 5.16 mF cm^{-2} whereas that of $\text{De-Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ is as high as 12.08 mF cm^{-2} . The ECSA has increased substantially after electrochemical tuning, also for $\text{De-Li}(\text{Ni}_{0.333}\text{Co}_{0.333}\text{Mn}_{0.333})\text{O}_2$ and $\text{De-Li}(\text{Ni}_{0.65}\text{Co}_{0.25}\text{Mn}_{0.1})\text{O}_2$. Apparently, the number of electrochemically active sites for water oxidation can be efficiently increased with generation of Li vacancies. Moreover, the electrochemical durability of $\text{De-Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ was evaluated by repeated cyclic voltammetry (CV) cycling for 500 times in 1 M KOH (**Figure 3c**). The current density is only slightly changed under applied voltage for $\text{De-Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$, demonstrating a high cyclic stability toward OER.

Besides the enhanced OER catalytic activity, an improved ORR performance is also observed. The ORR experiments were conducted using $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ and $\text{De-Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ as a reference catalyst pair in the electrochemical test. As shown in **Figure S7a**, a clear oxygen reduction peak at 0.58 V vs. RHE in the CV curves of $\text{De-Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ was observed in O_2 -saturated 0.1 M KOH solution. However, the oxygen reduction peak at 0.50 V vs. RHE in the CV curves of $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ is much weakened (**Figure S7b**), indicating $\text{De-Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ is more active to catalyze the ORR than the pristine one. Their LSV curves were collected on a rotating disk electrode (RDE) in O_2 -saturated solution of 0.1 M KOH at 1600 rpm (**Figure 3d**). The onset potential of $\text{De-Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ is $\sim 0.85 \text{ V}$ (vs. RHE) and its half-wave potential is $\sim 0.71 \text{ V}$ (vs. RHE), which is much better than that of the $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ electrode (~ 0.71 and ~ 0.63 vs. RHE). The same trend is observed for the other two samples (see **Figure S8**). The improved ORR performance after electrochemical tuning may be ascribed to the modification of carrier concentration and electrical conductivity of the Li vacancies [33-35]. To gain deeper insight into the ORR catalytic activity, $\text{De-Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ and $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ fibers were chosen to perform the LSV curves using an RDE rotating at speeds from 400 to 2025 rpm (**Figure 3e** and **Figure S9**). The electron-transfer number (n) is calculated from 0.35 to 0.50 V (vs. RHE) from the slope of the Koutecky-Levich (K-L) plots (inset of **Figure 3e** and **Figure S9**). The calculated n value of $\text{De-Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ is 4.0 and the calculated n value of $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ is 3.1. That represents that the ORR at the $\text{De-Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ electrode is more closer to a $4e^-$

reduction pathway compared with $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ [36,37]. Furthermore, the durability of $\text{De-Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ and $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ was tested at a constant voltage of 0.46 V vs. RHE for 29 000 s in an O_2 -saturated 0.1 M KOH solution at a rotation rate of 1600 rpm (**Figure 3f**). The corresponding current-time (*i-t*) chronoamperometric response of $\text{De-Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ exhibits a current loss (4 %) over 29 000 s, which is much lower than that of $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ (21 %). Apparently, the electrochemical tuning also enhanced durability in alkaline medium.

Fig 4. (a, b) The schematic of (a) pristine $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ and (b) $\text{De-Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$. The Li, O, Mn, Co, Ni are represented by green, red, silver, purple, and blue spheres, respectively. The green dotted circles represented the migration of Li ions. (c, d) TDOS and PDOS (the Fermi energy level was set to zero). (e) Calculated geometry of $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ adsorbing water (i) and oxygen (ii); Calculated geometry of $\text{De-Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ adsorbing water (iii) and oxygen (iv), DFT-calculated adsorption energy of O_2 and H_2O molecules on the surfaces of $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ and $\text{De-Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$. (f, g) Free energy diagram for pristine $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ and $\text{De-Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ for OER (f) and ORR (g).

To elucidate the underlying catalytic mechanism of Li vacancies on boosting OER and ORR, DFT calculations were performed to investigate both oxygen catalysis processes. As shown in **Figure 4a** and **4b**, we adopted the modules of $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ with and without Li vacancies to represent the $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ and $\text{De-Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ samples. We

described the total densities of states (TDOS) as well as the partial densities of states (PDOS) for De-Li ($\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2}\text{O}_2$) and $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2}\text{O}_2)$, respectively (**Figure 4c** and **4d**). De-Li($\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2}\text{O}_2$) and $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2}\text{O}_2)$ both exhibit very small bandgap near the Fermi level and are metal-like with good charge-transfer efficiency. However, there are significantly increased TDOS and Co-*d* PDOS values around the Fermi level in De-Li($\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2}\text{O}_2$). This indicates that De-Li($\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2}\text{O}_2$) has improved carrier concentration and electrical conductivity, especially in the Co-*d* orbits near the site of Li vacancies. In general, the ability of electrocatalysts to adsorb O_2 and H_2O plays a crucial role for ORR and OER activity [21,36]. The binding energies of H_2O and O_2 are shown in **Figure 4e**. **Figure 4 i-iv** exhibits the optimized adsorption structure. The adsorption energies of O_2 and H_2O on the pristine $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2}\text{O}_2)$ are 2.18 and 3.02 eV, respectively, while De-Li($\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2}\text{O}_2$) has significantly increased adsorption energies of O_2 (2.75 eV) and H_2O (3.34 eV). We plotted the free energy diagrams in **Figure 4f** and **4g** to describe the associative $4e^-$ reaction pathway of OER and ORR, which gives the different reaction mechanisms in pristine $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2}\text{O}_2)$ and De-Li($\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2}\text{O}_2$). For De-Li($\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2}\text{O}_2$), the OER rate determining step (RDS) of all reaction pathways was the transformation from O^* to OH^* . In contrast, the OER RDS of pristine $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2}\text{O}_2)$ was the formation of chemisorbed OOH^* . The ORR RDSs for De-Li($\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2}\text{O}_2$) and pristine $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2}\text{O}_2)$ are the formation of H_2O and chemisorbed OH^* , respectively. As presented in **Figure 4f**, the overpotential for De-Li($\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2}\text{O}_2$) is greatly reduced to 0.31 V compared with the pristine $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2}\text{O}_2)$ (0.38 V) in the whole OER. In **Figure 4g**, De-Li($\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2}\text{O}_2$) shows the overpotential of 0.48 V and the pristine $\text{Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2}\text{O}_2)$ is with 0.62 V in the whole ORR. Clearly, the introduction of Li vacancies is crucial to boost the OER and ORR performance of $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ materials.

Fig 5. (a) Schematic illustration of the ZABs prepared of the multi-shelled $\text{De-Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ hollow fibers. (b) Charge-discharge cycling performance at 5 mA cm^{-2} of the ZAB with bifunctional $\text{De-Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ catalyst as an air cathode. (c) Charge and discharge polarization curves of the ZABs with bifunctional $\text{De-Li}(\text{Ni}_{0.2}\text{Co}_{0.6}\text{Mn}_{0.2})\text{O}_2$ catalyst as an air cathode. (d) 22 LED light ($\sim 1.2 \text{ V}$, 38.0 mA) powered by two ZABs in series.

To demonstrate electrochemically bifunctional catalytic performance of De-Li(Ni_xCo_yMn_z)O₂ in realistic environments, electrically rechargeable ZAB prototypes were fabricated and their electrochemical performance were evaluated. ZABs are easier to handle and can be operated with little safety concern compared with lithium-air batteries [38]. In addition, ZABs experience a much less parasitic corrosion reaction in aqueous solution of alkaline than Al-air batteries [39]. **Figure 5a** shows the physical design of the ZAB in this study with 1D De-Li(Ni_{0.2}Co_{0.6}Mn_{0.2})O₂ catalyst. The stability experiment was performed by charging and discharging using a constant current rate of 5 mA cm⁻². The final charge and discharge potentials of De-Li(Ni_{0.2}Co_{0.6}Mn_{0.2})O₂ were about 1.97 V and 1.23 V after 441 h, whereas the initial values were about 1.95 V and 1.22 V, respectively. The round-trip overpotential after 441 h is ~ 0.74 V, which is a small increase of 0.01 V compared with the initial round-trip overpotential (~ 0.73 V) (**Figure 5b**). This catalyst gives the best cycle performances reported so far for ZABs in alkaline (**Table S2**). **Figure 5c** shows the discharge and charge polarization curves of a three-electrode rechargeable zinc-air battery using De-Li(Ni_{0.2}Co_{0.6}Mn_{0.2})O₂ catalyst on carbon papers as both the ORR and OER electrodes. For comparison, precious Pt/C and IrO₂/C were also employed in the electrodes as the ORR and OER catalysts, respectively. The charge-discharge voltage gap of De-Li(Ni_{0.2}Co_{0.6}Mn_{0.2})O₂ is lower than Pt/C-IrO₂/C (e.g. 1.05 V at 50 mA cm⁻², 1.50 V at 100 mA cm⁻², 2.15 V at 200 mA cm⁻² for De-Li(Ni_{0.2}Co_{0.6}Mn_{0.2})O₂ vs. 1.06 V at 50 mA cm⁻², 1.67 V at 100 mA cm⁻², 2.33 V at 200 mA cm⁻² for Pt/C-IrO₂/C), indicating better rechargeability. The Nyquist plots and corresponding analysis of the equivalent circuit are shown in **Figure S10**. The parameters of the fitting circuit element are shown in **Table S3**. The charge-transfer resistance (R_{ct}) values at the interface between the electrode and electrolyte are 3.724 Ω for De-Li(Ni_{0.2}Co_{0.6}Mn_{0.2})O₂, 9.739 Ω for IrO₂/C, and 4.463 Ω for Pt/C, respectively. This means De-Li(Ni_{0.2}Co_{0.6}Mn_{0.2})O₂ has a lower polarization than IrO₂/C and Pt/C. This value is much lower than those measured with NCNT/CoO-Co (1.50 V) [40], NCNT/CoO-NiO-NiCo (1.20 V) [18], and the reported Pt/C+IrO₂ counterparts (1.19 V) [18]. To demonstrate its potential application, two ZABs were connected in series to generate a sufficiently high open circuit potential of 1.3 V and high circuit current of 39.1 mA to power 22 LED lights (~1.2 V, 39.0 mA), as exemplified in **Figure 5d**.

Conclusions

In summary, 1D multi-shelled $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ hollow fibers have been synthesized and the $\text{De-Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ obtained after delithiated process, which were demonstrated to exhibit an enhanced catalytic performance with improved catalytic activity, fast kinetics and splendid durability in both the OER and ORR processes. As a consequence, the delithiated catalyst exhibits excellent ZAB performance. It is mainly attributed to the electrochemical tuning process, from which the Li vacancies can bring an improved carrier concentration and electrical conductivity. The study represents a successful application of electrochemical tuning beyond layered oxides and the resulting material exhibits tremendous potential for applications in renewable energy storage and conversion. Furthermore, the clearly demonstrated general efficacy of the methodology opens up new avenues to tune existing materials for more efficient and durable heterogeneous catalysts in the area of energy research.

Acknowledgements

This work is financially supported by the National Natural Science Foundation of China (Nos. 51473081 and 51672143), Taishan Scholars Program, Outstanding Youth of Natural Science in Shandong Province (JQ201713), and ARC Discovery Project (No. 170103317).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi

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Graphical Abstract

Generating Lithium Vacancies through Delithiation of $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ towards Bifunctional Electrocatalysts for Rechargeable Zinc-air Batteries

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PII: S2405-8297(18)30194-6
DOI: <https://doi.org/10.1016/j.ensm.2018.04.005>
Reference: ENSM357

To appear in: *Energy Storage Materials*

Received date: 24 February 2018
Revised date: 30 March 2018
Accepted date: 5 April 2018

Cite this article as: Yihui Zou, Guojing Chang, Yi (Alec) Jia, Rongsheng Cai, Shuai Chen, Yanzhi Xia, Wolfgang Theis, Dongjiang Yang and Xiangdong Yao, Generating Lithium Vacancies through Delithiation of $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ towards Bifunctional Electrocatalysts for Rechargeable Zinc-air Batteries, *Energy Storage Materials*, <https://doi.org/10.1016/j.ensm.2018.04.005>

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