CHEMISTRY OF MATERIALS

Electronic, Structural, and Electrochemical Properties of LiNi_xCu_yMn_{2-x-y}O₄ (0 < x < 0.5, 0 < y < 0.5) High-Voltage Spinel Materials

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Supporting Information

ABSTRACT: First principles computation is carried out for investigating the electronic, structural, and electrochemical properties of $\text{LiM}_{1/2}\text{Mn}_{3/2}O_4$ (M = Ti, V, Cr, Fe, Co, Ni, and Cu). The computation results suggest that doping with Co or Cu can potentially lower Li diffusion barrier as compared to Ni doping. Our experimental research has focused on $\text{LiNi}_x\text{Cu}_{y^-}$ $\text{Mn}_{2-x-y}O_4$ (0 < x < 0.5, 0 < y < 0.5), and we found that the amount of Cu will affect the lattice parameters, the cation disorder in the spinel lattice, the particle morphology, as well as the electrochemical properties. Crystal structures, electronic structures, and electrochemical properties of LiNi_x . Cu_yMn_{2-x-y}O₄ (0 < x < 0.5, 0 < y < 0.5) are studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray absorption spectroscopy (XAS), and electrochemical measurements including potentiostatic intermittent titration technique (PITT). With detailed electrochemical measurements



and in situ XAS experiments of $LiNi_{0.25}Cu_{0.25}Mn_{1.50}O_4$, the proposed explanation of the voltage profile by the first principles computation was proven, a second plateau at 4.2 V originates from the oxidation of Cu^{2+} to Cu^{3+} , and the plateau at 4.95 V may originate from extra electrons provided by oxygen ions. Although the reversible discharge capacity decreases with increasing Cu amount, optimized composition such as $LiCu_{0.25}Ni_{0.25}Mn_{1.5}O_4$ exhibits high capacities at high rates.

KEYWORDS: first principles computation, high-voltage spinel, Li-ion batteries

■ INTRODUCTION

LiMn₂O₄ spinel is an attractive compound as a cathode material in lithium-ion batteries, due to its economical, environment, and safety advantages over LiCoO₂. LiMn₂O₄ adopts the spinel structure with the space group $Fd\overline{3}m$, in which the Li and Mn occupy the 8a tetrahedral and 16d octahedral sites of the cubic close-packed oxygen ions framework, respectively. However, LiMn₂O₄ tends to exhibit capacity fade in the 4 V region, particularly at elevated temperatures. Factors such as Mn dissolution into the electrolyte and the development of microstrains^{1,2} during cycling have been suggested to be the main sources of capacity fade. The poor cycling performance could be improved by partial substitution of Mn with other metals, an approach to making the $\text{LiM}_x\text{Mn}_{2-x}O_4$ (M = Co, Mg, Cr, Ni, Fe, Al, Ti, Cu, Zn, etc.) electrode material.^{3–5} It has been found that a higher voltage plateau (>4 V) accompanies some transition metal doping.³ Among all LiM_xMn_{2-x}O₄ materials, LiNi_{0.5}- $Mn_{1.5}O_4$ is an attractive high voltage cathode material because it offers a flat voltage plateau at 4.7 V and demonstrates a reversible capacity >135 mAh/g.^{6,7} Several strategies were developed to improve the rate capability of LiNi_{0.5}Mn_{1.5}O₄. Arrebola et al.

obtained excellent rate properties by homogeneously mixing nano- and micro-size LiNi0.5Mn1.5O4 powders,8 or by adding polyethyleneglycol (PEG) to increase the crystallinity and decrease the strain.⁹ The rate capability was also affected by the atomistic structure of the spinel material, as proposed by Kunduraci et al.¹⁰ It is found that nonstoichiometric LiNi0.5- $Mn_{1.5}O_{4-\delta}$ (*Fd*3*m*) exhibited better structural reversibility at high rate as compared to stoichiometric LiNi0.5Mn1.5O4 $(P4_332)$. The oxygen deficiency leads to the presence of a small amount of Mn³⁺ in the pristine materials, which leads to better electronic conductivities in the material. The Cu-doped spinel materials were investigated by a few research groups.¹ Although the Cu-rich spinel electrodes provide lower discharge capacity than Ni-rich spinel electrodes, it is more stable during electrochemical cycling. Moreover, $LiCu_rMn_{2-r}O_4$ has a higher electronic conductivity than do other spinel LiM_xMn_{2-x}O₄ materials (Cr, Fe, Co, Ni),¹⁵ because Cu can participate in the

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Received: January 6, 2011
Revised: April 20, 2011
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charge transport process. All of the previous work focused mainly on the electronic conductivity in the doped spinel $\text{LiM}_x\text{Mn}_{2-x}O_4$ materials. Little has been explored to enhance the lithium ionic diffusivity in this family of materials. Using ab initio computational modeling, it is possible to rapidly screen the effect of different doping elements on the lithium diffusion activation barrier, as well as the redox potentials in the spinel structure. Ab initio computational method was first used by Van der Ven et al. to determine the energy barrier of Li diffusion in layered transition metal oxides.¹⁶ Kang et al. also used this method to identify the factors that limit Li⁺-ion hopping in layered oxide and successfully synthesize an optimized layered material with superior rate capability.¹⁷

Many researchers have already shown that the cycling performance of $LiNi_{0.5}Mn_{1.5}O_4$ can be improved by doping with different transition metal ions.^{18–21} However, a systematic understanding on the effects of co-doped elements is still lacking. In this work, first principles computation, based on density functional theory (DFT), is used to examine the voltage profile and electronic structures of the $LiM_xMn_{2-x}O_4$ (M = Ti, V, Cr, Fe, Co, Ni, Cu). The Li diffusion activation barriers in each material are calculated and compared. On the basis of the computational prescreening, our experimental research focuses on LiNi_xCu_yMn_{2-x-y}O₄ (0 < x < 0.5, 0 < y < 0.5), which have the potential to achieve high voltage, high rate, and good cycling performance, while keeping relatively high capacity. The materials with different Cu/Ni concentrations are synthesized using the sol-gel process. Their crystal structures, electronic structures, and electrochemical properties are then characterized and studied experimentally.

COMPUTATIONAL METHODS

In this work, a supercell composed of eight formula units of $Li_x M_{1/2}$ - $Mn_{3/2}O_4$ (M = Ti, V, Cr, Fe, Co, Ni, and Cu) is used. The doped spinel with ordered cation arrangement belongs to the space group $P4_332$. O ions occupy the 8c and 24e sites, forming a close-packed fcc lattice. Mn ions occupy the 12d octahedral sites, while M ions occupy the 4b octahedral sites. The 8c tetrahedral sites are filled with Li ions. For Li_xCu_{1/2}Mn_{3/2}O₄, an additional model of Cu ions exchanging sites with one-half of the Li ions was built and investigated. Calculations were performed using density functional theory (DFT) in the spin-polarized generalized gradient approximation (GGA) and in the GGA with Hubbard U correction (GGA+U). Core electron states were represented by the projector augmented-wave method²² as implemented in the Vienna ab initio simulation package (VASP).^{23–25} The Perdew– Burke–Ernzerhof exchange correlation²⁶ and a plane wave representation for the wave function with a cutoff energy of 370 eV were used. The Brillouin zone was sampled with a $5 \times 5 \times 5$ mesh by Gamma packing. The atomic positions and cell parameters are fully relaxed to obtain total energy and optimized cell structure. To obtain the accurate electronic density of states (DOS), a static self-consistent calculation was run, followed by a non-self-consistent calculation using the calculated charge densities from the first step. The cell volume was fixed with internal relaxation of the ions in the second step calculation. A supercell with one vacancy out of eight Li sites (Li₇M₄Mn₁₂O₃₂) was used to calculate the Li diffusion activation barriers in the Li-rich phase with GGA approximation. The Hubbard U correction was introduced to describe the effect of localized d electrons of transition metal ions when investigating the valence states and electronic structures of the ions. Previous work has shown that the U values can be calculated in a self-consistent way and the U values of Mn and Ni ions in the spinel structure are well established.^{27–29} These values are taken as the references. In the doped spinel system, the same transition metal ions with different valence states may coexist; therefore, small adjustments are made to the reference U values, so that each transition metal ion has a unique effective U value applied in the rotationally invariant LSDA+U approach.³⁰ In this work, the applied effective U value given to Mn ions is 5 eV, to Ni ions is 5.96 eV, and to Cu ions is 7 eV.

EXPERIMENTAL METHODS

Sample Preparation. Six samples were synthesized using the sol-gel method: LiNi_{0.5}Mn_{1.5}O₄, LiNi_{0.45}Mn_{1.55}O₄, LiCu_{0.05}Ni_{0.45}-Mn_{1.5}O₄, LiCu_{0.1}Ni_{0.4}Mn_{1.5}O₄, LiCu_{0.25}Mn_{1.5}O₄, and LiCu_{0.5}-Mn_{1.5}O₄. The sol solutions were prepared from the stoichiometric mixtures of Li(CH₃COO) \cdot 2H₂O (Fisher), Ni(CH₃COO)₂ \cdot 4H₂O (Fisher), Cu(CH₃COO)₂ \cdot H₂O (Fisher), and Mn(CH₃COO)₂ \cdot 4H₂O (Fisher) in distilled water. Next, the solution was added dropwise to a continuously stirred aqueous solution of citric acid. The pH of the mixed solution was adjusted to 6.5 by adding an ammonium hydroxide solution. The solution was then heated at 75 °C overnight; a transparent gel was obtained. The resulting gel precursors were decomposed at 450 °C for 10 h in air and calcined at 800 °C for 10 h.

X-ray Diffraction. Powder diffractions of all samples were collected using a high-resolution synchrotron powder X-ray diffractometer at beamline 11-BM at the Advanced Photon Source (APS), Argonne National Laboratory (U.S.). The conditions for the data collection were continuous scanning of a detector covering an angular range from 0.5° to 40° with a step size of 0.0001° and wavelengths of $\lambda = 0.413964$ Å. The diffraction patterns were analyzed by the Rietveld refinement software, FullProf.³¹ The ex situ XRD data were collected by a laboratory X-ray diffractometer equipped with a curved position sensitive detector (Inel CPS120, detection range 0–120°), a Cu X-ray tube source, and a Gobel mirror on the incident beam. The collection time for each XRD spectrum was 20 min. The samples for ex situ XRD were recovered by disassembling cycled batteries in an argon-filled glovebox, and the powder mixture was scraped from the aluminum disks.

ICP-AES. The chemical compositions of the samples were analyzed by inductive coupled plasma atomic emission spectroscopy (ICP-AES Perkin-Elmer Plasma 3200). The instrument is equipped with two monochromators covering the spectral range of 167-785 nm with a grated ruling of 3600 lines/mm. The system is capable of analyzing materials in both organic and aqueous matrices with a detection limit range of less than 1 ppm. The instrument was initially calibrated using commercial LiCoO₂ and LiFePO₄ powders.

SEM. Field emission secondary electron microscopy (FEG-SEM, JEOL JSM-6335F) was carried out to investigate the particle size and morphologies. Images were collected with an accelerating voltage of 15 kV.

In Situ XAS. X-ray absorption spectroscopy (XAS) at the Ni, Mn, and Cu K-edges was obtained in transmission mode at the National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan, to observe the changes in nickel, manganese, and copper oxidation states for $LiCu_{0.25}Ni_{0.25}Mn_{1.5}O_4$ during the charging process. A Si (111) double crystal monochromator was employed for energy selection. The coin cell 2016 was charged to target voltage (4.1–5 V) and rested for 40 min (10 min to reach equilibrium, 30 min to get spectrum) to obtain the spectroscopy. The spectrum was collected every 0.1 V.

Electrochemistry. The electrochemical properties of all cathode electrodes were measured using 2016 coin cells consisting of metallic lithium as an anode and an electrolyte comprised of 1 M LiPF₆ in a 1:1 volume fraction of ethylene carbonate (EC)/dimethyl carbonate (DMC). Celgard model C480 separator (Celgard Inc.,U.S.) was used as separator. Cathode films were prepared from slurries of LiCu_y-Ni_xMn_{2-x-y}O₄ with 7.5% polyvinylidene fluoride (PVDF) and 7.5% acetylene carbon black dissolved in *N*-methyl-2-pyrrolidinone (NMP).



Figure 1. Local environments of transition metal ion rings. (a) Three M ions in the ring. (b) One M ion in the ring.

The mixtures were cast onto Al foil using a doctor blade and dried at 100 °C overnight. Electrode discs were cut into cathodes containing 5–10 mg of active materials before storing them in an argon-filled glovebox (H₂O level <2 ppm). The coin-cells were assembled in an argon-filled glovebox and tested using an Arbin BT2000 instrument in galvanostatic mode. The tests were conducted between 3.0 and 5.0 V at a constant current rate of *C*/20, *C*/10, *C*/5, and *C*/2. The samples for ex situ XRD were recovered by disassembling charged batteries and washed using acetonitrile to remove residual electrolyte in an argon-filled glovebox. To measure the chemical diffusion coefficient, the potentiostatic intermittent titration technique (PITT) was performed by applying a voltage step of 10 mV. The potential was stepped to the next level when the current decreased below 3 × 10 μ A (which is equivalent to *C*/200 rate). The voltage window was set from 4.5 to 4.9 V.

RESULTS AND DISCUSSION

First Principles Calculations. Previous research has shown that, when Li ions diffuse in the undoped LiMn₂O₄ spinel structure, the diffusion activation barriers are reached when Li ions occupy the intermediate 16c sites, which are surrounded by six Mn ions forming a Mn ring.²⁹ A similar situation occurs in the doped spinel $\text{Li}_x M_{1/2} \text{Mn}_{3/2} O_4$ (M = Ti, V, Cr, Fe, Co, Ni, and Cu); however, the rings are now composed of two types of metal ions: Mn and the doped transition metal ion M. In the supercell used for this work, for each dopant, two distinct local environments of transition metal ion rings can be found. One is composed of three doped M ions and three Mn ions alternatively arranged (Figure 1a). The other one is composed of one doped M ions and five Mn ions (Figure 1b). The corresponding Li diffusion barriers with different dopants (M = Ti, V, Cr, Fe, Co, Ni, and Cu) are calculated using the GGA method (Figure 2). The Li diffusion barrier in undoped Mn spinel²⁹ is also provided as the reference. As compared to the undoped Mn spinel material, the average Li diffusion barrier remains largely unchanged when Ni and Fe ions are present. The average diffusion barrier increases with Ti, V, Cr doping and decreases with Co and Cu doping. Specifically, when only one Cu or three Co ions appears in the ring, the Li diffusion barrier can be reduced to as low as 256 meV, respectively.

As was shown in previous work,²⁹ the introduction of the Hubbard U correction accurately captures the charge/discharge voltages of the Li-intercalation spinel materials. More importantly, different valence states of the same transition metal ions can be distinguished. Calculations using the GGA+U method are performed on LiCu_{1/2}Mn_{3/2}O₄ spinel with different Li concentrations. In the first model, where Cu ions occupy 4b octahedral sites and Li ions occupy 8c tetrahedral sites, the calculated average voltage of Li_xCu_{1/2}Mn_{3/2}O₄ (0.5 < x < 1) is 4.44 V, which is 7% higher than the experimental low



Figure 2. Li diffusion barriers in $LiM_{0.5}Mn_{1.5}O_4$ (M = Cr, Fe, Co, Ni, Cu, Mn) calculated by GGA.

voltage plateau. In addition, the calculated average voltage of $Li_x Cu_{1/2} Mn_{3/2} O_4$ (0 < x < 0.5) is 5.36 V, which is 9% higher than the experimental high voltage plateau. The projected electronic density of states (DOS) of Cu 3d orbitals in $Li_xCu_{1/2}Mn_{3/2}O_4$ (x = 1, 1/2, 0) are calculated and presented in Figure 3a-c, respectively. In the proposed spinel model, the octahedral crystal field splits the Cu 3d orbitals into two parts. d_{xy} , d_{yz} , and d_{xy} orbitals belong to the t_{2g} orbitals with lower energy levels, while d_{z2} and d_{x2-y^2} belong to the e_g orbitals with a higher energy level.³² Figure 3a shows the projected DOS of Cu ions in the fully lithiated phase $LiCu_{1/2}Mn_{3/2}O_{4.}$ Both spin-up and spin-down states of the three ${\rm t_{2g}}$ orbitals are below the Fermi energy, which means the t_{2g} orbitals are completely occupied. For eg orbitals, the d_{z2} orbital is occupied, but the spin-up state of the d_{x2-y2} orbital is above the Fermi energy, indicating that the d_{x2-y2} orbital is half empty. The DOS plot is consistent with the t_{2g} electron configuration of Cu2+ ions. The projected DOS of Cu ions in the half-delithiated phase Li1/2Cu1/2Mn3/2O4 (Figure 3b) and in the fully delithiated phase Cu_{1/2}Mn_{3/2}O₄ (Figure 3c) are generally the same minus trivial differences in shape. It suggests that Cu ions are in the same valence state in the two compositions. The spin-up states of the eg orbitals are completely empty, while all of the other electronic states are occupied. The DOS plots indicate the electron configuration of $t_{2g}^{6}e_{g}^{2}$ consistent with Cu³⁺ ions. On the basis of these results from first-principles calculation, the Cu valence in doped spinel $LiCu_{1/2}Mn_{3/2}O_4$ is Cu^{2+} at fully lithiated state. The Cu^{2+} ions can be oxidized to Cu^{3+} ions when one-half of the Li ions are extracted. Valence higher than 3+ cannot be obtained, and the calculated voltage of the Cu^{2+}/Cu^{3+} redox couple is 4.44 V. When more than one-half of the Li ions are extracted, the charge densities of oxygen ions change significantly, suggesting that the extra electrons may be provided by oxygen ions.

If one exchanges the sites of Cu ions with one-half of the Li ions, a defect spinel model can be created with tetrahedral Cu and octahedral Li included. For the defect spinel system, its total energy is 493 meV per formula higher than the perfect spinel system, and therefore the structure should be thermodynamically less stable. However, the experimental synthesis is often conducted at relatively high temperatures (>700 °C), and a certain amount of transition metal and lithium ion site mixing occurs. The change of Cu valence versus Li concentration is investigated



Figure 3. Calculated DOS of Cu in $\text{Li}_x \text{Cu}_{1/2} \text{Mn}_{3/2} O_4((a) x = 1, (b) x = 1/2, (c) x = 0).$

using a method similar to that described above. Tetrahedral Cu^{2+} can also be oxidized to Cu^{3+} , but no higher valence can be obtained. In the defect spinel model, Li ions in octahedral sites are preferred to be extracted first, and the calculated voltage is



Figure 4. X-ray diffraction patterns of LiNi_xCu_yMn_{2-x-y}O₄.

4.58 V. The calculated voltage step for removing the remaining tetrahedral Li is 4.99 V, a surprisingly high value.

As compared to the NiMn spinel LiNi_{1/2}Mn_{3/2}O₄, in which Ni²⁺ can be oxidized to Ni⁴⁺ providing two electrons per ion, the reversible capacity of Cu doped spinel may be reduced as Cu ions can only provide one electron per ion. However, when doped with a small amount of Cu, it is possible to lower the Li diffusion activation barriers so that better rate capability can be obtained. To further understand the crystal structure, electronic structure, and electrochemical properties in a new series of bidopant spinel materials, we successfully synthesized and studied the LiNi_x. Cu_yMn_{2-x-y}O₄ with different amount of dopants (x = 0, 0.05, 0.10, 0.25, and 0.5).

Chemical Composition Analysis. The atomic compositions of $\text{LiNi}_x\text{Cu}_y\text{Mn}_{2-x-y}O_4$ electrode materials calcinated at 800 °C were obtained from ICP-AES analysis. Although a nickel oxide and a copper oxide impurity phase appear, respectively, in $\text{LiNi}_{0.5}\text{Mn}_{1.5}O_4$ and $\text{LiCu}_{0.5}\text{Mn}_{1.5}O_4$ samples, the molar ratio of Li, Ni, and Mn is in good agreement with the theoretical ratio of all samples.

X-ray Diffraction of $\text{LiNi}_x\text{Cu}_y\text{Mn}_{2-x-y}\text{O}_4$. X-ray diffraction patterns for $\text{LiNi}_x \text{Cu}_y \text{Mn}_{2-x-y} O_4$ are depicted in Figure 4. Detailed Rietveld refinement fitting results of LiNixCuv- $Mn_{2-x-y}O_4$ are shown in the Supporting Information (Figures S1–S6). The spinel structure with space group $Fd\overline{3}m$ can be identified according to the indexed major peaks. In some samples, small amounts of impurities are present, such as nickel oxide in LiNi_{0.5}Mn_{1.5}O₄ and copper oxide in LiCu_{0.5}Mn_{1.5}O₄ as shown in the inset in Figure 4. The impurities may be tied with the solubility limit of nickel or copper in the spinel LiNix- $Cu_{\nu}Mn_{2-x-\nu}O_4$ as nickel or copper approach 0.5, which supports the findings of other research groups.^{12,33} It is also consistent with previous reports^{34,35} that oxygen deficiency is usually found in $LiCu_{0.5}Mn_{1.5}O_4$. The results show that the impurity phase can be eliminated by slightly changing the Ni-Mn stoichiometry (LiNi_{0.45}Mn_{1.55}O₄, Figure 4a) or by doping Cu into the NiMn spinel (Figure 4c-e).

According to Ohzuku et al., the integrated intensity ratios of the (400)/(311) peaks in spinel structure represent the extent of occupancy of the substituent ions on the tetrahedral site (8a).^{36,37} From Table 1, the integrated intensity ratio of (400)/(311) peaks generally decreases with the increase of Cu content. Exceptions are found in LiNi_{0.5}Mn_{1.5}O₄ and LiCu_{0.5}Mn_{1.5}O₄ where the oxide impurities are involved and may affect the related

Table 1. I(400)/(311) Integrated Intensity Ratios of XRD Spectrum of LiNi_xCu_yMn_{2-x-y}O₄

	I(400)/(311) integrated intensity
LiNi _{0.45} Mn _{1.55} O ₄	1.354
LiNi 0.5Mn1.5O4	1.278
LiCu _{0.05} Ni _{0.45} Mn _{1.5} O ₄	1.294
$LiCu_{0.1}Ni_{0.40}Mn_{1.5}O_4$	1.121
LiCu _{0.25} Ni _{0.25} Mn _{1.5} O ₄	0.854
$LiCu_{0.5}Mn_{1.5}O_4$	0.983

Table 2.	Rietveld	Refinement	Fitting	Results	of
LiNi _x Cu,	Mn_{2-x-y}	O ₄			

sample	
$LiNi_{0.5}Mn_{1.50}O_4 \\$	$a = 8.1809 \pm 0.0001$
	$Z(O) = 0.2625 \pm 0.0001$
NEO	$K_{wp} = 0.35, K_B = 2.32$
NIO	$a = 4.151/ \pm 0.0001$
	$K_{\rm wp} = 5.15, K_{\rm B} = 4.25$
$LiN_{0.45}Mn_{1.55}O_4$	$a = 8.1/39 \pm 0.0001$
	$Z(O) = 0.2623 \pm 0.0001$
	$R_{\rm wp} = 4.62, R_{\rm B} = 4.87$
LiNi _{0.45} Cu _{0.05} Mn _{1.5} O ₄	$a = 8.1693 \pm 0.0001$
	$Z(O) = 0.2618 \pm 0.0001$
	$n \text{ Cu (in Li site)} = 0.012 \pm 0.001$
	$R_{\rm wp} = 5.02, R_{\rm B} = 4.44$
$LiNi_{0.4}Cu_{0.1}Mn_{1.5}O_{4}$	$a = 8.1795 \pm 0.0001$
	$Z(O) = 0.2621 \pm 0.0001$
	n Cu (in Li site) = 0.040 \pm 0.001
	$R_{\rm wp} = 8.03, R_{\rm B} = 4.08$
LiNi _{0.25} Cu _{0.25} Mn _{1.5} O ₄	$a = 8.1991 \pm 0.0001$
	$Z(O) = 0.2633 \pm 0.0001$
	<i>n</i> Cu (in Li site) = 0.133 ± 0.010
	$R_{\rm wp} = 8.56, R_{\rm B} = 4.10$
LiCu _{0.5} Mn _{1.5} O ₄	$a = 8.2131 \pm 0.0001$
	$Z(O) = 0.2646 \pm 0.0001$
	$n \mathrm{Cu} \mathrm{(in Li site)} = 0.112 \pm 0.010$
	$R_{\rm wp} = 7.24, R_{\rm B} = 5.62$

peak intensities. The decrease of the integrated intensity ratio of (400)/(311) peaks indicates that the occupancy of the substituent Cu in the tetrahedral sites (8a) increases when the Cu amount increases.

For LiNi_{0.5-y}Cu_yMn_{1.5}O₄ samples, refinements are performed and Rietveld fitting results of LiNi_xCu_yMn_{2-x-y}O₄ are shown in Table 2, and the trend of lattice parameters change with respect to *y* is depicted in Figure 5. From the plot, the lattice parameter decreases from y = 0 to y = 0.05, and then increases with the increase of *y*. The trend generally agrees with the results reported in previous literature. The site refinements also suggest that some Cu ions occupy the 8a tetrahedral sites instead of the 16d octahedral sites.

Scanning Electron Microscopy (SEM). SEM was performed to examine the particle size and morphologies of LiNi_{x-} $\text{Cu}_y\text{Mn}_{2-x-y}\text{O}_4$ after 800 °C calcination. Figure 6a–c shows that in samples with no Cu or small amounts of Cu doping,



Figure 5. Lattice parameters of $LiNi_{0.5-x}Cu_xMn_{1.5}O_4$ (*x* = 0, 0.05, 0.1, 0.25, 0.5).



Figure 6. FESEM images of $LiN_{1x}Cu_yMn_{2-x-y}O_4$: (a) $LiN_{10,45}Mn_{1.55}O_4$, (b) $LiN_{10,5}Mn_{1.5}O_4$, (c) $LiN_{10,45}Cu_{0.05}Mn_{1.5}O_4$, (d) $LiN_{10,4-}Cu_{0.1}Mn_{1.5}O_4$, (e) $LiN_{10,25}Cu_{0.25}Mn_{1.5}O_4$, and (f) $LiCu_{0.5}Mn_{1.5}O_4$.

spherical particles with 100 nm diameter were formed. It is also noted that when the amount of doped Cu increases (Figure 6d–f), the particle size increases and the shape of the particles becomes more faceted. For the LiCu_{0.5}Mn_{1.5}O₄ sample, the particle size is in the range of 300–500 nm, while the particle size for NiMn spinel sample is in the range of 50–100 nm.



Figure 7. (a) Charge curves of $LiNi_xCu_yMn_{2-x-y}O_4$. (b) Discharge curves of $LiNi_xCu_yMn_{2-x-y}O_4$. Voltage window of 5.0-3.0 V was used.

Electrochemical Properties of $\text{LiNi}_x\text{Cu}_y\text{Mn}_{2-x-y}\text{O}_4$. The electrochemical properties of $LiNi_xCu_yMn_{2-x-y}O_4$ (0 < x < 0.5, 0 < y < 0.5) were investigated in lithium half-cells. The charge/discharge profiles between 3.0 and 5.0 V are shown in Figure 7a and b. The cells were tested with a constant current of 0.1 mA/cm² applied to the cells. The LiNi_{0.45}Mn_{1.55}O₄ example exhibits the highest reversible capacity of 139.8 mAh/g, which is about 10 mAh/g higher than that of $LiNi_{0.5}Mn_{1.5}O_4$. The small capacity reduction in LiNi0.5Mn1.5O4 sample is attributed to the presence of NiO impurity. These two cells both have two distinct voltage plateaus around 4.7 V, which corresponds to the Ni²⁺-Ni⁴⁺ redox potential. A relatively small plateau can be found in the region around 4.0 V. This is attributed to the Mn³⁺-Mn⁴⁺ redox couple. Previous work has shown that calcination temperature may cause oxygen loss and can lower the average oxidation state of Mn and introduce Mn³⁺ ions.¹⁰ For the LiNi_{0.45}Mn_{1.55}O₄ sample, the average oxidation state of manganese decreases further due to the decrease of Ni/Mn ratio; therefore, the capacity of the LiNi_{0.45}Mn_{1.5}O₄ sample at the 4.0 V region is larger than that of the LiNi_{0.5}Mn_{1.5}O₄ sample. When Cu ions are doped, the voltage plateau shifts from 4.7 to

Table 3. Charge Capacity (mAh/g) of $LiNi_xCu_yMn_{2-x-y}O_4$ at Low Voltage Range

	capacity (mAh/g) of 4 V	capacity (mAh/g) from 4.2 to 4.6 V
LiNi _{0.45} Mn _{1.55} O ₄	23.18	0.00
LiNi _{0.5} Mn _{1.5} O ₄	17.63	0.00
LiCu _{0.05} Ni _{0.45} Mn _{1.5} O ₄	21.27	0.00
LiCu _{0.1} Ni _{0.40} Mn _{1.5} O ₄	21.31	10.54
LiCu _{0.25} Ni _{0.25} Mn _{1.5} O ₄	23.12	20.83
$LiCu_{0.5}Mn_{1.5}O_4 \\$	23.14	28.46



Figure 8. Rate capability of $LiNi_xCu_yMn_{2-x-y}O_4$.

4.95 V, and a new plateau appears between 4.2 and 4.6 V. When the doped Cu amount increases, the total capacity decreases, while the capacity between 4.0 and 4.6 V increases. Capacities contributed by the plateau around 4.0 V and by the plateau between 4.2 and 4.6 V in different materials are listed, respectively, in Table 3.

Rate Capability Testing. To study the rate capability of LiNi_xCu_yMn_{2-x-y}O₄ (0 < x < 0.5, 0 < y < 0.5), electrodes were made with similar loading of active materials in each cell (about 20 mg of active material/ cm^2). For each material, the cells were charged to 5.0 V at constant low current rate (C/20) and discharged to 3.0 V at various current rates (C/20, C/10, C/5, and C/2). The measured discharge capacities are shown in Figure 8. For LiCu_{0.25}Ni_{0.25}Mn_{1.5}O₄ and LiCu_{0.5}Mn_{1.5}O₄, the discharge capacities are highly retained when tested at a high discharge rate, while for Cu-free NiMn spinel samples the discharge capacity drops significantly at a high discharge rate. Note that the rate capability tests of LiCu_{0.25}Ni_{0.25}Mn_{1.5}O₄, LiNi_{0.5}Mn_{1.5}O₄, and LiNi_{0.45}Mn_{1.55}O₄ were also performed using a set of electrodes with much lower loading of active materials (about 10 mg active material/ cm^2) in each cell. The results are shown in Supporting Information Figure S7. A similar trend is seen in that LiCu_{0.25}Ni_{0.25}Mn_{1.5}O₄ has better rate capability than do the Cu-free NiMn spinel materials.

X-ray Absorption Near Edge Structure (XANES). X-ray absorption near edge structure (XANES) measurement was performed on the $LiCu_{0.25}Ni_{0.25}Mn_{1.5}O_4$ cathode material to study the active redox couple(s) in different voltage range.



Figure 9. Charge curve of ${\rm LiNi}_{0.25}{\rm Cu}_{0.25}{\rm Mn}_{1.5}{\rm O}_4$ for XANES experiment.



Figure 10. (a) The Cu K-XANES spectra of $LiCu_{0.25}Ni_{0.25}Mn_{1.5}O_4$ measured as a function of voltage. (b) Second-order derivative of Cu K-edge XANES spectra of $LiCu_{0.25}Ni_{0.25}Mn_{1.5}O_4$ measured as a function of voltage.

Figure 9 shows the charge curve for a $LiCu_{0.25}Ni_{0.25}Mn_{1.5}O_4$ half cell that is used for in situ XAS experiment. The Cu, Ni, and Mn K-edge XANES spectra of $LiCu_{0.25}Ni_{0.25}Mn_{1.5}O_4$ measured as a function of voltage are shown in Figures 10–12. In each figure,



Figure 11. (a) The Ni K-XANES spectra of $LiCu_{0.25}Ni_{0.25}Mn_{1.5}O_4$ measured as a function of voltage. (b) Second-order derivative of Ni K-edge XANES spectra of $LiCu_{0.25}Ni_{0.25}Mn_{1.5}O_4$ measured as a function of voltage.

(a) is the original spectra, and its second-order derivative is shown in (b) to investigate the distinct energy shifts. The spectra of related oxides are also provided as references for comparison. The pre-peak region of K-edge absorption peak of pristine sample is in the same position as the pre-edge peak for the CuO reference. This indicates that the oxidation states of Cu in the two materials are the same; thus Cu is +2 in the pristine LiCu_{0.25}Ni_{0.25}Mn_{1.5}O₄. During the charging process, the position of Cu K-edge absorption peak remains unchanged until the voltage reaches 4.2 V. After that, the peak begins to shift to the higher energy side. The shift stops at around 4.7 V, and no significant energy shift can be observed at high voltage region between 4.7 and 5.0 V. The Cu spectra show that the Cu valence only changes between 4.2 and 4.7 V. Similar methodology was applied on Ni and Mn spectra. Ni is Ni²⁺ in the pristine sample, and it starts to be oxidized from 4.7 V, and the K-edge energy shift continues until 4.9 V is reached. The Mn valence is +4 in the pristine sample, and it remains unchanged during the entire charging process.

Ex Situ XRD Measurements. Ex situ XRD patterns for LiNi_{0.25}Cu_{0.25}Mn_{1.5}O₄ at different states of charge were measured between 4.2 and 5.0 V, to investigate the possible phase transition during Li deintercalation. Figure 13 shows the XRD



Figure 12. (a) The Mn K-XANES spectra of $LiCu_{0.25}Ni_{0.25}Mn_{1.5}O_4$ measured as a function of voltage. (b) Second-order derivative of Mn K-edge XANES spectra of $LiCu_{0.25}Ni_{0.25}Mn_{1.5}O_4$ measured as a function of voltage.

patterns of the LiNi_{0.25}Cu_{0.25}Mn_{1.5}O₄ sample at different charged voltages during the second charging process. At low voltages between 4.2 and 4.6 V, the diffraction peaks shift to higher angles with increasing voltage, indicating that the lattice parameters are decreasing. However, at high voltages, no shifts in the diffraction peaks were observed, indicating the lattice parameters remain mostly constant. Although the amount and direction of shift may change with state-of-charge, no additional peaks appear during the entire charging process, suggesting the reaction remains single phase throughout the charging.

Potentiostatic Intermittent Titration Technique (PITT). The potentiostatic intermittent titration technique was performed to identify the lithium diffusion coefficient associated with the high voltage plateau observed in the second charging cycle of the electrochemical curve. The diffusion coefficient can be extracted from the current response assuming a standard Cottrell solution for the lithium flux at the surface.³⁸ Figure 14a shows the PITT profile for LiNi_{0.25}Cu_{0.25}Mn_{1.5}O₄ sample between 4.5 and 4.9 V. Within this region, the current decays quickly at first, then takes 7 h to reach the limit value. The trends are consistent when different sets of samples are tested. Figure 14b shows the variation of chemical diffusion coefficients of Li ions in LiNi_{0.45}Mn_{1.55}O₄, LiNi_{0.5}Mn_{1.5}O₄, and



Figure 13. The XRD pattern of the LiNi $_{0.25}$ Cu $_{0.25}$ Mn $_{1.5}$ O $_4$ sample at different voltages during the second charge process.

 $LiCu_{0.25}Ni_{0.25}Mn_{1.5}O_4$. The lithium diffusion coefficient is determined from the following equation where *I* is the current and L is the particle size. *L* is estimated from SEM images (Figure 6).

$$\tilde{D}_{\rm Li} = -\frac{\mathrm{d}\ln(I)}{\mathrm{d}t}\frac{4L^2}{\pi^2}$$

The diffusion coefficient of lithium, D_{Li} , can be calculated from the slope of the linear region in the plot of $\ln I(t)$ versus t. D_{Li} changes with the lithium content. This trend shown in Figure 14b is similar to previous literature, but the values of the diffusion coefficient from our results are 1–2 orders of magnitude smaller than those obtained by Xia et al.³⁹ The main source of discrepancy may come from the errors in estimiation of the diffusion length for powered composite electrode as oppose to thin film electrode. The minimum of D_{Li} appears between 4.7 and 4.8 V. These coincide with the oxidation of Ni²⁺ to Ni⁴⁺. Among the three samples, D_{Li} of $\text{LiCu}_{0.25}\text{Ni}_{0.25}\text{Mn}_{1.5}\text{O}_4$ is 1 order of magnitude higher than that of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{LiNi}_{0.45}$ -Mn_{1.55}O₄.

General Discussion on LiNi_xCu_yMn_{2-x-y}O₄. 1. The Crystal Structure of $LiNi_xCu_yMn_{2-x-y}O_4$. Although the results from first principles calculations performed at 0 K suggest that tetrahedral Cu is energetically less favored, results from XRD indicate that Cu ions do occupy tetrahedral sites in materials synthesized at high temperature. According to Shannon et al., the effective ionic radius of Cu^{2+} (0.57 Å) is slightly smaller than that of Li^+ (0.59 Å) if the atoms are tetrahedrally coordinated.⁴⁰ When a small amount of Cu ions are doped into the NiMn spinel materials, most of the Cu²⁺ ions may occupy the tetrahedral sites, leading to a smaller lattice parameter than undoped materials. However, when more Cu ions are doped, Cu²⁺ will also occupy the octahedral sites that were originally occupied by Ni^{2+} ions. Because the effective ionic radius of octahedral Cu^{2+} (0.73 Å) is larger than that of octahedral Ni^{2+} (0.69 Å),³⁹ the decrease of lattice parameter is gradually compensated, and the lattice parameters will finally increase with the increase of doped Cu amount.

2. The Voltage Profile and Capacities of LiNi_xCu_yMn_{2-x-y}O₄. Although in previous research,^{13,14} the high voltage plateau of 4.95 V was attributed to the oxidization of Cu²⁺ to Cu³⁺, our results show that this may not be true. The calculated voltage corresponding to the oxidization from Cu²⁺ to Cu³⁺ in



Figure 14. (a) PITT profile for LiNi $_{0.25}$ Cu $_{0.25}$ Mn $_{1.5}$ O₄ sample. (b) Diffusion coefficient of LiNi $_{0.45}$ Mn $_{1.55}$ O₄, LiNi $_{0.5}$ Mn $_{1.5}$ O₄, and LiNi $_{0.25}$ -Cu $_{0.25}$ Mn $_{1.5}$ O₄.

nondefect spinel LiCu_{0.5}Mn_{1.5}O₄ is only 4.44 V, much lower than the experimentally measured high voltage plateau at around 4.95 V, but quite close to the low voltage step at around 4.2 V. Cu³⁺ ions cannot be further oxidized to higher valences, and this conclusion is also supported by our XANES results obtained from LiNi_{0.25}Cu_{0.25}Mn_{1.5}O₄, in which Cu ions are only oxidized at low voltages between 4.2 and 4.7 V. Mn ions are inactive, and the high voltage plateau is caused by the Ni²⁺ oxidization, together with possible oxygen charge-loss mechanism as suggested by first principles computation in this work, but cannot be detected by XANES. The cycling performance of these samples is shown in Supporting Information Figure S8. The 4.95 V plateau is reversible, and there is no cycling stability issue for these materials.

In regards to the electrochemical charge –discharge results of $\text{LiNi}_x \text{Cu}_y \text{Mn}_{2-x-y} O_4$, the capacity contributed by the second plateau between 4.2 and 4.6 V increases with the increase of doped Cu amount (Table 3). This trend is consistent with the above conclusion, as more Cu^{2+} ions are present and oxidized to Cu^{3+} ions. However, when more Cu ions are doped, the total capacity of $\text{LiNi}_x \text{Cu}_y \text{Mn}_{2-x-y} O_4$ keeps on decreasing. The capacity of $\text{LiCu}_{0.5} \text{Mn}_{1.5} O_4$ is just slightly higher than one-half of the capacities of undoped NiMn spinel materials. It suggests that in Cu-doped NiMn spinel, not all Li ions can be electrochemically extracted. Two reasons may be attributed to this phenomenon. (1) As Cu ions can only provide one electron per

atom, extra electron sources are not absolutely confirmed from experiments. Calculation results suggest a possibility that extra electrons may be extracted from oxygen ions, although further investigation is necessary to confirm the exact electron sources. (2) The first principles calculations show that when tetrahedral Cu ions are presented, Li in octahedral sites prefer to be extracted first. However, with tetrahedral Li and Cu ions blocking the diffusion paths, some octahedral Li ions may never be extracted. On the other hand, it is possible that voltage plateaus higher than 5 V may exist but cannot be obtained due to the cut off voltage limit imposed by the electrolyte decomposition.

3. Rate Capabilities of $LiNi_xCu_yMn_{2-x-y}O_4$. Although the reversible capacity is partially affected, a suitable amount of Cu doping in NiMn spinel may significantly improve the rate capability of the materials. As shown in Figure 8, LiCu_{0.25}-Ni_{0.25}Mn_{1.5}O₄ shows the best rate performance among all of the materials. The discharge capacity of LiNi_{0.25}Cu_{0.25}Mn_{1.5}O₄ at C/20 is around 95 mAh/g, and 97% of them can be retained at C/2. On the other hand, the discharge capacity of LiNi_{0.5}M $n_{1.5}O_4$ at C/20 is 122 mAh/g, but it drops to 76 mAh/g at C/2. The improvement of rate performance of LiNi_{0.25}Cu_{0.25}Mn_{1.5}O₄ may come from two major sources. (1) The ionic conductivity of the materials is improved by the enhancement of Li mobility. As shown in Figure 14b, the measured lithium diffusion coefficient of LiCu_{0.25}Ni_{0.25}Mn_{1.5}O₄ is significantly larger than that of LiNi_{0.5}Mn_{1.5}O₄ or LiNi_{0.45}Mn_{1.55}O₄. A possible reason is that the cation distribution of LiNi_xCu_yMn_{2-x-y}O₄ varies with the change of cation composition. When the amount of Cu doping is in a certain range, the corresponding cation arrangements can provide more local environments that are similar to Figure 1b, and therefore may significantly reduce the Li diffusion barriers and improve the overall Li mobility. (2) The LiCu_{0.25}Ni_{0.25}-Mn_{1.5}O₄ system experiences smaller strains during the Liextraction than the nondoped NiMn spinel. For LiNi_{0.5}Mn_{1.5}O₄ and LiMn₂O₄, a second or third cubic phase will form during the charging stage.⁴¹ As the coexistence of two phases usually causes lattice mismatch, high stress and strain may be introduced into the nondoped NiMn spinel and affect the stabilities of the systems, especially at high rate. For LiCu_{0.25}Ni_{0.25}Mn_{1.5}O₄, however, the ex situ XRD results (Figure 13) show that only single cubic phase is present during the charging stage. No phase transition occurs inside the materials, as the experienced strains are much less and the system is therefore more stable at high rate. Besides the above two sources, the effect of electrical conductivity may also play a role. It was already reported by Kunduraci et al.¹⁰ that cation ordered P4₃32 spinel exhibits less capacity retention than does the disordered spinel at fast discharge rates. This phenomenon is attributed to the higher electronic conductivity of the disordered spinel. Molenda et al.¹⁵ also showed that the electrical conductivity of LiCu_xMn_{2-x}O₄ would increase with the Cu amount. There are factors that may negatively affect the rate capability of the materials as well, such as the increased particle sizes for Cu-doped NiMn spinel and the presence of unmovable tetrahedral Cu that may block the Li diffusion channels. From the experimental results obtained in this work, however, these factors can be compensated by the positive effects discussed previously.

CONCLUSION

In this work, a series of bidoped spinel oxides of LiNi_{x} - $\text{Cu}_{v}\text{Mn}_{2-x-v}O_{4}$ (0 < x < 0.5, 0 < y < 0.5) have been studied.

Their crystal structure, electronic structure, and electrochemical properties are compared. A new explanation of the voltage profile for $LiNi_xCu_yMn_{2-x-y}O_4$ is proposed, supported by the results from first principles computation, and confirmed by electrochemical property measurement and in situ XAS experiment. We have shown that Ni, Cu, and Mn are 2+, 2+, and 4+, respectively, in the pristine sample. Cu cannot be further oxidized to Cu^{4+} , and the plateau at 4.95 V originates from extra electrons possibly provided by oxygen ions. Li diffusion activation barriers of $LiM_{1/2}Mn_{3/2}O_4$ (M = Ti, V, Cr, Fe, Co, Ni, and Cu) are calculated. The results show that different dopants can have significant effects on the Li diffusion barriers. Although the capacity of the doped spinel materials decreases with the increasing doped Cu amount, LiCu_{0.25}Ni_{0.25}Mn_{1.5}O₄ spinel oxide exhibits higher capacity than does undoped LiNi05Mn1.5O4 spinel at high rates. The good rate capability of LiCu_{0.25}Ni_{0.25}-Mn_{1.5}O₄ spinel oxide is attributed to the single phase reaction during charging, the lower Li diffusion barrier induced by Cu doping, and possibly higher electronic conductivity contributed by Cu doping.

ASSOCIATED CONTENT

Supporting Information. Detailed Rietveld refinement fitting results of $\text{LiNi}_x \text{Cu}_y \text{Mn}_{2-x-y} O_4$, rate testing with lower loading, and cycling performance (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

M.-C. Yang acknowledges the financial support from Florida Energy System Consortium (FESC) through University of Florida and the assistance from C. R. Fell and J.-W. Shin. B. Xu acknowledges the support by the U.S. Department of Energy, Office of Basic Energy Sciences under Award Number DE-SC0002357. B. Xu thanks S. Curtarolo and co-workers for providing aconvasp code. Y. S. Meng acknowledges the support as part of NECCES, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Basic Energy Sciences under Award Number DE-SC0001294. We thank the Major Analytical Instrumentation Center at the University of Florida for research facilities. XAS data were obtained at the National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan.

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