Evaluation of Low-cost Natrochalcite $\text{Na}[\text{Cu}_2(\text{OH})(\text{H}_2\text{O})(\text{SO}_4)_2]$ as an Anode Material for Li- and Na-ion Batteries

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ABSTRACT: Here we report the evaluation of natrochalcite ($\text{Na}[\text{Cu}_2(\text{OH})(\text{H}_2\text{O})(\text{SO}_4)_2]$), an anionic layered structure $[\text{Cu}_2(\text{OH})(\text{H}_2\text{O})(\text{SO}_4)_2]^-$ charge-balanced by Na^+ , as an anode material for both Li- and Na-ion batteries. It delivers 224 mAh/g and 175 mAh/g in the first discharge in the Li^+ - and Na^+ -cells respectively, and decomposes to form amorphous matrixes during this step. In the subsequent charge, the original layered structure is unusually partially recrystallized back from the matrixes, resulting in 53 mAh/g and 35 mAh/g discharge capacities in the second discharge respectively. In subsequent cycling, Li^+ in the electrolyte is found to replace the original Na^+ during cycling in the Li^+ -cell and the electrode in the Li^+ -cell demonstrates better capacity retention rates than that in the Na^+ -cell, possibly due to Li^+ being smaller than Na^+ and thus decomposition-recrystallization cycles being more reversible during cycling in the Li^+ -cell.

Keywords: natrochalcite, anode, conversion electrode, sodium ion battery, lithium ion battery

1. Introduction

As rechargeable lithium-ion batteries (LIBs) have been widely used in powering consumer electronics and electric vehicles [1], they have also been considered promising candidates for large-scale grid applications [2]. The vast needs for rechargeable batteries make it vital to make alternative electrodes and batteries at low cost. Therefore, rechargeable sodium-ion batteries (SIBs) have gained momentum toward commercialization due to their performances comparable to those of LIBs and the abundance and low-cost of sodium resources [3], while compounds containing earth-abundant elements (e.g. Fe [4] and Cu [5]) have received extensive interest as electrode materials for both LIBs and SIBs.

Meanwhile, compounds containing SO_4^{2-} have been extensively researched since they tend to demonstrate higher operation potentials than oxides and other salts such as phosphates and molybdates [6–8]. While $\text{Fe}^{3+/2+}$ - SO_4^{2-} -based compounds have been widely investigated as cathodes toward Li^+ - and Na^+ insertion-extraction in LIBs and SIBs [8–13], less studied Cu^{2+} - SO_4^{2-} -based compounds were revealed to have more versatile operation potentials. For example, the discharge potentials of one-dimensional (1D) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ [14] and the brochantite $\text{Cu}_4(\text{SO}_4)(\text{OH})_6$ of 3D structure [15] are around 3.0 V and 1.6 V (vs. Li^+/Li) respectively, suggesting the potential of tuning the operation potentials via tuning the chemical compositions and structures. However, both compounds demonstrate fast capacity decay during cycling when used as electrode materials for LIBs. Meanwhile, the kröhnkite $\text{Na}_2\text{Cu}(\text{SO}_4)_2(\text{H}_2\text{O})_2$ [16] of 1D crystal structure and 3D CuSO_4 and $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ [14] were revealed to demonstrate very limited Na^+ or Li^+ insertion-extraction when evaluated as cathode materials.

In this paper, we report a new synthetic route to and electrochemical activities of natrochalcite ($\text{Na}[\text{Cu}_2(\text{OH})(\text{H}_2\text{O})(\text{SO}_4)_2]$) toward Li^+ and Na^+ insertion-extraction. This synthetic route is more

facile than reported syntheses of pure natrochalcite [17–19]. While revealed as a poor cathode material for LIBs and SIBs, this compound represents the first 2D-structured and bimetallic copper hydroxysulfate that delivers reasonable capacities as anode materials for both LIBs and SIBs. In comparison to previously evaluated Cu^{2+} - SO_4^{2-} -based compounds, it demonstrates significantly improved capacity retention rates toward Li^+ and Na^+ insertion-extraction. The mechanisms responsible for the similarities and differences of the cycling and rate performances as an anode material for LIBs and SIBs are also investigated.

2. Experimental Methods

2.1. Materials

EtOH (99.8%) and DMSO (99%) were purchased from Tianjin Fuyu Fine Chemical Co., Ltd. Na_2SO_4 (99%) was purchased from Tianjin Bodi Chemical Co., Ltd. CuSO_4 (98%) was purchased from Beijing Chemical Factory. Terephthalic acid (99%) was purchased from Aladdin. All chemicals including solvents were used as received.

2.2. Syntheses of $\text{Na}[\text{Cu}_2(\text{OH})(\text{H}_2\text{O})(\text{SO}_4)_2]$

0.06 mmol Na_2SO_4 , 0.08 mmol CuSO_4 , and 0.03 mmol terephthalic acid were added to 3.0 mL mixture of $\text{H}_2\text{O}/\text{EtOH}/\text{DMSO}$ ($v/v/v = 2/1/3$) which was then stirred for 2 mins at room temperature to afford a suspension. Then the suspension was heated at 115 °C for 2 days in a 25 mL autoclave liner, and let slowly cooled down. The obtained green crystals were washed with DMSO and then let dry in air. Yield: 75.0% (based on Cu).

2.3. X-ray structure determination

A single crystal of this compound was selected and attached to a quartz fiber for single-crystal X-ray analysis. Intensity data were measured at 293(2) K on a Bruker SMART APEX II CCD area detector system and corrected for absorption effects using the multi-scan technique (SADABS)

[20]. Structure was solved and refined using the Bruker SHELXTL (Version 6.1) Software Package [21]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to OH⁻ and H₂O were located from the difference Fourier map and refined with restrained O–H distance. Important crystal and structure refinement data are given in Table 1.

2.4. Materials characterizations

Powder X-ray powder diffraction patterns were collected with Rigaku MiniFlex Desktop X-ray diffractometer using Cu-K α radiation ($\lambda = 1.54056 \text{ \AA}$) at 30 kV and 15 mA under ambient conditions. A continuous scan mode was used to collect the diffraction data from 10° to 50° at a speed of 0.5°/min. Raman spectra were measured using a Lab Raman HR Evolution spectrometer (Horiba JY, France) with a solid state 633 nm laser at room temperature. The morphologies were investigated by an FEI Nova NanoSEM scanning electron microscope (SEM) equipped with a field emission gun operated at 10 kV. To minimize charging problems, samples for SEM were coated with thin Au layers. High-resolution transmission electron microscopy (HRTEM) image was obtained from FEI Titan 80-300 TEM equipment. X-ray photoelectron spectroscopy (XPS) surface analysis was done using PHI VersaProbe XPS instrument and the peak positions were corrected using C1s as the internal reference.

2.5. Electrochemical Measurements

The working electrode was prepared by mixing the compound, super P carbon black, and polyvinylidene fluoride (PVDF) in a weight ratio of 80:10:10 under Ar atmosphere. The resulting slurry was then cast onto an Al foil which was then dried in vacuum at room temperature overnight. Then, the electrode was pressed at ~ 20 MPa using a PHI manual compression press and punched into electrodes of ~ 8 mm in diameter. The loading and thickness of each electrode was 1–2 mg cm⁻² and ~ 50 μ m, respectively. 2032-type coin cells were assembled in an MBraun glove box

(O₂, H₂O < 2 ppm) while a Celgard 3501 microporous membrane was used as the separator. Cyclic voltammetry was performed on a Solartron SI 1287 Electrochemical Interface at a scan rate of 0.05 mV/s while galvanostatic tests were performed on a BT 2000 battery tester. For testing as electrodes for LIBs, 1M LiPF₆ in ethylene carbonate, dimethyl carbonate and ethylmethyl carbonate (EC/DMC/EMC, v/v/v = 1:1:1) and Li foil were used as the electrolyte and counter electrode. For testing as electrodes for SIBs, 1M NaClO₄ in EC/DMC (w/w = 1:2) and Na foil were used as the electrolyte and counter electrode. For *ex-situ* X-ray diffraction analysis of electrodes during cycling, button cells were disassembled and thoroughly washed with ethanol and dried at ambient conditions. The electrochemical impedance spectroscopy (EIS) measurements were carried out over the frequency range of 1M Hz to 0.01 Hz, with an amplitude of 5 mV using a CHI660D electrochemical analyzer.

3. Results and Discussion

3.1. Synthesis and crystal structure of natrochalcite

It is worthy to note that this compound could not be obtained in the absence of terephthalic acid under the same reaction condition using water as the solvent. In comparison, in the absence of terephthalic acid the reaction between Na₂SO₄ and CuSO₄ in H₂O/EtOH/ below 80 °C led to the formation of the Kröhnkite Na₂Cu(SO₄)₂·2H₂O [16]. Furthermore, our synthetic route is more facile than previously reported routes. For example, in a procedure developed by G. Giester *et al.* the hydrothermal reaction between CuO and Na₂SO₄ at 180–240 °C in the presence of small amount of H₂SO₄ for several days led to the formation of a few mixed phases that contained natrochalcite [18]. For another example, in another procedure developed by G. Chevrier *et al.* the low-hydrothermal synthesis took two to three months [19]. Therefore, both terephthalic acid and

Na^+ could serve as structure-directing agents (SDAs) in the formation of this 2D anionic layered structure.

In the crystal structure, each Cu^{2+} is six-coordinated by four O atoms from four SO_4^{2-} and two O atoms from one OH^- and one H_2O while two neighbouring Cu^{2+} are linked by two SO_4^{2-} and one OH^- or H_2O to afford chains along the b direction (Fig. 1a). Each 4-coordinated SO_4^{2-} uses two O atoms to coordinate two Cu^{2+} in one chain respectively, uses a third O atom to further bridge another two Cu^{2+} in a neighbouring chain, and leaves the fourth O atom uncoordinated. Thus neighbouring chains are connected into anionic $[\text{Cu}_2(\text{OH})(\text{H}_2\text{O})(\text{SO}_4)_2]^-$ layers extending along the ab plane (Fig. 1b) that are separated and charge-balanced by Na^+ (Fig. 1c). Each Na^+ is weakly coordinated in a distorted square prism by eight O atoms from six SO_4^{2-} (Fig. 1d) with the Na–O bond lengths ranging from 0.2574(3) nm to 0.2638(3) nm. Both the Na^+ -framework weak interactions and interlayer spaces could allow the Na^+ movement and further insertion-extraction of Li^+ and Na^+ .

The experimental powder X-ray powder diffraction (PXRD) pattern matched that of the simulated (Fig. 2a). The peak at 38.10° , which was too weak to be seen in the simulated PXRD pattern, showed up in the experimental PXRD pattern. Such difference of relative peak intensities is quite common for polycrystalline samples [22] and well explained [23]. The additional peaks at 18.07° and 29.62° in experimental PXRD pattern may come from preferred orientations from the sample preparation [14] or tiny amount of impurities. As shown later, both peaks disappeared in the PXRD patterns of as-made electrodes, indicating they may come from preferred orientations of samples. The experimental Raman spectrum of the powder matched the standard [24] (Fig. 2b), further confirming the pure phase of the product. The bands at 1049 and 998 cm^{-1} were attributed to the antisymmetric and symmetric stretching modes of SO_4^{2-} , the bands at 636 and 607 cm^{-1} to

the out-of-plane bending modes and the bands at 466, 445, 429 and 402 cm^{-1} to the in-plane bending modes of SO_4^{2-} [24]. Scanning electron microscope (SEM) analysis of the powder before being mixed with binders and conductors showed that the particles before electrode fabrication range from submicrometer to a few micrometers in size (Figure 2c). In the high-resolution transmission electron microscope (HRTEM) image, the d -spacing of 0.46 nm could be indexed to the (200) planes.

3.2 Electrochemical performances of natrochalcite as an anode material in Li^+ -cell

Since the assembled cell displayed an open circuit voltage (OCV) at ~ 2.65 V, galvanostatic charge-discharge cycling tests were run in the range of 0.5 V to 2.7 V at the current of 2.5 mA/g (Fig. 3a). This compound delivered a negligible capacity from 2.65 V to 1.80 V, 55 mAh/g from 1.80 V to 0.90 V. Then there were two quasi-plateaus at 0.90 V and 0.60 V respectively both of which were combined to contribute the majority discharge capacity, leading to 224 mAh/g in total during the first discharge. The second, fifth, and tenth discharge capacities were 53, 51, and 52 mAh/g respectively, and all of them were $\sim 24\%$ of the first discharge capacity. All the charge capacities from the first to the tenth cycle were ~ 60 mAh/g and quite close to each other.

To understand the cycling performances, cyclic voltammetry (CV) analysis was performed (Fig. 3b). During the first negative scan from 2.4 V, the two irreversible cathodic peaks at 1.20 V and 0.69 V should correspond to the reduction of Cu^{2+} to Cu^+ and then to Cu [25], possibly accompanied by the electrochemical formation of a solid electrolyte interphase (SEI) layer and the structural decomposition [26–27]. The current at 1.20 V being significantly larger than that at 0.69 V also indicates the copper stripping process. The cathodic peak at 1.20 V should correspond to the quasi plateau at 0.90 V in Fig. 3a while the potential difference could be due to different discharge rates. The cathodic peak at 0.69 V should correspond to the quasi-plateau at 0.60 V in

Fig. 3a. In subsequent scans, the first to the fifth positive scans almost overlapped with broad anodic shelves stretching from 0.60 V to 1.20 V possibly due to some structural reorganization and the charge process from other species [28]; the second to the fifth negative scans overlapped with sharp cathodic peaks near 0.50 V. The CV analysis results match the galvanostatic cycling profiles in Fig. 3a.

To further understand the electrochemical performances, *ex-situ* PXRD analysis was used to compare the electrode before, during, and after cycling (Fig. 4a). The major (001) peaks at $2\theta = 13.58^\circ$ correspond to the packing of the layers along the *c* axis, and their peak intensities were normalized by the masses of the starting compounds for quantitative analysis. The PXRD pattern of the pristine electrode maintained major peaks from the starting compound while some peaks' relative intensities changed (Fig. 2 and Fig. 4a), indicating the maintenance of the compound's framework and possible accompanied structural rearrangement [14] during electrode fabrications.

During the first discharge, the layered structure was maintained when the electrode was discharged to 0.85 V. In this stage, two peaks at $2\theta = 35.54^\circ$ and 42.10° neither match the (111) and (200) peaks $2\theta = 36.4^\circ$ and 42.3° of cubic Cu_2O (JCPDF 005-0667) [29] nor match any peaks of hexagonal Cu_2S (JCPDS 026-1116) [30]. Instead, these two peaks come from the layered structure, and their increased intensities should be due to the structural rearrangement accompanying the Li^+ -insertion. When the electrode was further discharged to 0.50 V, the resultant electrode was found to be amorphous (Fig. 4a). Interestingly, after the subsequent charge, the starting structure was recrystallized back to a significant extent though some peaks' relative intensities (e.g. 13.58° vs. 39.18°) changed possibly due to structural rearrangement (Fig. 4a). The peak intensity at $2\theta \approx 13.58^\circ$ from the electrode after the first cycle was c.a. 25% of that from the as-made electrode. This percentage is close to the ratio of the second discharge capacity versus the

first discharge capacity. Such reversible decomposition-recrystallization process continued during the second discharge-charge cycle at different rates (Fig. 4a). The peak at $2\theta \approx 13.58^\circ$ was found to slightly shift to 13.64° ($\Delta\theta = 0.06^\circ$, Fig. 4b), indicating the decrease of the crystal lattice which should be due to the partial or complete replacement of Na^+ by Li^+ during cycling.

To further reveal the structural changes and Cu-ion evolution during cycling, *ex-situ* measurement of XPS spectra was done on electrode before and during the first cycling (Fig. 4c). The XPS spectrum of this compound is very similar to that of brochantite $\text{Cu}_4(\text{SO}_4)(\text{OH})_6$ [15]. The Cu 2p peaks in Cu^{2+} are broader than those in Cu^+ and Cu, due to the coupling between unpaired electrons in the paramagnetic Cu^{2+} , while the satellite peaks from Cu^{2+} come from the charge transfer transitions from the bound ligands into the unfilled d^9 valence level of Cu^{2+} [31]. Both the intermediates obtained from being discharged to 0.85 V and the discharged product obtained from being discharged to 0.50 V were revealed to contain no Cu^{2+} . Based on all the above results, the following two-step reductions during discharge are proposed:

Here the intermediate is different from those obtained during the first-step of discharging CuO [32] and CuS [33]. Those intermediates, i.e., Li_xCuO and Li_xCuS respectively, contained both Cu^{2+} and Cu^+ . While CuS, like natrochalcite, also experiences two-step reductions to afford metallic copper during discharge [33], CuO could experience four different processes [32]. All the differences and similarities indicate the electrochemical activities of Cu^{2+} toward Li^+ -insertion are sensitive to its environment. The formation of Cu^0 -containing amorphous matrix was also observed in the case of $\text{Cu}_4(\text{OH})_6\text{SO}_4$ possibly due to that the discharge products such as Cu metal, LiOH, Li_2SO_4 , etc formed an amorphous matrix [15]. While X-ray photoelectron spectroscopy

(XPS) was unable to differentiate Cu and Cu⁺ due to their very similar binding energies (932.3 eV vs. 932.4 eV) and peak widths [34–35], only high-resolution XRD using a synchrotron source was proved to be able to detect the discharge products of Cu-containing electrode materials [36]. EDX, SEM, and backscattered electron (BSE) imaging of the counter Li metal did not find metallic Cu, confirming the significant capacity decay after the first discharge was not due to the dissolution of metallic Cu generated from the reduction of Cu²⁺ by water-contaminated electrolyte [15].

Interestingly when recharged to 2.70 V, the electrode was revealed by XPS spectra to contain small amount of Cu²⁺, as indicated by the weak peaks from Cu²⁺. Possible reason could be due to the low charge potential. Actually even when charged to 4.0 V, a significant portion of Cu remained to be Cu⁺ or Cu in the case of brochantite [15]. Combining both PXRD and XPS data, we may conclude there may be no or very small amount of Cu²⁺-containing compounds other than the recrystallized natrochalcite structure in the first charged electrode. In other words, only the recrystallized natrochalcite structure contributed to the subsequent discharge capacities, resulting in well-maintained discharge capacities under different rates for 48 cycles (Fig. 5a). It is worthy to note that the columbic efficiencies (CEs) were higher than 100.0% and could reach up to 111.9%. Actually, CEs being higher than 100.0% is not that unusual. For example, composites of polyacrylonitrile-Ketjenblack carbon and sulfur, when serving as a cathode material, demonstrated CEs being higher than 100.0% during the first 24 cycles partially due to some side reactions [37]. For another example, the CEs of carbon-coated LiFePO₄ were occasionally higher than 100.0% though no reasons were proposed [38]. So in our case some side reactions and the ion-exchange between Li⁺ and Na⁺ during cycling might possibly contribute to the CEs being higher than 100.0%. Understanding of the exact reasons is ongoing.

Fig. 5b shows the electrochemical impedance spectroscopy (EIS) of the electrode after different cycles. The semi-circle in the middle-high frequency range correlates with the charge transfer resistances. After the first cycle, the electrode appeared to have a stable charge transfer resistance. When the potential window was enlarged to cover 0.3 V–3.4 V, the first discharge capacity increased to 312 mAh/g at the rate of 5.0 mA/g (Fig. S1). The near 90 mAh increased capacity came from the potential window of 0.5 V–0.3 V, indicating more possible capacities at lower potentials. However, the capacities were found to decay faster. Optimization of all components to optimize the capacities and capacity retention rates are ongoing.

Similar reversible decomposition-recrystallization processes of active electrode materials during cycling accompanied with copper extrusion-insertion processes were observed when $\text{Cu}_{2.33}\text{V}_4\text{O}_{11}$ was evaluated as a cathode for LIBs [5]. This compound and $\text{Cu}_{2.33}\text{V}_4\text{O}_{11}$ have both similarities and differences in both the crystal structure and the structural evolution during cycling. First, both of them are 2D structures with anionic layers. While this compound utilizes Cu^{2+} as building units of extended layers charge-balanced by Na^+ , $\text{Cu}_{2.33}\text{V}_4\text{O}_{11}$ utilizes $\text{Cu}^{2+}/\text{Cu}^+$ to charge-balance extended layers built of V^{5+} as building units. Second, $\text{Cu}_{2.33}\text{V}_4\text{O}_{11}$ mainly registers $\text{V}^{5+}/\text{V}^{4+}$ redox chemistry, though accompanied by $\text{Cu}^{2+}/\text{Cu}^+/\text{Cu}$ redox chemistry, during cycling, while this compound totally registers $\text{Cu}^{2+}/\text{Cu}^+/\text{Cu}$ redox chemistry. Therefore, the recrystallization in this case could be more difficult than the case of $\text{Cu}_{2.33}\text{V}_4\text{O}_{11}$, resulting in lower recovery rates (i.e. the percentage of the active electrode materials recrystallized) during the charge ($\sim 25\%$ vs. $\sim 100\%$).

3.3. Electrochemical performances of natrochalcite as an anode material in Na^+ -cell.

Galvanostatic charge-discharge cycling tests of this compound as an anode for SIBs were run at the current of 2.5 mA/g in the range of 0.2 V to 2.1 V vs. Na^+/Na . (Fig. 6a). This compound

delivered a specific capacity of 175 mAh/g during the first discharge, and $\sim 78\%$ of that in the Li^+ -cell. A quasi potential plateau was observed in the range of $\sim 0.5\text{ V} - \sim 0.7\text{ V}$. The second discharge capacity was 35 mAh/g and $\sim 20\%$ of the first discharge capacity. The discharge capacities then slowly decreased to reach 25 mAh/g during the fifth cycle and then stabilized towards the tenth cycle. Meanwhile, the charge capacities from the first to the tenth cycles were 23–25 mAh/g and very close to each other.

Cyclic voltammetry (CV) analysis (Fig. 6b) revealed two irreversible cathodic peaks at 0.69 V and 0.40 V during the first negative sweep from 2.2 V, which should correspond to the reduction of Cu^{2+} to Cu^+ and then to Cu [25]. Since these two peaks have a smaller potential gap (0.29 V) than that in the case of Fig. 3b (0.51 V), thus the corresponding potential plateaus during the discharge could not be differentiated and thus only a quasi potential plateau was observed (Fig. 6a). The current at 0.69 V was significantly larger than that at 0.40 V, suggesting the copper stripping process at 0.69 V. In subsequent scans, the redox chemistry was quite reversible, though appeared to be less reversible than that in the Li^+ -cell (Fig. 3b). All the CV analysis results support the galvanostatic cycling profiles in Fig. 6a.

PXRD analysis reveals the structural evolution of this compound in the Na^+ -cell during cycling is similar to that in the Li^+ -cell (Fig. 7a). During the first discharge, the layered structure was also maintained when the electrode was discharged to 0.65 V. XPS spectrum of the electrode at this stage indicated the absence of Cu^{2+} (Fig. 7b). The resultant electrode became amorphous when the electrode was further discharged to 0.50 V (results not shown here) and 0.20 V. All these results indicate the insertion of Na^+ and the evolution of Cu ions during the first discharge in Na-ion cell are similar to those in the Li-ion cell.

After the first discharge and a significant percentage of the layered structure was recrystallized back after the subsequent charge (Fig. 7a), which is similar to the case in the Li^+ -cell. While the intensity of the main peak $2\theta = \sim 13.58^\circ$ decreased significantly, the relative intensities of some peaks (e.g. 13.58° vs. 37.56°) also changed possibly due to structural rearrangement. The decrease of the peak intensity at $2\theta = \sim 13.58^\circ$ in this case was slightly larger than that in the case of the Li^+ -cell, which could explain less capacity retention rate was achieved in the second discharge in the Na^+ -cell than in the Li^+ -cell ($\sim 20\%$ vs. $\sim 24\%$). After two discharge-charge cycles, the main layered structure was also maintained, as evidenced by the maintenance of the peak at $2\theta = \sim 13.58^\circ$. The peak intensity at $2\theta = \sim 35.40^\circ$ was enhanced possibly due to some structural rearrangement. Compared to the Li-ion cell, the Na-ion cell had smaller capacities and was more affected by charging-discharging currents (Fig. 8a). All the CEs were lower than 100.0%, and ranged from 90.0% to 98.6% at various C-rates with a few exceptions. Since there was no ion-exchange in this Na-ion cell during cycling, we proposed the ion-exchange did play some role in making the CEs in the case of Li-ion cell higher than 100.0% (Fig. 5a). The electrochemical impedance spectroscopy (EIS) of this electrode in Na-ion cell indicated both the solid electrolyte interface (SEI) and the charge transfer in the Na-cell had higher resistance those in the Li-ion cell (Fig. 8b).

3.4 Possible roles played by Li^+/Na^+ in the recrystallization of the layered structure during cycling.

This compound demonstrates much better capacity retention rates in the Li^+ - and Na^+ -cells from the second cycle than other copper sulfates [14] and $\text{Cu}_4(\text{SO}_4)(\text{OH})_6$ [15] both of which contain no alkaline ions as counter cations. $\text{Cu}_4(\text{SO}_4)(\text{OH})_6$ appeared not to be recrystallized from the amorphous matrixes of discharged products during the charge, this might contribute to the low

capacity retention rates from the second cycle onwards [15]. A possible reason responsible for the difference could be that Li^+ and Na^+ here possibly serve as SDAs to help recrystallize the crystal structure from the amorphous matrixes of discharged products. Indeed, hydrated alkali-metal cations were proved to demonstrate directing effects in organizing building units into zeolites with extended frameworks [39]. It is worthy to note that both the Na^+ in this compound (Fig. 1d) and the above reported hydrated alkali-metal cations are coordinated by large numbers of O atoms. The low water concentration in the cell may be partially responsible to the relatively low rate of recrystallization. In contrast, the small amount of water in commercially available reagents can help crystals to grow with large yields in hydrothermal reactions under vacuum systems [40]

3.5. Natrochalcite revealed to be a poor cathode material in both Li^+ -cell and Na^+ -cell.

Both galvanostatic tests and CV analysis revealed this compound to be a poor cathode material for both LIBs (Fig. S2†) and SIBs (Fig. S3†). The capacities observed in galvanostatic cycling profiles (Fig. S2a†, and Fig. S3a–S3b†) should mainly attribute to double-layer capacitance [16]. The first charge capacity in the Na^+ -cell is significantly higher than that in the Li^+ -cell, possibly due to the more difficulty of extracting Na^+ in the presence of the Na^+ -containing electrolyte. In the first scan during the CV analyses, both the anodic peak at 3.51 V vs. Li^+/Li in the Li^+ -cell (Fig. S2b†) and the anodic peak at 2.68 V vs. Na^+/Na in the Na^+ -cell were observed due to the oxidation of Cu^{2+} into Cu^{3+} . However, the current (mA/g) in the Li^+ -cell was much lower than those of cathodic peaks observed in Fig. 3b, indicating here negligible amount of Na^+ could be extracted. In the reverse scans, no cathodic peaks were observed possibly due to very low extent insertion of Li^+ (Fig. S2b†) and Na^+ (Fig. S3c†). In subsequent scans, anodic peaks diminished and moved positively while no cathodic peaks appeared, further confirming the above assessment.

Conclusions

In this report, $\text{Na}[\text{Cu}_2(\text{OH})(\text{H}_2\text{O})(\text{SO}_4)_2]$ was evaluated as anode and cathode materials for LIBs and SIBs since the Cu^{2+} in $\text{Na}[\text{Cu}_2(\text{OH})(\text{H}_2\text{O})(\text{SO}_4)_2]$ can be reduced and oxidized at lower and higher potentials. When evaluated as a cathode material for both LIBs and SIBs, very limited amount of Na^+ and Li^+ can be extracted and inserted. In contrast, this compound can be a workable anode material for LIBs and SIBs. Here the natrochalcite particles range from submicrometers to a few micrometers in size. Natrochalcite nanoparticles are expected to demonstrate significantly enhanced electrochemical performances due to much larger surface areas and more efficient charge transport [41]. For example, the capacities of brochantite nanoparticles were almost seven times of those of brochantite microparticles [15]. Natrochalcite nanoparticles may even have higher rates of recrystallization during the cycling. Development of natrochalcite nanomaterials and optimization of all components and testing conditions, e.g. wider testing potential windows and correspondingly proper current collectors, are ongoing to optimize the capacities and capacity retention rates.

Here natrochalcite delivers reasonably good discharge capacities during the first discharge, the layered structure decomposes in this stage and then is partially recrystallized during the subsequent charge. Such decomposition-recrystallization cycles are found to be quite reversible from the second cycle, and the discharge capacities should come from both the recrystallized layered structure. Li^+ in the electrolyte is found to replace Na^+ during cycling of the electrode in the Li^+ -cell. Further, here the electrode in the Li^+ -cell demonstrates higher capacities and capacity retention rates than that in the Na^+ -cell, possibly due to smaller size of Li^+ versus Na^+ , thus higher extent of ion insertion-retraction and more reversible decomposition-recrystallization cycles. While Na^+ could serve as a SDA during the preparation of this layered structure, both Li^+ and Na^+

could serve as SDAs in recrystallizing this layered structure during charge from the “amorphous” discharged products.

Though a same compound can be used as anode and cathode materials for a same rechargeable battery [42], to the best of our knowledge this compound was the first Cu^{2+} - SO_4^{2-} -based compound evaluated in this way. It is worthy to note that here the observed potential associate with $\text{Cu}^{2+}/\text{Cu}^+$ is lower than that of nanosized $\text{Cu}_4(\text{SO}_4)(\text{OH})_6$ of 3D crystal structure (1.55 V vs. Li^+/Li) [15] and significantly lower than that of 1D $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ (> 3.0 V vs. Li^+/Li) [14]. The large differences could be due to the different coordination environment around Cu^{2+} and connection modes, suggesting great potentiality for engineering the potentials and cycling stability through engineering the crystal structures. In summary, this work demonstrates the great potential of Cu^{2+} - SO_4^{2-} -based bimetallic compounds as electrode materials for rechargeable LIBs and SIBs, and sheds new light on utilizing Cu^{2+} -containing compounds as electrode materials with excellent capacity retention rates.

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Table 1. Crystal data and structure refinement of Na[Cu₂(OH)(H₂O)(SO₄)₂]

Formula [molecular weight]	Cu ₂ H ₃ NaO ₁₀ S ₂ [377.21 g/mol]
Crystal system, space group	Monoclinic, C2/m (# 12)
Unit cell parameters, theoretical density	a = 8.8118(19) Å, b = 6.1834(13) Å, c = 7.506(3) Å, β = 118.746(2)°, Z = 2, V = 358.59(16) Å ³ , 3.494 g·cm ⁻³
F(000), θ range, reflections collected/unique	368, 3.10 to 25.00°, 920 / 356
R(int), goodness-of-fit on F ²	0.0131, 1.020
R ₁ ^a), wR ₂ ^b) (I > 2σ (I))	R ₁ = 0.0193, wR ₂ = 0.0584
All data	R ₁ = 0.0196, wR ₂ = 0.0586

$$^a) R_1 = \frac{\sum (||F_o| - |F_c||)}{\sum |F_o|}, \quad ^b) wR_2 = \left\{ \frac{\sum w [(F_o^2 - F_c^2)]}{\sum w [(F_o^2)^2]} \right\}^{0.5}, \quad w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1},$$

where $P = (F_o^2 + 2F_c^2)/3$. $a = 0.0434$, $b = 1.3013$.

Figures and Captions

Fig. 1. Crystal structural description of $\text{Na}[\text{Cu}_2(\text{OH})(\text{H}_2\text{O})(\text{SO}_4)_2]$: (a) 1D chain built from the connection of Cu^{2+} by SO_4^{2-} , OH^- , and H_2O , (b) The 2D anionic layer structure 1D chain built from the connection of chains, (c) The packing of the layers that are separated by Na^+ , and (d) The coordination environment of Na^+ .

Fig. 2. (a) Experimental and simulated PXRD patterns; (b) Experimental and standard Raman spectra; (c) Scanning electron microscope (SEM) image of powders before electrode fabrication and for both PXRD analysis. Inset scale bar: 10 μm . (d) High-resolution transmission electron microscope (HRTEM) image; the d -spacing of 0.46 nm could be indexed to the (200) planes.

Fig. 3. (a) Galvanostatic charge-discharge cycling profiles at 2.5 mA/g in the potential range of 0.5–2.7 V in a Li^+ -cell; (b) Cyclic voltammograms at the scan rate of 0.05 mV/s for the first five cycles in the range of 0.5–2.4 V vs. Li^+/Li ; the black arrow indicates the starting point.

Fig. 4. (a) *Ex-situ* PXRD patterns of electrodes before and during cycling in the Li^+ -cell in comparison with that of powders before the electrode fabrication; (b) *Ex-situ* PXRD patterns of the as-made electrode and the electrode after two discharge-charge cycles in the Li^+ -cell focusing on the (001) peak and one peak from Al; (c) *Ex-situ* XPS spectra of electrodes before and during the first cycling. In both (a–c), the peaks labelled with squares come from the layered structure.

Fig. 5. (a) Charge–discharge capacities and Columbic efficiencies at different rates in the Li^+ -cell from the 2nd to 48th cycles. (b) Nyquist plots of the cell at different cycles.

Fig. 6. (a) Galvanostatic charge-discharge cycling profiles at 2.5 mA/g in the potential range of 0.2–2.1 V in a Na⁺-cell; (b) Cyclic voltammograms at the scan rate of 0.05 mV/s for the first five cycles in the range of 0.2–2.2 V vs. Na⁺/Na; the black arrow indicates the starting point.

Fig. 7. (a) *Ex-situ* PXRD patterns of electrodes before and during cycling in the Na^+ -cell in comparison with that of powders before the electrode fabrication. (b) XPS patterns of the as-made electrode and the electrode discharged to 0.65 V.

Fig. 8. (a) Charge–discharge capacities and Columbic efficiencies at different rates in the Na⁺-cell from the 2nd to 48th cycles. (b) Nyquist plots of the cell at different cycles.