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Nature of Alkali Ion Conduction and Reversible Na-Ion Storage in Hybrid Formate Framework Materials

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Cite This: J. Phys. Chem. C 2020, 124, 26714–26721



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ABSTRACT: The cost advantage of Na-ion batteries has spurred intensive research effort in the last 10 years to develop reversible Na⁺ storage materials. Although classic host materials—analogous to those in the Li-ion system—are potentially straightforward targets, sluggish Na⁺ diffusion in many inorganic structures limits options. In this regard, open framework inorganic—organic hybrids such as metal—organic framework materials are considered as viable alternatives. Herein, we introduce heterometallic formate frameworks as potential candidates for reversible Na⁺ storage. As a first, we present a microwave solvothermal strategy for rapid synthesis of phase-pure microcrystalline Na₂Co(HCO₂)₄ and AB(HCO₂)₃ (A: Li/Na; B: Co/Mn). By combining in-depth impedance analysis with ab initio molecular dynamics simulation,



we reveal that the Li^+/Na^+ conduction—which follows a "pinball" mechanism—in these materials is extrinsic defect-dominated. Calculation suggests that a librational motion of the formate anions facilitates the diffusion of Na⁺ compared to Li⁺, explaining the origin of anomalously higher ionic conductivity for the Na analogue compared to the Li one. Preliminary electrochemical investigation reveals reversible Na⁺ storage in Na₂Co(HCO₂)₄ and NaMn(HCO₂)₃ at an average voltage of 2.5–3 V.

INTRODUCTION

Once forsaken for higher-energy Li-ion batteries (LIBs), research on Na-ion batteries (NIBs) has attracted tremendous attention in the last decade owing to sodium's high abundance and inexpensiveness, which make NIBs attractive for largescale and renewable energy storage.¹⁻³ In the search for Na⁺ host materials, many Na analogues of classic inorganic Li hosts have been developed, but the larger size of Na⁺ (1:06 Å) compared to Li⁺ (0:76 Å) results in different-most often inferior—electrochemical charge storage behavior.^{3,4} Thus, the development of novel materials, specifically based on open structures, is essential. To this end, inorganic-organic hybrids-where metal centers are three-dimensionally (3D) templated by organic ligands—offer numerous possibilities.^{5,6} They combine the advantages of both inorganic and organic materials. Organic compounds are presumably more sustainable and offer a molecular toolbox of diverse redox functions, but their solubility in typical organic electrolytes is detrimental for long-term cycling.⁷ Organic-inorganic hybrids are however intrinsically insoluble in organic solvents like the inorganic materials.⁸⁻¹¹ These coordination polymers are closely related to metal-organic framework (MOF) compounds which have been the subject of considerable interest for diverse energy storage-related applications.^{12,13} A vast majority of them are based on the carboxylate group containing organic ligands, which coordinate with the metal ions.¹⁴⁻¹⁷ While several MOFs have been studied for LIB cathodes^{8,18,19} and anode

applications,^{14,20,21} the number remains low, and besides hexacyanoferrate materials that are generally classified as purely inorganic systems, report on MOFs for Na⁺ storage is rare.²²

Heterometallic formates, such as $A_2B(HCO_2)_4$ and $AB-(HCO_2)_3$ (A: Li/Na; B: Mn/Co), belong to the organicinorganic hybrid class of materials. Strictly speaking, these materials cannot be termed as MOFs as they contain M–O– M (M: metal) units or single oxygen bridging two metal centers. Based on an autoclave-assisted solvothermal method, the synthesis of single crystals of $Na_2Co(HCO_2)_4$,²³ NaMn- $(HCO_2)_3$,²⁴ LiCo $(HCO_2)_3$,²⁵ and LiMn $(HCO_2)_3$,²⁵ and their crystal structures was reported earlier. The interest in these materials was mainly owing to their magnetic behavior, facilitated by the rather short formate anion $HCOO^-$ which allows magnetic coupling between the transition metals. From the redox chemistry perspective, all four compounds may undergo Co/Mn oxidation/reduction between 2+ and 3+ oxidation states, leading to reversible Na⁺/Li⁺ storage. Whereas structurally considering, the Na ions in between the Co

Received: October 29, 2020 Revised: November 11, 2020 Published: December 1, 2020









Figure 1. Powder XRD pattern of the as-synthesized polycrystalline (a) $Na_2Co(HCO_2)_4$, (b) $NaMn(HCO_2)_3$, (c) $LiCo(HCO_2)_3$, and (d) $LiMn(HCO_2)_3$. The corresponding reference patterns are shown in blue.



Figure 2. Typical SEM images showing the morphology of the as-synthesized (a) $Na_2Co(HCO_2)_4$, (b) $NaMn(HCO_2)_3$, (c) $LiCo(HCO_2)_3$, and (d) and $LiMn(HCO_2)_3$.

formate layers in monoclinic $Na_2Co(HCO_2)_4$ (Figure 1a) and Na/Li ions residing in the tunnels in cubic $AM(HCO_2)_3$ (Figure 1b; A: Na/Li and M: Co/Mn) are likely to be mobile. Additionally, the soft formate anionic framework is expected to bind the alkali ions weakly, which can potentially aid the alkali ion mobility in these structures.

As we showcase here, the microcrystalline heterometallic formates can be synthesized by a rapid microwave solvothermal technique that has not been demonstrated earlier for hybrid formate materials. The materials display a "pinball" ionic conduction mechanism with anomalously higher ionic conductivity for the Na analogue compared to the Li one—as revealed by impedance spectroscopy analysis and molecular dynamics simulation. Preliminary electrochemical cycling confirms reversible Na⁺ storage behavior.

RESULTS AND DISCUSSION

Synthesis and Characterization. Phase-pure micro- or nanocrystalline powder material is essential for physicochemical and electrochemical analysis relevant to battery material application. Solvothermal reactions that have been applied so far to synthesize the target formate compounds typically result in large crystals and often accompany impurities. Therefore, a microwave heat treatment-mediated solvothermal synthesis route was developed that dramatically brought down the reaction time from 48 to 72 h-required for regular solvothermal synthesis-to only 30 min (see Experimental Methods). This is the first time a rapid microwave solvothermal technique is demonstrated for the synthesis of heterometallic formate frameworks. The phase purity of the assynthesized Na₂Co(HCO₂)₄, NaMn(HCO₂)₃, LiCo(HCO₂)₃, and $LiMn(HCO_2)_3$ was confirmed from powder X-ray diffraction (XRD) patterns, as shown in Figure 1c-f. No impurity peaks were observed, and all patterns matched well with the corresponding reference pattern generated from the single crystal data reported earlier. Efforts to synthesize $NaCo(HCO_2)_3$ led to the formation of an unidentified white color impurity along with the pink target material, which was confirmed by XRD (Figure S1). The chemical identity of the compounds-consisting of the formate anionic frameworkwas further validated by infrared spectroscopic analysis (Figure S2). All the formates have almost identical spectra—which are

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primarily dominated by fingerprints of formate and confirm the absence of any solvent impurity.

Thermal analysis data as presented in Figure S3 reveal that the as-synthesized materials are stable up to 200-250 °C and thus possess adequate oxidative stability for their use in battery electrode application. The formates are expected to decompose to metal oxides, accompanying the release of CO, H₂O, and possibly H₂. Elemental microanalysis was performed to determine the carbon content in the form of the formate anion. Based on carbon analysis data presented in Table S1, it can be said that the carbon content of the pure compounds agrees well with their nominal composition. Morphology of the materials as investigated by scanning electron microscopy (SEM) study is shown in Figure 2. As evident from Figure 2a, $Na_2Co(HCO_2)_4$ consists of rod-shaped particles that are between 30 and 100 μ m in length and 5–7 μ m in diameter. The Na to Co ratio was confirmed to be 2:1 by energy dispersive X-ray analysis (see EDX data in Figure S4). The cubic-structure AM(HCO₂)₃ (A: Li/Na and M: Co/Mn) materials are comparable in dimension with particle size ranging from 200 nm to 2 μ m and display somewhat similar irregular polyhedral morphology. The polyhedral shapes are discernible for $LiCo(HCO_2)_3$ (Figure 2c) but deformed for $NaMn(HCO_2)_3$ (Figure 2b) and $LiMn(HCO_2)_3$ (Figure 2d). EDX analysis of the Na to Mn ratio on $NaMn(HCO_2)_3$ particles confirmed the nominal composition.

Li⁺/Na⁺ Conductivity Study. Mobility of the Li/Na ions in the formate frameworks, which is necessary for their electrochemical cycling, was probed by electrochemical impedance spectroscopy. Figure 3a-d shows the Nyquist impedance plots at different temperatures, and the corresponding plots depicting the variation of the bulk ionic conductivity (natural logarithm) as a function of temperature are presented in Figure 3e-h. The bulk ionic conductivities were extracted by fitting the impedance data with an equivalent circuit (Figure S5), and the activation energies for the Li/Na-ion mobility were revealed by Arrhenius-type fitting shown in Figure 3e-h. The parameters obtained from fitting are presented in Table S2. From the Arrhenius plot of $Na_2Co(HCO_2)_4$ in Figure 3e, it is apparent that the nature of Na-ion diffusion changes with increasing temperature. Until 90 °C, the activation energy is 0.28 eV atom⁻¹, which is relatively low. In the window up to 130 °C the barrier is a high 0.62 eV atom⁻¹ but decreases to a very low 0.07 eV atom⁻¹ above 130 °C. Such jumps in the activation barrier most likely stem from a change in the ionic conduction mechanism from an extrinsic type at lower temperatures to an intrinsic one at higher temperatures when intrinsic defects such as vacancies can be formed, which dominate the ionic mobility. Usually intrinsic defects are formed at much higher temperatures than observed here, but as the thermal stability of $Na_2Co(HCO_2)_4$ is much lower, defects are not unlikely at low temperatures. NaMn(HCO₂)₃ displays a similar behavior (Figure 3f) where the activation energy of Na-ion migration increases from 0.07 to 0.70 eV atom⁻¹ at around 110 °C. The Li compounds $LiCo(HCO_2)_3$ and LiMn(HCO₂)₃ show activation barriers of 0.20 and 0.34 eV atom⁻¹, respectively, with only one Arrhenius slope and thus no change in ionic conduction mechanism with increasing temperature. Room-temperature bulk ionic conductivity of each compound was extrapolated from the linear fit of the corresponding Arrhenius plot (Table S3). While Na₂Co- $(HCO_2)_4$ and $LiCo(HCO_2)_3$ have similar ionic conductivity $(\sim 10^{-6} \text{ S cm}^{-1})$, NaMn $(HCO_2)_3$ displays a rather high ionic





Figure 3. AC impedance data (left column) as a function of temperature and Arrhenius-type fitting of the bulk ionic conductivity values (right column) for (a,e) Na₂Co(HCO₂)₄, (b,f) NaMn-(HCO₂)₃, (c,g) LiCo(HCO₂)₃, and (d,h) LiMn(HCO₂)₃. The fitted lines are in solid red.

conductivity of ~10⁻⁴ S cm⁻¹ that is 4 orders of magnitude higher than that of LiMn(HCO₂)₃, despite Na⁺ being larger than Li⁺ and both compounds having identical structures.

To further understand and characterize the ionic conductivity of heterometallic formate frameworks, we performed first-principles simulations based on density functional theory (DFT).²⁶ Ionic diffusion involves highly anharmonic and *T*dependent processes;²⁷ thus, we employed *ab initio* molecular dynamics (AIMD) simulations to accurately describe them (Supporting Information). Ionic transport was characterized by estimating the mean-squared displacement, MSD, and diffusion coefficient, *D*, of all the atomic species in LiMn-(HCO₂)₃ and NaMn(HCO₂)₃ (Supporting Information).

By considering perfectly ordered and stoichiometric systems, we estimated small lithium and sodium diffusion coefficients of $D < 10^{-8}$ cm² s⁻¹, which cannot explain the experimental observation. Likewise, for perfectly ordered and off-stoichio-

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Figure 4. First-principles calculation of the ionic transport properties of bulk $LiMn(HCO_2)_3$ and $NaMn(HCO_2)_3$. Estimation of the ionic meansquared displacements (MSD) for bulk (a) $LiMn(HCO_2)_3$ and (b) $NaMn(HCO_2)_3$ at T = 900 K. The AIMD trajectory of a (c) mobile Li ion in bulk $LiMn(HCO_2)_3$ and a (d) mobile Na ion in bulk $NaMn(HCO_2)_3$. Li, Na, O, H, and C ions are represented as dark-green, gold, red, pink, and brown spheres, respectively. The mobile Li and Na ions are represented as blue and light-green spheres, respectively.

metric crystals-generated by removing few ions from the simulation cell—we obtained negligible D_{Li^+} and D_{Na^+} values. These results indicate that the likely cause for the large ionic diffusion observed in our experiments is not the creation of intrinsic defects induced by temperature. In fact, the formation energy of Li⁺ and Na⁺ Frenkel defects (i.e., simultaneous generation of one vacancy and one interstitial in the crystal) that we calculated for $LiMn(HCO_2)_3$ and $NaMn(HCO_2)_3$, $E_{\rm Frenkel} \sim 3$ eV, is noticeably larger than the defect energies estimated for intrinsic superionic materials (e.g., $E_{\text{Frenkel}} \sim 2 \text{ eV}$ in CaF_2^{28}). The physical origin of this result is the attractive interactions between the alkali metal ions and highly distorted O_6 octahedra that surround them (Figure 4c,d), which severely restrict the Li⁺ and Na⁺ mobility. Nevertheless, by considering a small concentration of Li⁺ and Na⁺ Frenkel defects (\sim 1%) in our simulations, we were able to reproduce significant ionic diffusion for LiMn(HCO₂)₃ and NaMn(HCO₂)₃ (Figure 4a,b), namely, $D_{Li} = 6.3 \cdot 10^{-7}$ and $D_{Na} = 2.5 \cdot 10^{-6}$ cm² s⁻¹ at T = 900 K. The agreement between the simulated D's and the corresponding experimental values is far from perfect. However, this quantitative disagreement can be regarded as normal because the origin of the observed ionic transport appears to be extrinsic defects, which are generated during the materials synthesis and cannot be quantified straightforwardly. On the other hand, at the qualitative level, our theoretical results are fully consistent with our experimental results because the diffusion coefficient of sodium ions is noticeably larger than that of lithium ions.

By analyzing the AIMD trajectories of mobile ions (Figure 4c,d), we were able to identify a characteristic ionic diffusion mechanism for heterometallic formate frameworks that resembles that of a metallic sphere in a "pinball" machine. In

particular, the diffusion of the alkali metal ions ("metallic balls") appears to be supported by the librational motion of the formate anions ("flippers"), which are light and flexible. Interestingly, we found that the interactions of formate anions with mobile Na ions are more attractive than those with Li ions. Despite of its larger size, the average distance between the mobile sodium ion and the formate anion, $\langle d_{\text{Na}-\text{FA}} \rangle = 1.90$ Å, is smaller than that for the mobile lithium ion, $\langle d_{\text{Li}-\text{FA}} \rangle = 1.98$ Å. We believe that the identified disparity in the chemical forces acting between "metallic balls" and "flippers" can explain the origin of the enhanced ionic diffusion observed for Nabased formate frameworks. It is worth noting that in terms of the relative available interstitial volume, both LiMn(HCO₂)₃ and NaMn(HCO₂)₃ compounds are pretty similar.

Reversible Na⁺ Storage Behavior. Preliminary electrochemical cycling at a 0.05 C rate revealed reversible Na⁺ storage in Na₂Co(HCO₂)₄ (Figure 5a) and NaMn(HCO₂)₃ (Figure 5b) at an average voltage of 2.5-3 V. For the cycling of both Na-ions accompanying Co^{2+}/Co^{3+} and Co^{3+}/Co^{4+} redox, the theoretical capacity of $Na_2Co(HCO_2)_4$ is 188 mA h g^{-1} , which is very close to that of high-capacity layered transition-metal oxides.² In comparison, $NaMn(HCO_2)_3$ can deliver a maximum of 126 mA h g^{-1} , corresponding to the Mn²⁺/Mn³⁺ redox. Polyanionic systems such as Na₃V₂(PO₄)₃ and NaFePO₄ possess comparable specific capacities. Experimentally, $Na_2Co(HCO_2)_4$ delivered a reversible capacity of 60 mA h g^{-1} corresponding to the cycling of only 0.6 Na⁺. Even though NaMn(HCO₂)₃ showed a higher initial reversible capacity of ~100 mÅ h g^{-1} , electrolyte decomposition—most likely catalyzed by the transition metal—is apparent at high charging voltages during the first few cycles. In comparison, $LiMn(HCO_2)_3$ displayed (Figure S6) a low capacity of 30 mA



Figure 5. Galvanostatic charge-discharge profiles of (a) $Na_2Co(HCO_2)_4$ and (b) $NaMn(HCO_2)_3$ against a metallic Na anode at a 0.05 C rate with 1 M NaClO₄ in EC/PC/FEC as the electrolyte. (c,d) The corresponding differential capacity plots for $Na_2Co(HCO_2)_4$ and $NaMn(HCO_2)_3$, respectively. The cyclability data and the Coulombic efficiency evolution of $-(e) Na_2Co(HCO_2)_4$ and (f) $NaMn(HCO_2)_3$.

h g^{-1} owing to its poor Li-ionic conductivity. Figure 5c,d shows the differential capacity plots corresponding to the galvanostatic data shown in Figure 5a,b, respectively. While reproducible profile in both plots confirms the reversible nature of the involved electrochemical processes, the large gap between the oxidation and reduction peaks highlights the large voltage polarization in both systems. For $Na_2Co(HCO_2)_4$, the oxidation peak at 3.9 V (first cycle) moves to 3.6 V and stabilizes after the second cycle, indicating an irreversible structural adjustment during the first cycle. Whereas, NaMn- $(HCO_2)_3$ peaks maintain their position throughout, but the peak current diminishes with cycling in accordance with capacity fading with increasing cycle number. Figure 5e,f presents the specific capacity and the Coulombic efficiency as a function of the cycle number for $Na_2Co(HCO_2)_4$ and $NaMn(HCO_2)_{31}$ respectively. Both show a significant discrepancy between the charge and the discharge capacities, leading to Coulombic efficiencies of ~90%. $Na_2Co(HCO_2)_4$ shows slightly better cyclability and Coulombic efficiency compared to $NaMn(HCO_2)_3$. Despite the incorporation of a significant amount (25%) of conductive carbon in the electrode mixture, large voltage polarization is common to both systems, which hinders attainment of full capacity and good cycling stability. While the ionic conductivity is relatively higher than most inorganic polyanion cathode hosts such as NASICON $Na_3\bar{V}_2(PO_4)_3^{29}$ or cubic $Na_3\mathrm{Ti}P_3O_9N^{30}$ (both ${\sim}10^{-7}~S$ cm⁻¹), it is likely that the performance limitation stems from

the low electronic conductivity and relatively large particle size of the formate materials. In this regard, the development of uniform nanostructured materials and conductive composite formation by conductive polymer coating or graphene wrapping—both of which can be achieved in situ by modifying the synthesis condition—are likely solutions. Nevertheless, galvanostatic cycling of the as-obtained microcrystalline formates clearly demonstrate reversible Na⁺ storage is feasible in the formate frameworks, which has not been reported in literature so far.

CONCLUSIONS

In summary, we have developed a microwave synthesis methodology for the rapid and versatile synthesis of heterometallic formate frameworks. The obtained phase-pure polycrystalline materials are thermally stable up to 200-250 °C and display intriguing Na⁺/Li⁺ conduction behavior. Particularly impressive is the 4 orders of magnitude-higher Na⁺ conductivity of NaMn(HCO₂)₃ compared to the Li⁺ conductivity of LiMn(HCO₂)₃, despite both having an identical crystal structure. Prevalence of interstitial defects in the as-synthesized compounds and librational motion of the formate anions which interact strongly with the Na ions appears to facilitate the diffusion of Na⁺ compared to Li⁺, as revealed by theoretical calculations. The capability of the Na-analogues to reversibly store Na⁺ is confirmed by preliminary electrochemical measurements.

EXPERIMENTAL METHODS

Synthesis. For the synthesis of $Na_2Co(HCO_2)_4$ and NaMn(HCO₂)₃, a mixture of 1 mmol Co(NO₃)₂·6H₂O (Acros Organics, 99% purity) or 1 mmol Mn(NO₃)₂·4 H₂O (Sigma-Aldrich, \geq 97.0% purity) and 6 mmol HCO₂Na (Sigma-Aldrich, > 99.0% purity) was dissolved in 10 mL of N.N-dimethylformamide (DMF, Fisher Chemical, extra pure) in a 35 mL pressure vessel (Pyrex, CEM). For $LiCo(HCO_2)_3$ and LiMn(HCO₂)₃, HCO₂Li·H₂O was used instead of HCO₂Na. After thoroughly stirring for at least an hour, the dispersion turned turbid. The vessel was placed inside a microwave synthesizer (CEM, Explorer 12 SP Hybrid) and heated up to 160 °C with a maximum power of 160 W. The mixture was kept at this temperature for 30 min. Each product was rinsed three times with ethanol (technical grade), using a centrifuge (Hettich, 14 model universal 320) and redispersed by vortex, followed by drying under vacuum overnight. After drying, the Na₂Co(HCO₂)₄ powder had a copper-rose color and NaMn(HCO₂)₃ as well as LiMn(HCO₂)₃ had a creambeige color, while $LiCo(HCO_2)_3$ was pink. The same synthesis was performed to obtain NaCo(HCO₂)₃, but the product was impure.

Physicochemical Characterization. The materials were characterized with XRD, SEM, elemental microanalysis, attenuated total reflection infrared spectroscopy, and thermal gravimetric analysis (TGA). XRD was measured on a PANalytical XpertPro equipped with an X'Celerator RTMS detector and a Cu K_{α} X-ray tube ($\lambda = 1.5405$ Å) in the range from 5 to 80° (2 θ) with a step size of 0.033°. SEM was performed on ZEISS Leo 1530 FEG equipped with an energy-dispersive X-ray spectroscopy (EDX) attachment. For TGA, a TA Instruments Q500 was used, with the samples heated from 30 to 900 °C under a nitrogen atmosphere at a heating rate of 10 °C min⁻¹. Infrared spectroscopic analysis was performed on ATR.

Ionic Conductivity and Electrochemical Studies. For temperature-dependent ionic conductivity measurements, pellets were pressed at 500 MPa with a uniaxial press (MTI corporation). The pellets were sintered at 150 °C overnight and sandwiched between two stainless-steel rods under an Ar atmosphere. Contact problems were eliminated by applying a conductive silver paste on both sides of the pellets and the stainless steel rods. Bulk resistance measurements were performed by two-probe ac impedance spectroscopy (SP-150, BioLogic) in the 400 kHz to 100 mHz range with a perturbation of 200 mV. Impedance data were recorded in the 50-170 °C window. The data were fitted with equivalent circuit models shown in Figure S5 using the EC-lab Z-fit software to extract the ionic conductivities. The activation energy for Na⁺/Li⁺ diffusion was obtained by linear fitting of the bulk ionic conductivity values at different temperatures by applying the Arrhenius equation with a temperature-dependent pre-exponential factor: $\sigma T = \sigma_0 \exp(-E_A/k_bT)$. σ is the temperature-dependent bulk ionic conductivity, σ_0 is the ionic conductivity at absolute zero temperature, E_A is the activation energy for ion migration, $k_{\rm b}$ is the Boltzmann constant, and T is the temperature in Kelvin.

For electrode fabrication, the formates were mixed with conductive carbon black Super P (Timcal) and polyvinylidene fluoride or PVDF (Sigma-Aldrich, $M_W \sim 534.000$) in 70:25:5 ratio. A small amount of *N*-methly-2-pyrrolidone (Sigma-Aldrich, 99% purity) was added to the mixture to obtain a

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viscous slurry that was spread with a doctor blade on an aluminum foil (MTI). The film was first dried under vacuum in a desiccator and then placed in a vacuum oven to dry overnight at 100 °C. Circular electrodes ($\phi = 11 \text{ mm}$) were punched out of the film. Swagelok-type cells were assembled with two pieces of glass fiber separator (GF/A) placed in between the electrodes, where the anode was Na metal. A total of 100 μ L of 1 M NaClO₄ in EC/PC/FEC (49:49:2 by volume) and 1 M LiPF6 in EC/DMC (1:1 by volume) were used as electrolytes.

Theoretical Calculations. AIMD simulations based on DFT were performed in the canonical (N,V,T) ensemble (constant number of particles, volume, and temperature). The temperature in the AIMD simulations was kept fluctuating around a set-point value by using Nose-Hoover thermostats. Large simulation boxes containing 448 atoms were employed, and periodic boundary conditions were applied along the three Cartesian directions. Off-stoichiometric systems were generated by removing one lithium or sodium atom from the stoichiometric simulation cell. Newton's equations of motion were integrated by using the Verlet algorithm with a time step of 10^{-3} ps. Γ -point sampling for Brillouin zone integration was employed in all the AIMD simulations. Our calculations comprised total simulation times of around 50 picoseconds (ps), and for each compound, we performed a total of seven AIMD simulations considering different temperatures and compositions.

To quantify the transport properties of the selected materials, we computed the corresponding mean-squared displacement (MSD), $\Delta r^2(t)$, and diffusion coefficient, *D*, for all the involved ionic species. The ionic mean-squared displacements were calculated according to the definition

$$\langle \Delta r_i^2(t) \rangle = \langle |r_i(t+t_0) - r_i(t_0)|^2 \rangle$$

where $r_i(t)$ is the position of the migrating ion labeled as *i* at time $t_i t_0$ an arbitrary time origin, and $\langle ... \rangle$ denotes average over atoms and time origins. By averaging over different time origins, we accumulated enough statistics to significantly reduce the MSD numerical fluctuations at long times, thus obtaining accurate *D* values.²⁷ Meanwhile, the ionic diffusion coefficients were estimated with the well-known formula

$$D = \lim_{t \to \infty} \frac{\langle |r_i(t+t_0) - r_i(t_0)|^2 \rangle}{6t}$$

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.0c09783.

Theoretical calculation details, X-ray data of NaCo- $(HCO_2)_3$ synthesis products, FTIR data, thermal analysis results, carbon analysis result, SEM–EDX data of Na₂Co(HCO₂)₄ and NaCo(HCO₂)₃, equivalent circuits used for impedance data fitting, parameters obtained from impedance data fitting, bulk ionic conductivities at room temperature, and reversible Li+ storage performance of LiMn(HCO₂)₃ (PDF)

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Author Contributions

D.K. conceived the idea and designed the experimental work with help from A.P. A.P. carried out all the experimental studies and data analysis, and C.C. performed the computational work. D.K. wrote the manuscript with help from all authors.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

D.K. acknowledges the Swiss National Science Foundation (SNSF) for the financial support for this work through their Ambizione grant. D.K. also acknowledges the UNSW for the support through the start-up grant.

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