Single Na and K ion-conducting sulfonated -NH- linked covalent organic frameworks

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Abstract

Highly ion-conductive solid electrolytes of non-lithium ions (sodium- or potassium-ions) are necessary for pursuing more cost-effective and sustainable energy storage. Here, new two classes of sulfonated -NH-linked covalent organic frameworks (COFs), specifically designed for sodium or potassium ion conduction (named i-COF-2 (Na or K) and i-COF-3 (Na or K)), was synthesized through a straightforward, one-step process using affordable starting materials. Remarkably, these COFs demonstrate high ionic conductivity at room temperature—3.17×10^{-4} S cm^{-1} and 1.02×10^{-4} S cm^{-1} for i-COF-2 (Na) and i-COF-2 (K) and 2.75×10^{-4} S cm^{-1} and 1.42×10^{-4} S cm^{-1} for i-COF-3 (Na) and i-COF-3 (K) —without the need for additional salt or solvent. This enhanced performance, including low activation energies of 0.21 eV for both i-COF-2 (Na) and i-COF-2 (K) and of 0.24 eV and 0.25 eV for i-COF-3 (Na) and i-COF-3 (K), is attributed to the strategic incorporation of sulfonate groups and the directional channels within the COF structure. The Na$^+$ and K$^+$ ion high conductivities, low cost and intrinsic framework stability of i-COF-2 (Na or K) and i-COF-3 (Na or K) provide promising solid electrolyte candidate for the exploration of sustainable energy storage.

Introduction

Covalent organic frameworks (COFs) are versatile materials employed across a diverse array of fields, including gas storage and separation, catalysis, sensing, drug delivery, water purification, and energy storage, owing to their inherent characteristics.[1] COFs are a category of porous polymers characterized by their well-defined channels and periodic structures in two or three dimensions, which are established through covalent linkages among monomers enriched with light elements such as carbon (C), oxygen (O), nitrogen (N), and hydrogen (H). These frameworks boast several beneficial features, including highly organized networks with precise pore sizes, shapes, and configurations, alongside high stability, low density, and the potential for functionalization.[2] Together, these attributes position COFs as an outstanding candidate for solid electrolytes in solid-state batteries.[3-6]

Solid-state batteries have garnered significant attention in both academic research and commercial development, as they address several limitations associated with the conventional liquid-based lithium-ion batteries, such as leakage risks, flammability, and constrained voltage ranges.[3-19] The adoption of solid electrolytes in solid-state batteries offers advantages in terms of improved thermal stability, non-flammability, and streamlined battery architecture. Nonetheless, certain challenges hinder the broader application of both inorganic and polymer solid electrolytes. A critical issue is the low ionic conductivity of solid electrolytes, which limits their practical use.[7,8] Unlike liquid electrolytes that provide a uniform pathway for ion transport, solid electrolytes feature complex, tortuous paths with boundaries that impede ion movement.

To overcome the limitations of inorganic solid electrolytes, various strategies have been employed, including doping, the integration of nanoparticles, microstructure control, interface engineering through coatings, and chemical composition optimization.[9-12] These techniques have successfully improved lithium-ion conductivity. Similarly, for polymer solid electrolytes, enhancements in lithium-ion conductivity have been achieved through methods

such as polymer matrix modifications, doping with ionic liquids or plasticizers, salt adjustments, the addition of nanofillers, and cross-linking.[13-16] These advancements signal promising directions for increasing the efficiency and practical viability of solid-state batteries.

However, most approaches to enhance the ion-conducting properties of solid electrolytes were based on lithium-ion. Because the lithium-ion has smaller size than the other metal cations such as sodium or potassium-ions. Smaller ionic size can have faster ion mobility, and lower energy barrier of ion migration. Therefore, some inorganic or polymer solid electrolytes which have some barriers for ion migration still can transport lithium-ions. However, to make more cost-effective energy storage applications, the lithium should be replaced with cheaper and abundant non-lithium sources such as sodium or potassium. Sodium- or potassium-ions batteries can have benefits in enhanced sustainability, cost-effectiveness, environmental and geopolitical benefits, and versatility across a range of applications.[17-19] However, as can be seen in **Scheme 1**, the energy barriers of sodium- and potassium- ions diffusion for inorganic or polymer solid electrolytes are larger than that of lithium-ion due to larger ionic sizes.[20,21] In inorganic solid electrolytes, atoms are typically arranged in a closely packed mode, leaving limited intrinsic void space, which prevents the diffusion of bulkier ions. On the other hand, in polymer solid electrolytes, ions are often wrapped by polymer chains, making it difficult for them to hop between coordination sites. To reduce the energy barrier of bulky ion diffusion, COFs can be a promising candidate as highly ion-conductive solid electrolyte that can replace the inorganic or polymer. The well-arranged directional pathway and ample void space of COFs can provide the rapid diffusion of various ions, leading to reduce the energy barrier of ion migration.[22] Additionally, when the ionic groups are incorporated in the COFs, the energy barrier can be further reduced with increased hopping sites and these ionic groups can contain the mobile ions, leading to make the COFs to be the single ion conductors without addition of any salt or solvent.[23,24]
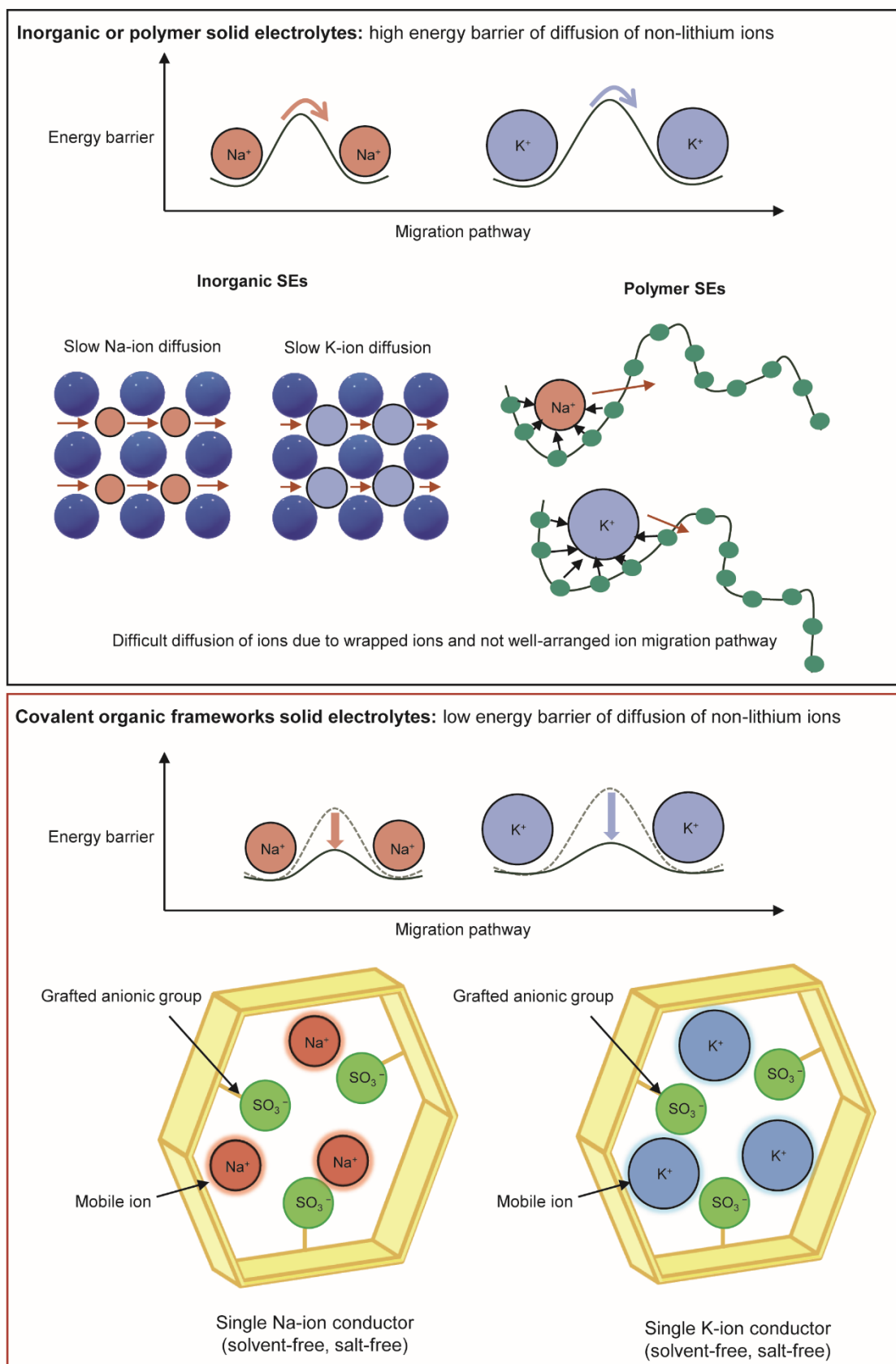
Scheme 1. Na- and K- ion-conducting mechanisms of inorganic, polymer, and COF SEs.

Herein, a new class of ionic COF specifically designed for sodium and potassium ion conduction—sodium sulfonated and potassium sulfonated NH-linked COF, designated as i-COF-2 (Na or K) and i-COF-3 (Na or K) respectively—were developed (**Fig. 1**). Both COFs contain the sulfonate groups and mobile ions, therefore, they can act as superior single ion conductors without addition of any salt or solvent. In addition, the simple structural modification of COFs could be investigated by simply tuning the monomer structure, and the ionic conducting properties and structural changes were also evaluated.

Results and discussion

Fig. 1 shows the synthetic scheme of newly designed two-dimensional (2D) COFs. There are mainly two types of COFs that were developed in this study. Firstly, i-COF-2 was synthesized through a process involving flexible C-NH-C linkages (**Fig. 1a and 1b**). TAZ-3P and 2,5-diaminobenzene sulfonic acid (para-position monomer) were used as starting materials to form covalent bonds and sodium or potassium carbonate was used as a base and converting the proton to sodium form in the sulfonate groups in the COFs. The reaction proceeds under reflux in an organic solvent for one day. Post-reaction, the mixtures are vacuum-filtered, and the resultant solid COF powders are dried overnight at 60°C in a vacuum oven. This reaction can lead to the formation of sodium or potassium phenolate as a byproduct that can be soluble in the organic solvent used during synthesis. Therefore, only i-COF-2 (Na) or i-COF-2 (K) crashed out as pure products. Second type of COF is i-COF-3 (**Fig. 1c and 1d**). The overall synthesizing method is same with that of i-COF-2. The only different point is that i-COF-3 was synthesized by using 1,3-diaminobezene sulfonic acid (ortho-position monomer) instead of 2,5-diaminobezene sulfonic acid (para-position monomer). This simply different position of reaction sites that form the covalent bonds can lead to make different structure of COF and the structural effect on ion conducting properties

also can be investigated. This synthesis method is both straightforward and cost-efficient, relying on readily available starting materials. The integration of $-SO_3^-$ groups and directional channels within the COF structure enhances the diffusivity of Na-ion or K-ion through a hopping mechanism, ensuring efficient pathways for rapid ion transport.)
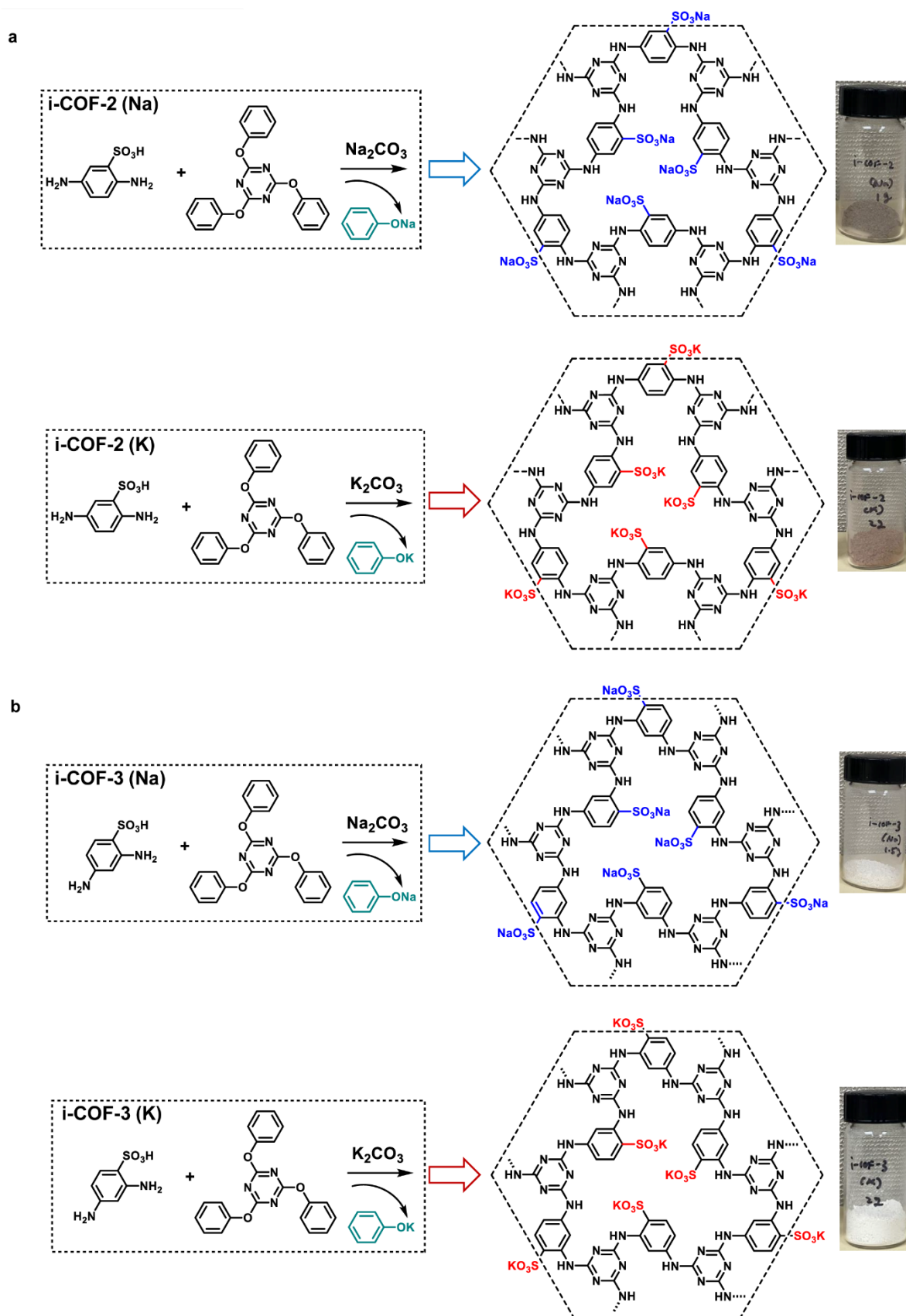
Fig. 1 Synthetic scheme of new design of (a) i-COF-2 (Na or K) and (b) i-COF-3 (Na or K) with different monomers.

To identify whether the covalent bonds were well formed, and sulfonate groups are integrated in the COF samples, the Fourier transform infrared (FT-IR) spectroscopy was used as analysis method (**Fig. 2**). The FT-IR spectrum of i-COF-2 (Na or K) showed characteristic peaks at 1409 cm^{-1}, indicating the formation of covalent bond. Furthermore, the emergence of a peak between 1050 and 1100 cm^{-1} in i-COF-2 (Na or K) and 2,5-diaminobenzene sulfonic acid corresponds to the sulfonate group, indicating successful integration of sulfonate ionic groups within the COF structures. Additionally, a peak at 1355 cm^{-1} was shown in both i-COF-2 (Na or K) and TAZ-3P, which confirmed the presence of a triazine core. Notably, a peak at 912 cm^{-1} observed in TAZ-3P was absent in i-COF-2 (Na or K), suggesting that the phenoxy groups from TAZ-3P were largely replaced with the 2,5-diaminobenzene sulfonic acid monomer. Similar alterations in IR transmittance were also observed for i-COF-3 (Na or K), indicating the parallel covalent bond formation and integration process of the sodium sulfonate group.

To investigate the amorphous or crystalline structures of synthesized COF powders and whether there is remaining residue, the powder X-ray diffraction (PXRD) analysis was performed (**Figs. S1-S4**). There were new peaks which are not relevant to the starting materials and possible byproduct in the PXRD analysis of COF samples, indicating the formation of COF. The data exhibited an amorphous structure.
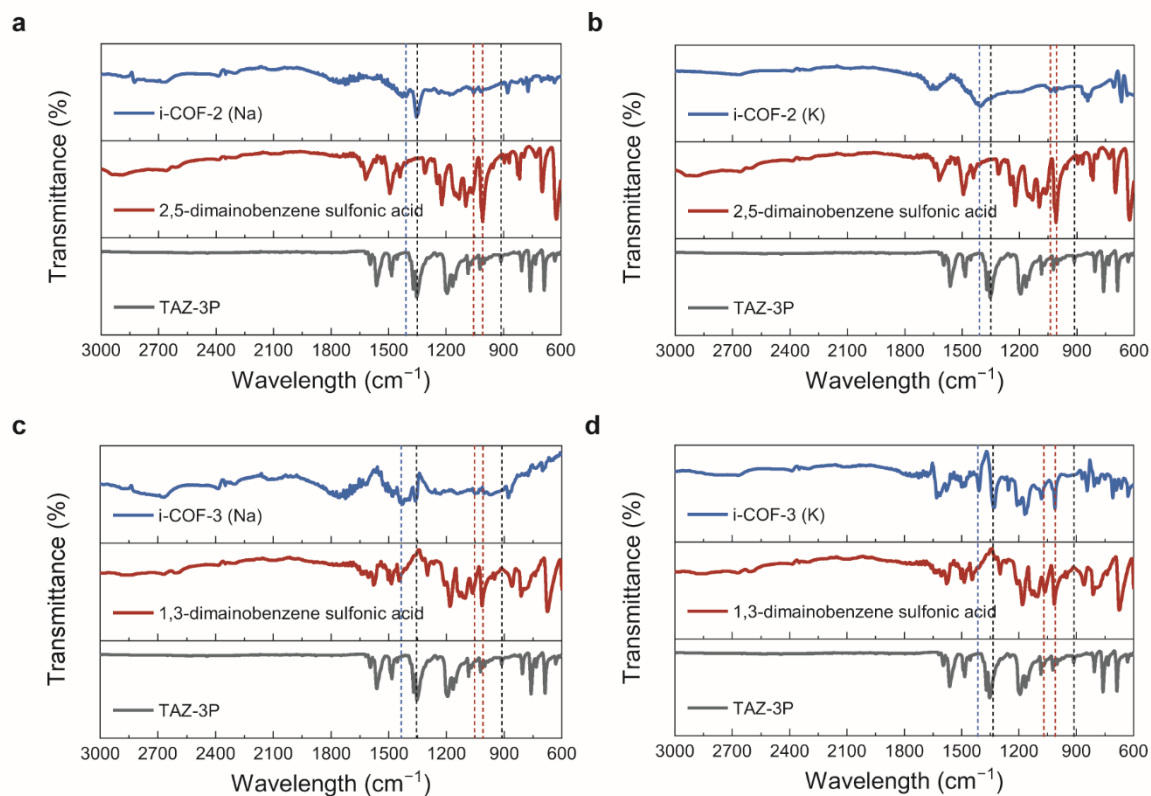
Fig. 2 ATR-FTIR of i-COF-2 (Na or K) and i-COF-3 (Na or K).
(a) and (b) ATR-FTIR of (a) i-COF-2 (Na) and (b) i-COF-2 (K).
(c) and (d) ATR-FTIR of (c) i-COF-3 (Na) and (d) i-COF-3 (K).

The ionic conducting properties of i-COF-2 (Na) and i-COF-2 (K) were evaluated through electrochemical measurements (**Fig. 3**). Initially, the ionic conductivity at room temperature (20°C) was determined using electrochemical impedance spectroscopy (EIS) (**Fig. 3a**). For assessing the ionic conductivity of the COF materials, the COF powders were placed between stainless steel electrodes in a split cell configuration, acting as a blocking cell. These were then compressed under a pressure of 10 MPa for 1 hour to form a uniform COF pellet. The ionic conductivities of i-COF-2 (Na) and i-COF-2 (K) at room temperature were determined to be 3.17×10^{-4} and 1.02×10^{-4} S cm^{-1}, respectively. The sodium-ion conductivity of i-COF-2 (Na) is higher than potassium-ion conductivity of i-COF-2 (K), indicating the smaller ionic size has faster ion mobility as explained above. These values, indicative of high ionic conductivity, underscore the unique and superior ionic mechanism facilitated by the ionic COF structure, which achieves significant conductivity despite the generally slow diffusivity of Na- or K-ions.

Further investigation into the ion-hopping activation energy (E_a) within i-COF-2 (Na) and i-COF-2 (K) was conducted through electrochemical EIS measurements of COF pellets at varying temperatures (20, 30, 40, 50, and 60°C) (**Fig. 3b-3d**). The results reveal a progressive increase in ionic conductivity with temperature. Specifically, the ionic conductivities of i-COF-2 (Na) ranged from 3.17×10^{-4} S cm^{-1} at 20°C to 8.44×10^{-4} S cm^{-1} at 60°C. Similarly, i-COF-2 (K) exhibited conductivities from 1.02×10^{-4} S cm^{-1} at 20°C to 2.70×10^{-4} S cm^{-1} at 60°C. The activation energies calculated for i-COF-2 (Na) and i-COF-2 (K) were both 0.21 eV. These relatively low E_a values highlight the efficient ion migration within i-COF-2, facilitated by the directional porous channels and the strategically integrated sulfonate groups.
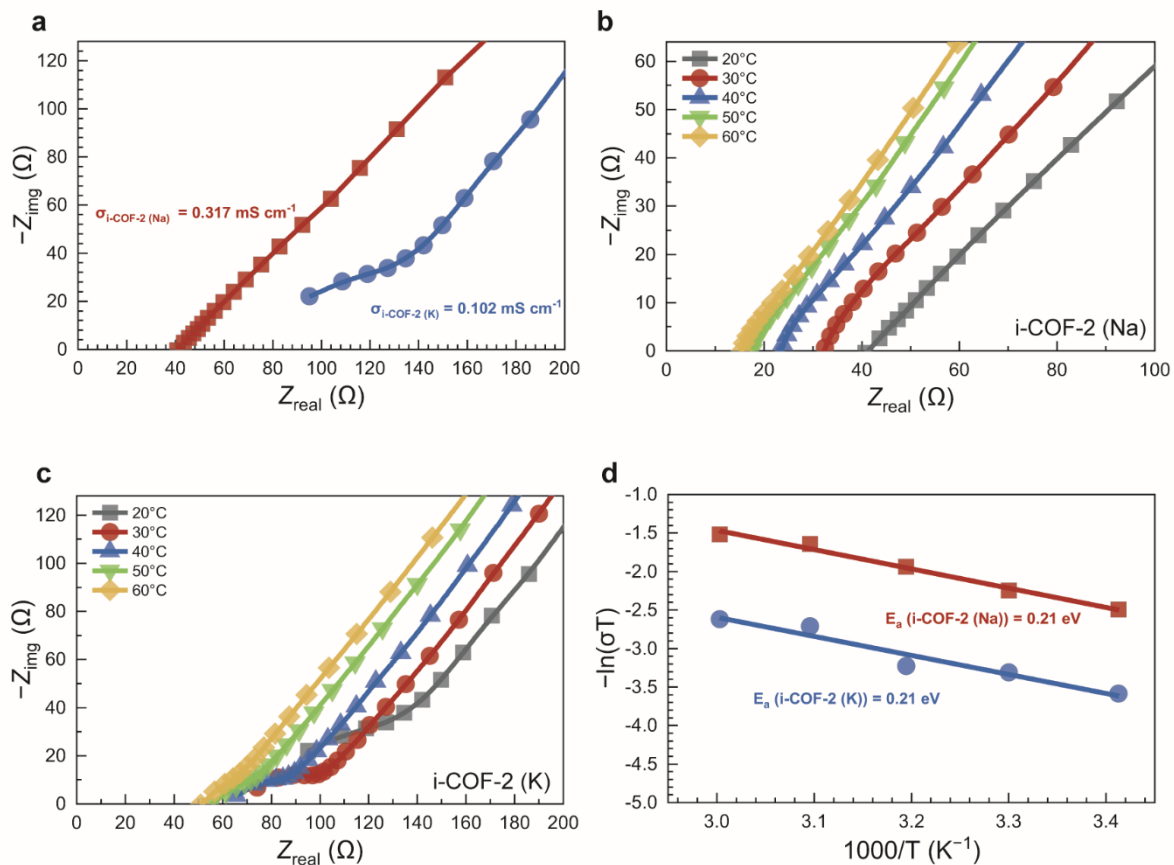
Fig. 3 Ionic conducting properties of i-COF-2 (Na) and i-COF-2 (K).
(a) Ionic conductivity at room temperature.
(b) and (c) EIS plots at different temperatures of (b) i-COF-2 (Na) and (c) i-COF-2 (K).
(d) Activation energy.

Similarly, the ionic conducting properties of i-COF-3 (Na) and i-COF-3 (K) were also investigated through electrochemical measurements (**Fig. 4**). The ionic conductivities of i-COF-3 (Na) and i-COF-3 (K) at room temperature were determined to be 2.75×10^{-4} and 1.42×10^{-4} S cm^{-1}, respectively. Further evaluation into the ion-hopping activation energy (E$_a$) within i-COF-3 (Na) and i-COF-3 (K) was conducted through same method at varying temperatures (20, 30, 40, 50, and 60°C) (**Fig. 4b-4d**). The ionic conductivities of i-COF-3 (Na) increased from 2.75×10^{-4} S cm^{-1} at 20°C to 8.43×10^{-4} S cm^{-1} at 60°C with increased temperature. In the same manner, i-COF-3 (K) showed conductivities from 1.42×10^{-4} S cm^{-1} at 20°C to 5.04×10^{-4} S cm^{-1} at 60°C. The activation energies calculated for i-COF-3 (Na) and i-COF-3 (K) were 0.24 eV and 0.25 eV, respectively, indicating low E$_a$ could be achieved by intrinsic properties of ionic COF. Here, the E$_a$ of i-COF-3 was higher than that of i-COF-2, meaning that there is the relationship between the structure of COF and ion conducting properties. The structural difference between i-COF-2 and i-COF-3 could be achieved by altering the position of reaction sites of one monomer (diaminobenzene sulfonic acid) used in the synthesis (para-positioned monomer for i-COF-2 and ortho-positioned monomer for i-COF-3). This simple difference could make the different COF structures, indicating the easy tunability of COF can be one of the advantages of COF has. The lower Ea of i-COF-2 than i-COF-3 may relate to the larger surface area and pore volume than those of i-COF-3 (**Fig. S5**). The larger surface area and pore volume can provide more free space for ion transport. However, there are many complex ion hopping pathways that should be considered further such as effect of interaction between sulfonate ion groups and mobile ions on ion conducting properties.
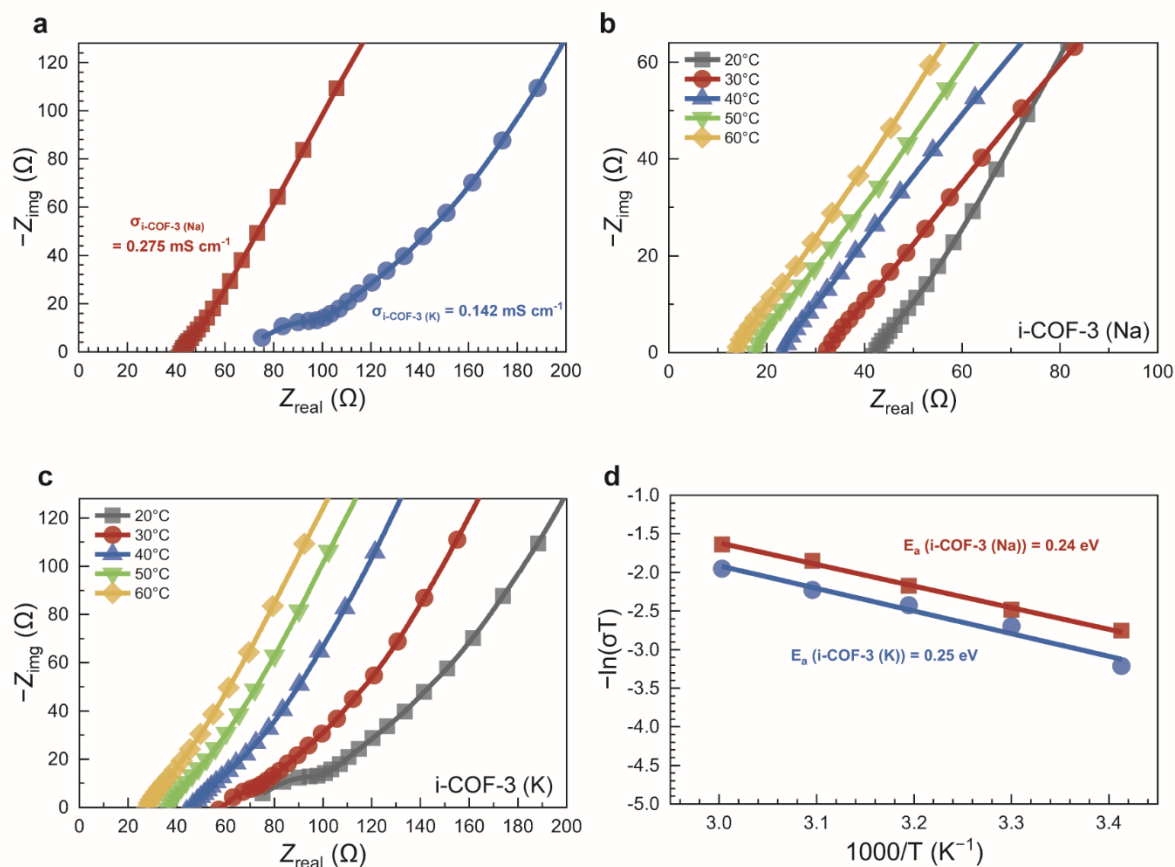
Fig. 4 Ionic conducting properties of i-COF-3 (Na) and i-COF-3 (K).
(a) Ionic conductivity at room temperature.
(b) and (c) EIS plots at different temperatures of (b) i-COF-3 (Na) and (c) i-COF-3 (K).
(d) Activation energy.

The ion conducting properties of i-COF-2 and i-COF-3 are comparable to, or exceed, those reported for other COFs or metal-organic frameworks (MOFs) (**Table 1**).[25-28] Some reported COFs or MOFs showed high ionic conductivity and low E_a. However, they involved additional solvent or salt when measure the conductivity. On the other hand, our COFs could show good ion conducting properties even without addition of any solvent or salt. This superior ion conductivity without any solvent or salt attributed to the sulfonate groups containing mobile ions already in the COF structure itself. The grafted sulfonate groups can provide more ion hopping sites, and already contained mobile ions (sodium-ion or potassium-ion) in the ionic groups during the synthesis could make the COF to be single ion conductors.

Table 1. Na- or K-ion conductivity comparison of newly developed ionic COF with other COFs or MOFs.

Solid electrolyte	Conducting ion	Additional solvent or salt	E_a eV	$\sigma_{(RT)}$ S cm^{-1}	Reference
NaOOC-COF	Na-ion	liquid electrolyte (10.0 µL, 1.0 M) of $NaPF_6$ (in propylene carbonate, PC)	0.24	2.68×10^{-4}	[R25]
TPDBD-CNa-QSSE	Na-ion	9 wt.% solvents (PC) with 5% FEC	0.204	1.30×10^{-4}	[R26]
MIL-121/Na	Na-ion	50 wt% of 1 M $NaClO_4$ in PC	0.36	1.0×10^{-4}	[R27]
MOF-808-SO_3K	K-ion	20 µL of anhydrous PC	0.32	3.1×10^{-5}	[R28]
i-COF-1 (Na)	Na-ion	-	0.28	1.41×10^{-4}	In progress
i-COF-1 (K)	K-ion	-	0.21	1.37×10^{-4}	
i-COF-2 (Na)	**Na-ion**	**-**	**0.21**	$\mathbf{3.17 \times 10^{-4}}$	**This work**
i-COF-2 (K)	**K-ion**	**-**	**0.21**	$\mathbf{1.02 \times 10^{-4}}$	
i-COF-3 (Na)	**Na-ion**	**-**	**0.24**	$\mathbf{2.75 \times 10^{-4}}$	
i-COF-3 (K)	**K-ion**	**-**	**0.25**	$\mathbf{1.42 \times 10^{-4}}$	

Furthermore, a comparative analysis with other solid electrolytes, including sulfide, halide, and beta-alumina SEs, reveals that the sodium-ion conductivity of these ionic COFs is comparable or slightly lower than that of other high-performance solid electrolytes (**Table 2**).

[29-40] Despite this, the ionic COFs distinguish themselves through their superior stability and cost-effectiveness, addressing the common challenges of high processing temperatures, expensive materials, and air sensitivity associated with inorganic or halide solid electrolytes that exhibit high Na-ion conductivity. Notably, the K-ion conductivity of the developed ionic COFs significantly surpasses that of other solid electrolytes, showcasing their exceptional ionic conducting properties. The ionic conductivity is related to the ion mobility and the number of ion concentration. When the ion mobility or the number of ion concentration increases, the ionic conductivity will increase. To compare the ion mobility between COF and inorganic solid electrolytes, the ion concentrations were calculated, and most inorganic solid electrolytes showed larger ion density than that in COF. Even though the developed COF samples have lower ion concentrations, they still could show high ion conductivity due to fast ion mobility. This result is matched with the ability of COF on reducing the energy barrier of ion diffusion. This advancement in ion conductivity positions ionic COFs as viable alternatives to expensive Li-ion batteries, leveraging the abundance and low cost of Na- or K-ions.

Table 2. Na- or K-ion conducting properties comparison of newly developed ionic COF with other SEs.

Solid electrolyte	Conducting ion	Mobile ion concentration Ions cm^{-3}	E_a eV	$\sigma_{(RT)}$ S cm^{-1}	Reference
Na$_{3.4}$Sc$_2$Si$_{0.4}$P$_{2.6}$O$_{12}$	Na-ion	3.99×10^{21}	0.33	6.9×10^{-4}	[R29]
Na$_{3.4}$Sc$_{0.4}$Zr$_{1.6}$Si$_2$PO$_{12}$	Na-ion	3.46×10^{21}	0.20	1.9×10^{-3}	[R30]
Na$_3$Zr$_2$(SiO$_4$)$_2$PO$_4$ (NZSP)	Na-ion	3.69×10^{21}	0.12	9.66×10^{-4}	[R31]
Na$_{3.125}$Zr$_{1.75}$Sc$_{0.125}$Ge$_{0.125}$Si$_2$PO$_{12}$	Na-ion	3.43×10^{21}	0.19	4.64×10^{-3}	[R32]
Na$_{3.3}$La$_{0.3}$Zr$_{1.7}$Si$_2$PO$_{12}$ (NLZSP0.3)	Na-ion	3.27×10^{21}	0.1	1.34×10^{-3}	[R33]
Na-β″-Al$_2$O$_3$	Na-ion	3.25×10^{21}	0.1	2.1×10^{-3}	[R34]
Na$_3$PS$_{3.85}$O$_{0.15}$	Na-ion	7.06×10^{21}	0.43	2.7×10^{-4}	[R35]
Na$_3$SbS$_4$	Na-ion	5.66×10^{21}	0.24	1.0×10^{-3}	[R36]
NaTaCl$_6$	Na-ion	3.61×10^{21}	-	4.0×10^{-3}	[R37]
Halide HSEs incorporating a UCl$_3$-type framework	Na-ion	3.24×10^{21}	-	2.7×10^{-3}	[R38]
0.5Na$_2$O$_2$-TaCl$_5$ (NTOC)	Na-ion	3.79×10^{21}	0.30	4.62×10^{-3}	[R39]
Na−LaCeZrHfTa−Cl	Na-ion	4.08×10^{21}	0.326	8.8×10^{-4}	[R40]
K−LaCeZrHfTa−Cl	K-ion	3.83×10^{21}	0.552	1.32×10^{-6} (at 55 °C)	[R40]
i-COF-1 (Na)	Na-ion	1.22×10^{21}	0.28	1.41×10^{-4}	In progress
i-COF-1 (K)	K-ion	1.22×10^{21}	0.21	1.37×10^{-4}	
i-COF-2 (Na)	**Na-ion**	**1.48×10^{21}**	**0.21**	**3.17×10^{-4}**	**This work**
i-COF-2 (K)	**K-ion**	**1.34×10^{21}**	**0.21**	**1.02×10^{-4}**	
i-COF-3 (Na)	**Na-ion**	**1.66×10^{21}**	**0.24**	**2.75×10^{-4}**	
i-COF-3 (K)	**K-ion**	**1.28×10^{21}**	**0.25**	**1.42×10^{-4}**	

Scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDS) analyses of i-COF-2, 3 (Na) and i-COF-2, 3 (K) pellets were conducted to examine the morphology of the ionic COFs and ensure the uniform distribution of their constituent elements (**Figs. S6-S9**). The SEM images highlighted the uniform packing of COF powders within the pellets, indicating successful compaction and structural integrity. Furthermore, EDS analysis provided a detailed elemental distribution within the pellets, confirming the presence and uniform distribution of carbon (C), nitrogen (N), oxygen (O), sulfur (S), and sodium (Na) in the i-COF-2, 3 (Na) pellets. Similarly, for the i-COF-2, 3 (K) pellets, elements including C,

N, O, S, and potassium (K) were uniformly distributed. These findings underscore that the sulfonate groups, -SO$_3$Na and -SO$_3$K, were effectively grafted into the COF structures, and the pellets were uniformly prepared through a pressing method at a relatively low pressure of only 10 MPa. This uniform elemental distribution and the integrity of the COF structure are crucial for ensuring consistent ionic conductivity and the overall performance of the COFs as solid electrolytes.

The detailed characterizations and electrochemical assessments provided in this study confirm that i-COF-2, 3 (Na) and i-COF-2, 3 (K) exhibit superior qualities, enabling high ionic conductivity for the cost-efficient and plentiful sodium and potassium ions. This significant discovery highlights the viability of these novel ionic covalent organic frameworks (COFs) as cost-effective materials, utilizing low-cost precursors that are markedly less expensive than most inorganic solid electrolytes (SEs). Although certain inorganic sulfide SEs may employ affordable materials, their vulnerability to atmospheric exposure curtails their utility due to stability issues. In stark contrast, COFs display outstanding air stability, marking them as favorable SE candidates in terms of both economic efficiency and long-term performance.

Conclusions

In summary, this research introduces the two new classes of non-lithium ions conductors with showing outstanding ion-conductive properties: sulfonated -NH- linked ionic COF containing sodium-ion or potassium-ion within their framework structures. One class of COF is designated as i-COF-2 (Na or K), and the other class of COF is names as i-COF-3 (Na or K). The different COF structures could be prepared with same straightforward synthesizing process by altering only one monomer (para-position monomer or ortho-position monomer). Such tunability not only results in diverse ion conducting properties but also paves the way for further investigations into the structural-property relationships of COFs by experimenting with

various monomers.

Both i-COF-2 (Na or K) and i-COF-3 (Na or K) showed remarkable ionic conductivity and low activation energy with reduced energy barrier of sodium- or potassium- ions diffusion with, facilitated by a well-organized porous structure and the incorporation of sulfonate anionic groups even without any addition of solvent or salt. This development not only offers a promising avenue for more sustainable energy storage solutions but also aligns with global efforts to transition away from reliance on expensive and less abundant materials.

Looking forward, the potential for scaling up the fabrication of freestanding SEs and optimizing the manufacturing process of COFs for large-scale applications presents an exciting avenue for practical implementation. Such materials must be not only economically viable but also scalable, ensuring their adoption can meet global demands. This research paves the way for future advancements in material science, promising a significant impact on the development of eco-friendly and efficient energy storage technologies.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information can be found with this article online.

Synthetic methods; characterization; electrochemical data; morphological analysis

■ AUTHOR INFORMATION

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Notes

The authors declare no competing financial interest.

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