

Cation-Assisted Water Oxidation with Crown Ether–Based Covalent Organic Frameworks

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ABSTRACT: Covalent Organic Framework-based electrocatalysts for water oxidation are usually designed by inducing polarization into an organic framework. The most common methodology, “heteroatom insertion” suffers from lower catalytic activity than metalated systems. Herein, we introduce a strategy of polarity induction into organic frameworks by complexing electrolyte’s alkali metal using crown ether. We have synthesized a series of porous crystalline covalent organic frameworks (COFs) with different sizes of crown ether units, having different alkali metal binding abilities. COF-catalysts having crown ethers in their backbone show oxygen and hydrogen evolution (OER & HER) performance in alkaline electrolytes. Electrocatalytic performances of various COF-catalysts have also been studied while changing the alkali metal of the electrolyte solution. The most efficient catalyst B18C achieved a current density of 20 and 100 mA cm⁻² at an overpotential (η_{20} and η_{100}) 287 ± 1 and 362 ± 8 mV (for OER) in 1 M KOH (pH = 13.6), with a good electrocatalytic stability (16 h chronopotentiometry study showed 2 mV potential change at 25 mA cm⁻² current density). Notably, B18C COF also exhibited good OER performance in a 1 M K₂SO₄ (pH = 6.3) with an overpotential (η_{20}) of 471 mV. Additionally, a promising alkaline HER activity of B18C ($\eta_{20} = 310 \pm 5$ mV) leads to an overall water-splitting performance in 1 M KOH ($E_{\text{cell}} = 1.784$ V @ 20 mA cm⁻²).

INTRODUCTION

Covalent Organic Frameworks (COFs) are a class of highly tunable materials known for their exceptional crystallinity, high porosity, and thermal and chemical stability.^[1] COFs can be engineered to provide specific catalytic centers by enabling precise functional group incorporation into their backbones, making them ideal for various catalytic processes, including electrocatalysis and photocatalysis.^[2] Noble metals and their oxides, along with transition metal-based systems, exhibit superior electrocatalytic oxygen evolution reaction (OER) and hydrogen evolution reaction (HER).^[3] However, their application is hindered by limitations such as susceptibility to gas poisoning, and the requirement for complex synthetic processes to obtain

specific phases.^[4] Recently, electrocatalysts, including heteroatom-doped carbon materials and porous organic polymers, have gained attention due to their chemical tunability, which is essential for catalyst design.^[5] However, these materials often suffer from lower catalytic activity than metalated systems, possibly due to insufficient polarization and poor intermediate stabilization.^[6] In an effort to overcome these challenges, we decided to introduce alkali metal binding sites into the COF frameworks. Crown ethers, widely known for their ability to selectively complex alkali metal ions, offer a unique approach to enhance polarization, local hydroxide ion concentration, and hydrophilicity in the COF backbone

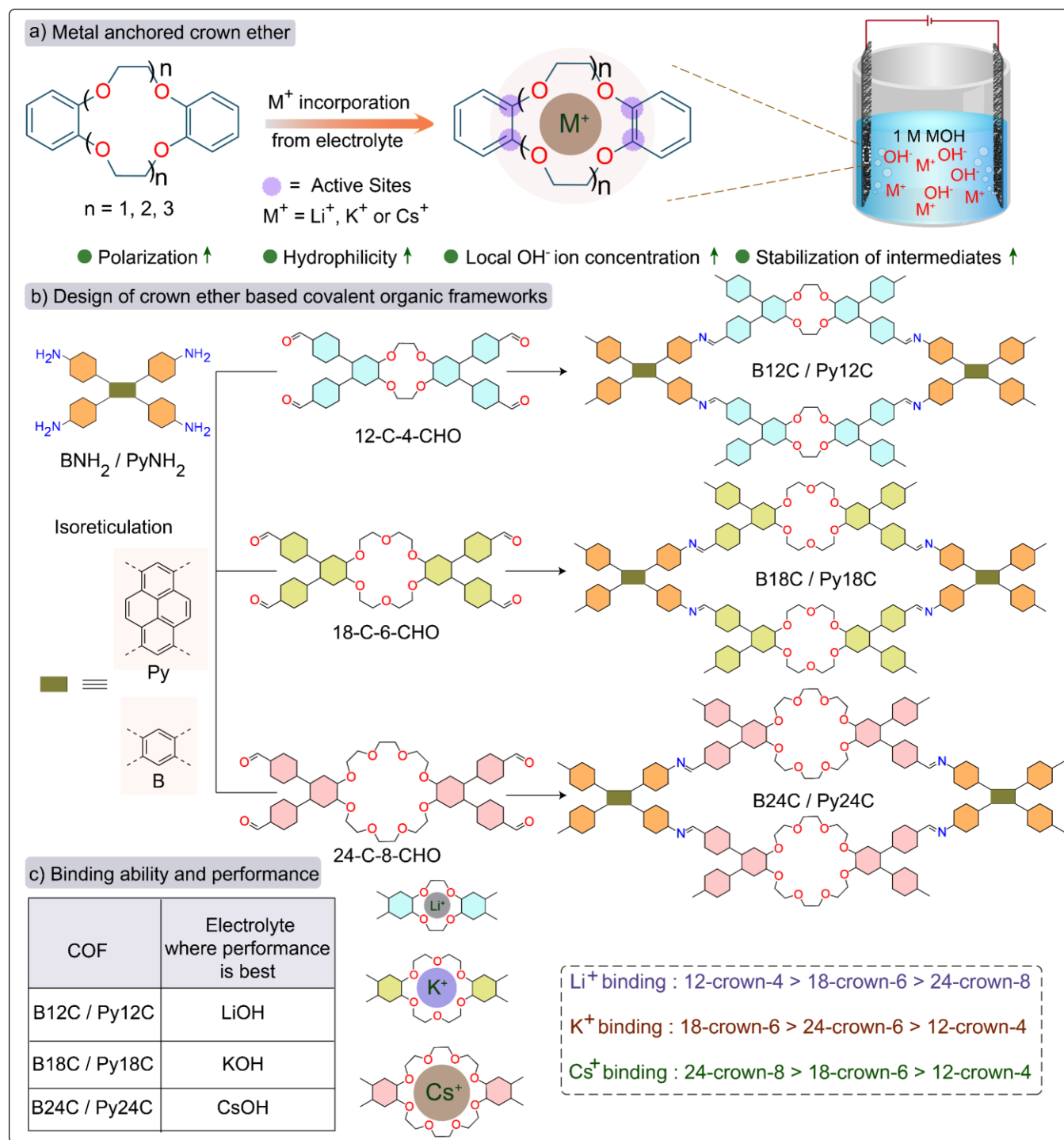


Figure 1. Crown ether COFs: a) Crown ethers as alkali metal binding sites b) Design of crown ether-based COFs c) Alkali metal binding ability of crown ethers and electrochemical performances.

thereby electrocatalytic performance of COFs.^[7] Previous studies have demonstrated the potential of crown ethers as phase-transfer catalysts, ion separators, stabilizers for reactive intermediates and boosters for electrochemical processes.^[8] Leveraging their ion-selective properties, we synthesized a series of crown ether-based COFs with varying alkali metal-binding abilities, significantly enhancing OER and HER performance. The crown ether-

functionalized COFs reported here with bifunctional activity in alkaline media, showcase an overpotential of 287 ± 1 mV for OER and 310 ± 5 mV for HER at 20 mA cm^{-2} , with stability over 1000 cycles and 16 h chronopotentiometry at 25 mA cm^{-2} . Therefore, by studying the relationship between crown-ether binding capabilities and catalytic performance, we could gain insights into designing advanced catalysts for efficient water oxidation.

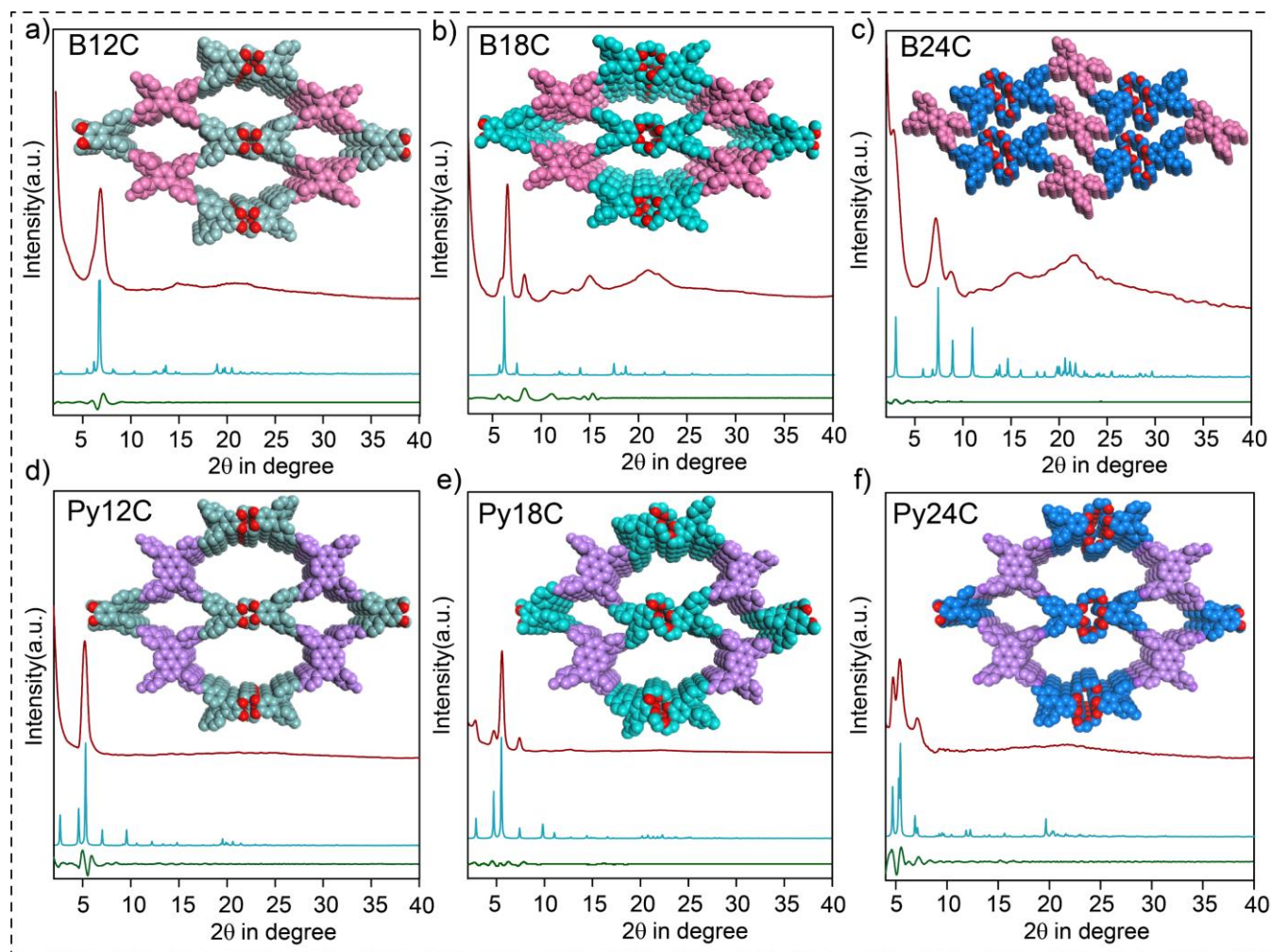


Figure 2. PXRD patterns of COFs: a) B12C b) B18C c) B24C d) Py12C e) Py18C, and f) Py24C. (Maroon: Experimental, sky: simulated, green: difference)

RESULT AND DISCUSSION

A series of six crown ether-based covalent organic frameworks (COFs)—B12C, B18C, B24C, Py12C, Py18C, and Py24C^[9]—were synthesized via a solvothermal method using Schiff-base condensation. The condensation involved crown ether aldehydes (12-C-4-CHO, 18-C-6-CHO, and 24-C-8-CHO) with 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl) tetra-aniline and 4,4',4'',4'''-(benzene-1,3,6,8-tetrayl) tetra-aniline (Figure 1b, Figures S31–S36). Powder X-ray diffraction (PXRD) analysis revealed that all synthesized COFs exhibited long-range order and strong diffraction patterns, indicative of high crystallinity. For B12C, the most prominent peaks were observed at 6.7° (2θ) and 6.0° (2θ), corresponding to reflections from the (110) and (100) planes. Similarly, B18C exhibited strong peaks at 6.5° (2θ) and 6.1° (2θ), also assigned to the (110) and (100) planes. B24C showed a peak at 7.1° (2θ) along with additional peaks at 2.9°, 8.4°, and 10.8° (2θ), corresponding to reflections from the (110), (010), (120), and (130) planes. For Py12C, the most intense peak appeared at 5.4° (2θ), originating from a combination of the (100) and (020) planes. Py18C exhibited its most prominent peak at 5.5° (2θ), along with peaks at 2.86°, 4.7°, and 7.4° (2θ), which were attributed to reflections from the (110), (100), (010), and (210) planes. Finally, Py24C displayed its most intense

peak at 5.2° (2θ), with additional peaks at 4.6° and 6.9° (2θ), corresponding to the (110), (010), and (210) planes, (Figure 2). The eclipsed AA stacking model showed good alignment with the experimental diffraction patterns. Furthermore, Pawley refinement confirmed the structure, with low R_p (0.98 – 5.28 %) and R_{wp} (1.49 – 7.32 %) values validating the reliability of the PXRD data (Figures S37–S42). However, one must note that the Pawley refinement may not achieve complete structural accuracy, as it modifies unit cell parameters, scale factors, background, peak shape, and intensities, but does not alter atomic positions or structure factors^[10] FT-IR analysis revealed a peak at ~1625 cm^{-1} , indicating the presence of imine bonds ($-\text{HC}=\text{N}-$), alongside a peak at ~1600 cm^{-1} attributed to aromatic $-\text{CH}=\text{CH}-$ stretching, and an attenuated peak at ~1695 cm^{-1} corresponding to residual $-\text{HC}=\text{O}$ functionalities (Figures S43–S49). We performed solid-state ^{13}C cross-polarization magic-angle spinning (CP-MAS) NMR spectroscopy to explore the bonding within the frameworks. The spectra displayed two distinct ^{13}C peaks at approximately 70 ppm and 160 ppm, assigned to aliphatic ($-\text{CH}_2-\text{O}-$) and imine ($-\text{HC}=\text{N}-$) carbons,^[9] Peaks corresponding to aromatic carbons were observed in the 110 to 150 ppm range, while a residual $-\text{CH}=\text{O}$ peak appeared at 190 ppm for Py12C and Py24C (Figure 3a,

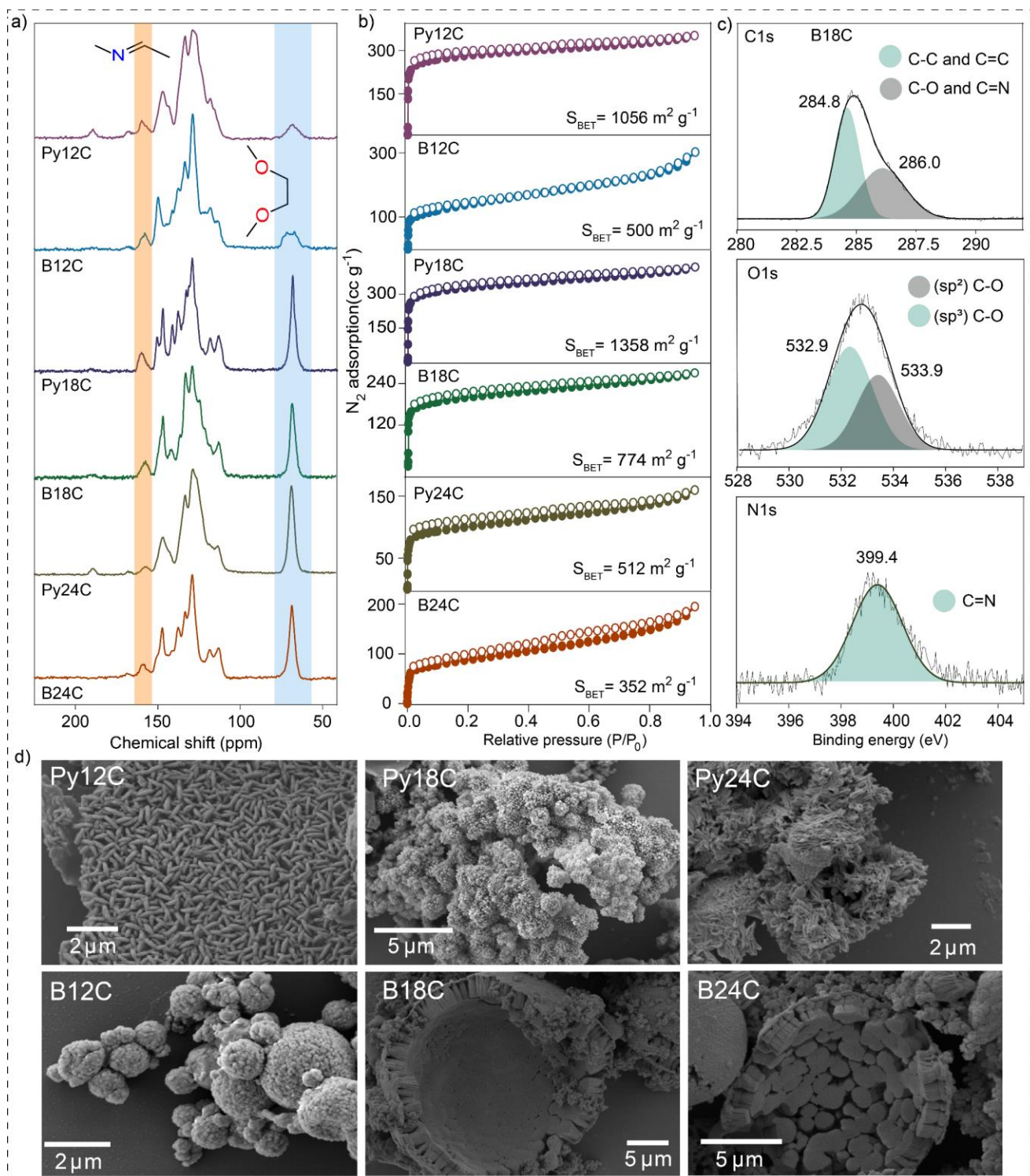


Figure 3. a) Solid state ^{13}C -CPMAS b) N_2 adsorption isotherm c) XPS spectra of C1s, O1s and N1s of B18C COF d) SEM images of B12C, B18C, B24C, Py12C, Py18C, and Py24C COFs.

Figures S50-S55).^[3e] These findings are consistent with the spectroscopic analyses of the COFs and the imine-bonded monomers of crown ether aldehydes (Figures S44-S47, S50-S53). The deconvoluted X-ray photoelectron spectroscopy (XPS) of C1s spectra exhibited two peaks at binding energies of ~ 284.7 – 284.8 eV, corresponding to $-\text{CH}_2-\text{CH}_2-$ and $-\text{CH}=\text{CH}-$ carbons, and 285.9 – 286.0 eV, attributed to sp^3 $-\text{CH}_2-\text{O}-$, sp^2 $=\text{CH}-\text{O}-$, and $-\text{CH}=\text{N}-$

carbons.^[11] The high-resolution O1s spectra revealed two signals at binding energies of ~ 532.1 – 532.4 eV and 533.3 – 533.6 eV, corresponding to sp^3 $-\text{CH}_2-\text{O}-$ and sp^2 $=\text{CH}-\text{O}-$ groups.^[12] The high-resolution N1s spectra also displayed a single peak at 399.1 – 399.6 eV, confirming the presence of imine ($-\text{HC}=\text{N}-$) bonded nitrogen (Figure 3c, Figures S57–S58).^[11b] The Brunauer–Emmett–Teller (BET) surface areas are found to be 1056 , 500 , 1358 , 774 , 512 , and 352 m^2 g^{-1}

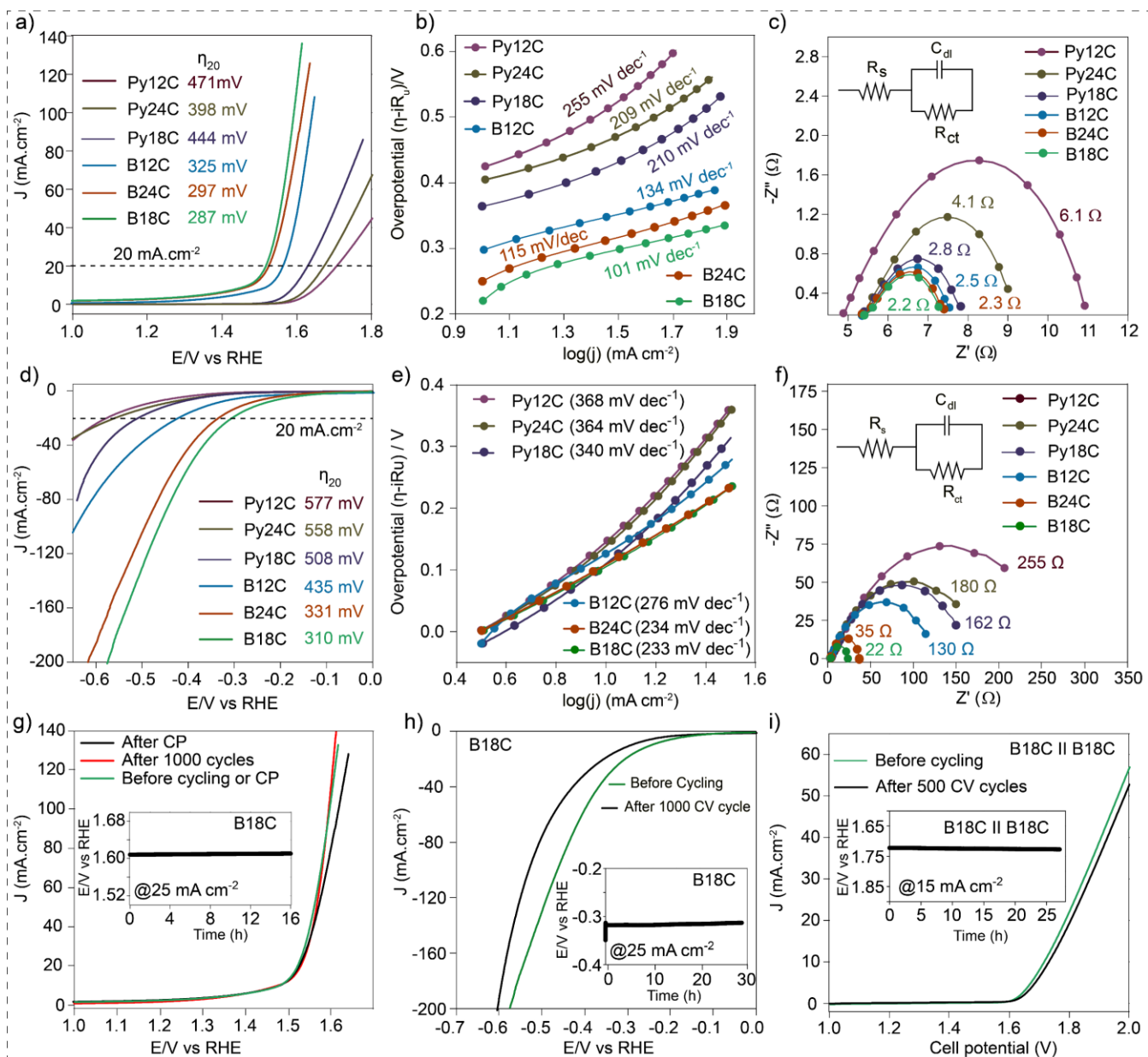


Figure 4. Electrochemical performances of the COFs: a) The mass normalized LSV curves for OER (measured at 5 mV sec⁻¹ scan rate) b) The Tafel plot for OER c) Electrochemical impedance spectroscopy for OER d) The mass normalized LSV curves for HER (measured at 5 mV sec⁻¹ scan rate) e) The Tafel plot for HER f) Electrochemical impedance spectroscopy for HER. g) Chronopotentiometry of B18C and AD study of B18C (1000 CV cycles) for OER h) Chronopotentiometry of B18C and AD study of B18C (1000 CV cycles) for HER. h) Full cell LSV, chronopotentiometry, AD study of the full cell (500 CV Cycles).

for Py12C, B12C, Py18C, B18C, Py24C and B24C (Figure 3b). The thermogravimetric analysis (TGA) of COFs indicates the thermal stability around 380–400°C (Figure S56). Scanning electron microscopy (SEM) analysis of these COFs showed agglomeration of tiny crystallites (Figure 3d, Figures S59–S64). Transmission electron microscopy (TEM) images of B12C and Py18C COFs revealed distinct lattice fringes indicating crystalline domains (Figures S59–S64). Inductively coupled plasma mass spectrometry (ICP-MS) analysis showed that B12C, B18C, and B24C COFs contained approximately 0.09 % (w/w), 0.08 % (w/w), and 0.07 % (w/w) iron, as well as 0.5 % (w/w), 0.4 % (w/w), and 0.6 % (w/w) palladium. These trace metals are attributed to

residual catalysts from the linker synthesis. Additionally, ICP-MS analysis of the KOH (purchased from Merck) detected approximately 0.03 % (w/w) iron. The stability of the COFs in the alkaline medium plays a crucial role in alkaline water splitting. The PXRD patterns after alkali treatment (3 M and 5 M KOH for 7 days at room temperature) retain the initial diffraction pattern with negligible change in crystallinity. Bond connectivity was also retained after alkali treatment, as evident from the FT-IR spectra (characteristic HC=N- ~ 1625 cm⁻¹ remains unchanged along with other peaks). After 5 M KOH treatment, binding energies of the COFs remain mostly unaltered with an additional peak in O1s spectra due to the

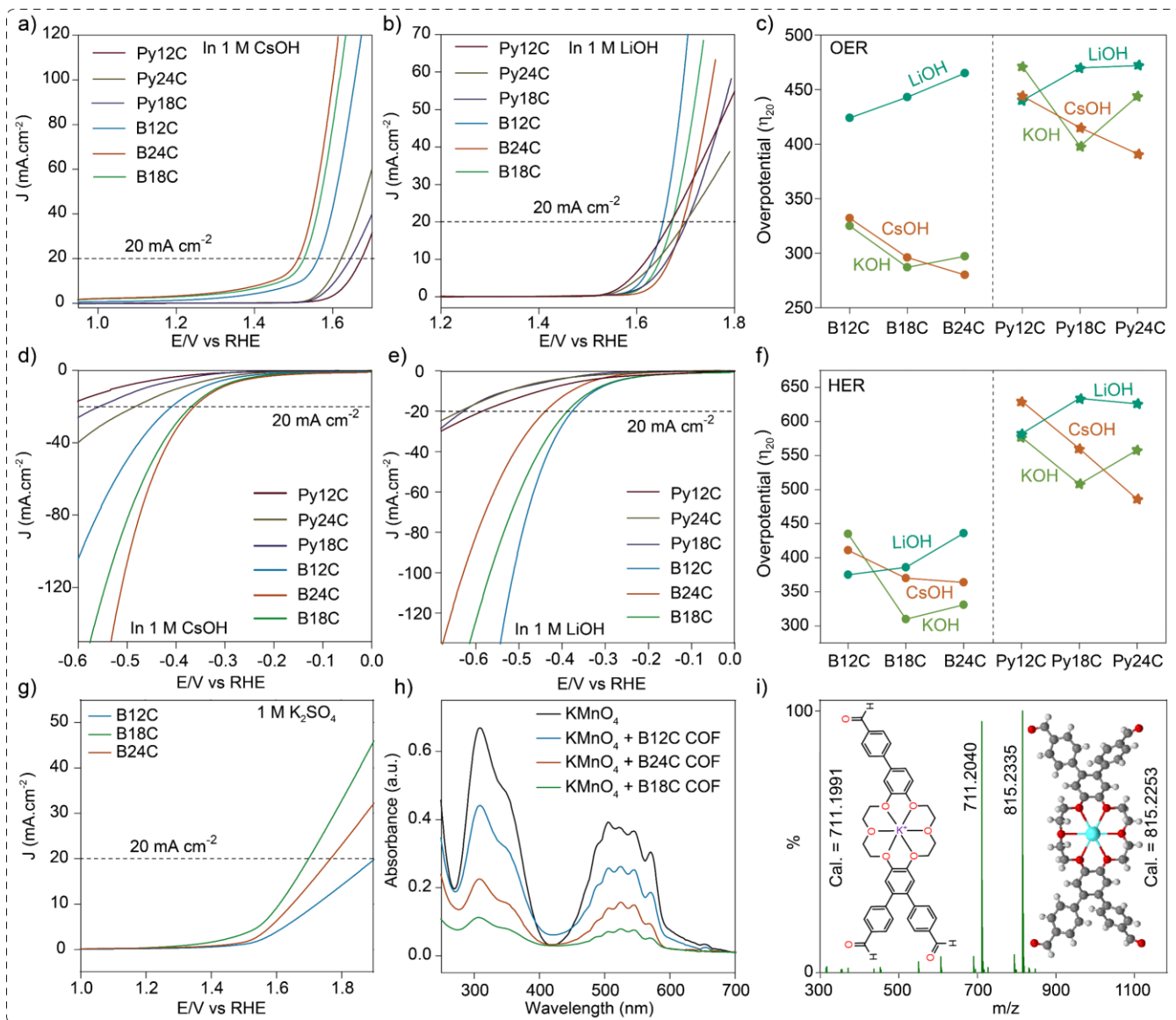


Figure 5: Electrocatalytic performance of the COFs: a) The mass normalized LSV curves (measured at 5 mV sec^{-1} scan rate) for OER in 1 M CsOH b) The mass normalized LSV curves (measured at 5 mV sec^{-1} scan rate) for OER in 1 M LiOH c) Comparative overpotential (η_{20}) for all the COFs reported here in different metal hydroxide electrolytes (LiOH, KOH, and CsOH) for OER d) The mass normalized LSV curves (measured at 5 mV sec^{-1} scan rate) for HER in 1 M CsOH e) The mass normalized LSV (measured at 5 mV sec^{-1} scan rate) curves for HER in 1 M LiOH f) Comparative overpotential (η_{20}) for all the COFs reported here in different metal hydroxide electrolytes (LiOH, KOH, and CsOH) for HER g) The mass normalized LSV curves (measured at 5 mV sec^{-1} scan rate) for OER in 1 M K_2SO_4 h) UV-visible experiment i) HR-MS of potassium bound 18-crown ether-based aldehydes.

adsorbed hydroxide ion, as evident from the XPS spectra. Additionally, there was no change in morphology after exposure to 3 M and 5 M KOH (Figures S65–S68). The BET surface area of the COFs decreased after treatment with 3 M and 5 M KOH. For instance, the surface area of Py18C COF decreased from $1356 \text{ m}^2 \text{ g}^{-1}$ to $1168 \text{ m}^2 \text{ g}^{-1}$ and $856 \text{ m}^2 \text{ g}^{-1}$ following 3 M and 5 M KOH treatments, respectively (Figures S65–S68). Similarly, the contact angle of pristine B18C COF, initially measured at 95° , was reduced to 79° after soaking in 1 M KOH for 12 hours at room temperature (Figure S90). This reduction indicates an increase in hydrophilicity attributed to the incorporation of K^+ ions into the 18-crown-6 ether core. To show the importance of

crown ether core, we also synthesized two similar types of COF Tet-COF and Py-COF without crown-ether units (Figures S100–S103).^[13c]

The electrocatalytic experiments for OER were carried out in 1 M KOH electrolyte using a typical three-electrode system. The catalyst's electrocatalytic performance was measured by coating the catalyst ink (COF: PVDF: Super P carbon = 3: 0.8: 0.25 wt. %) on a carbon cloth electrode (Tables S1–S6). The Linear Sweep Voltammetry (LSV) analysis of these COFs exhibited capacitive current before 1.23 V; therefore, we compared the overpotentials at higher current densities (20, 50, and 100 mA cm^{-2}) for more accurate evolution of the catalyst's performance. LSV

showed the overpotential (η_{20} and η_{100}) 287 ± 1 mV and 362 ± 8 for B18C to reach 20 mA cm^{-2} and 100 mA cm^{-2} current density, followed by B24C [297 ± 1 mV (η_{20}) and 389 ± 5 (η_{100})] and B12C [325 ± 5 mV (η_{20}) and 413 ± 7 (η_{100})] (Figure 4a, Table S15). The overpotential (η_{20} and η_{50}) of the Py12C (471 ± 5 and 580 ± 9 mV), Py18C (398 ± 2 and 472 ± 5 mV), and Py24C (444 ± 8 and 527 ± 13 mV) followed a similar performance trend. We have also presented the LSV curves without iR-correction in Figure S84. The Faradaic efficiency normalized LSV curve for B18C is illustrated in Figure S86c. The observed trend indicates that the OER performance of these COFs is primarily governed by the potassium ion (K^+) binding ability of the crown ether backbone, which follows the order: 12-crown-4 < 24-crown-8 < 18-crown-6 (Figure 1c).^[9,13a-13b] The Tafel slope provides information about the kinetics of the electrochemical reactions.^[14] B12C, B18C, B24C, Py12C, Py18C, and Py24C displayed Tafel slopes of 134, 101, 115, 255, 210 and 209 mV dec^{-1} (Figure 4b). The lower value of Tafel slope B18C indicates the faster kinetics for B18C among all the COFs reported here. Electrochemical Impedance Spectroscopy (EIS) ^[15] measurements provided additional insights into charge transfer properties. The Nyquist plots revealed charge transfer resistance for all COFs, with values of 2.5, 2.2, 2.3, 6.1, 2.8, and 4.1 Ω for B12C, B18C, B24C, Py12C, Py18C, and Py24C, implying the enhanced charge transfer at the electrode-electrolyte interface (Figure 4c). Double-layer capacitance (C_{dl}) at the electrode-electrolyte interface was measured by ΔJ vs scan rate plot.^[16] The calculated C_{dl} values were 88.8, 94.4, 92.4, 72.8, 81.8, and 73.8 mF cm^{-2} for B12C, B18C, B24C, Py12C, Py18C, and Py24C (Figures S69-S70, S71a). The electrochemical active surface area (ECSA) displayed values of 2217, 2360, 2309, 1820, 2045, and 1845 cm^2 for B12C, B18C, B24C, Py12C, Py18C, and Py24C indicating a high accessible active site available for catalytic reaction (Figure S71b).^[17] To assess the intrinsic electrocatalytic performance of the COFs, we plotted their ECSA normalized LSV polarization curves for both OER and HER (Figure S86). The Faradaic efficiency of the most promising catalyst, B18C, was evaluated using a rotating ring-disk electrode (RRDE) experiment ^[18] conducted at 1.65 V vs. RHE (Figure S73). The oxygen generated at the disk electrode was reduced by sweeping the potential at the ring electrode. The Faradaic efficiency B18C, was determined to be 89 % from the ratio of the currents measured at the disk and ring electrodes. Chronopotentiometry at 25 mA cm^{-2} demonstrated the durability of the B18C COF in OER conditions, with a 0.002 V change in potential observed after 16 h. (Figure 4g). The dynamic stability of B18C was demonstrated by 1000 CV cycling, which showed less than 5 mV change in overpotential (η_{20}) (Figure 4g). The chronopotentiometry study of B18C COF at 250 mA cm^{-2} current density in OER condition showed a 0.54 V change in potential after 10 h (Figure S88a). To explore the electrode-dependency on the electro-catalytic performance of our catalysts, LSV measurements have been carried out using glassy carbon as a support in the working electrode in 1 M KOH. B12C, B18C, and B24C COFs exhibited an overpotential (η_{20}) of 343, 285, and 322 mV for OER and 477, 339, and 387 mV for HER, which are comparable with the carbon-cloth electrode (Figure S87). On top of that, the LSV study of the bare carbon

cloth as well as PVDF (0.8 mg) and super P carbon (0.35 mg) loaded carbon cloth exhibited the overpotential (η_{20}) of > 700 mV (for bare carbon cloth) and > 600 mV (for PVDF and super P carbon loaded carbon cloth) for OER and HER (Figures S72b, S76e) in 1 M KOH. The PXRD pattern of B18C after 1000 CV cycles in OER conditions showed the retention of the peaks accompanied by the emergence of new peaks due to PVDF binder at approximately 18.2° and $20.1 (2\theta)$, with a drop in crystallinity (Figure S98d). High-resolution XPS spectra showed N1s peak shifted to higher binding energy, which is attributable to the oxidation of the imine-bonded nitrogen on the catalyst surface during electrocatalysis. The O1s spectra after OER showed the appearance of a new peak at ~ 531 eV, indicating the C=O formation during the electrocatalysis by oxidation of aromatic carbons (Figure S98c). Post-catalytic SEM and TEM images indicate a retention of the morphology of catalyst surface (Figures S98b, S98e). The post-catalytic FT-IR spectra indicate the formation of a -C=O peak at 1670 cm^{-1} , which suggests surface oxidation of the catalyst in long-term electrolysis (Figure S98a).^[19] The GC-MS data collected after 1 hour of chronoamperometry at 1.48 V and 1.6 V showed no evidence of CO_2 or CO formation via overoxidation of the COF catalyst (Figure S73b). Post-catalytic ICP-MS analysis exhibits the presence of $\sim 0.085 \%$ (w/w) Fe and $\sim 0.41 \%$ (w/w) of Pd for B18C COF after the chronopotentiometry for 10 h. To eliminate any possibility of iron content from the electrolyte itself, we purified the KOH following the previously reported procedure.^[20] The LSV study using these for B18C results in an overpotential of 280 mV at 20 mA cm^{-2} current density (Figure S89). To explore the HER performance, we have carried out the LSV measurement in 1 M KOH electrolyte. Among all COFs B18C demonstrated the lowest overpotential (η_{20}) of 310 ± 5 mV, while B12C and B24C showed overpotential (η_{20}) of 435 ± 13 and 331 ± 3 mV (Figures 4d, 5f, Table S16). Py12C, Py18C, and Py24C showed a consistent trend with an overpotential of 577, 508, and 558 mV (Figures 4d, 5f). The LSV curves without iR-correction are shown in Figure S85. The Faradaic efficiency normalized LSV curve for B18C is illustrated in Figure S86d. These superior performances of B18C over B12C and B24C in 1 M KOH are attributed to the stronger K^+ ion binding affinity of the 18-crown-6 core compared to other crown units.^[10,13] The Tafel slopes of B12C, B18C, B24C, Py12C, Py18C, and Py24C were calculated as 276, 233, 234, 368, 340, and 364 mV dec^{-1} (Figure 4e). The R_{ct} values obtained from EIS study were 130, 22, 35, 255, 152, and 180 Ω for B12C, B18C, B24C, Py12C, Py18C, and Py24C (Figure 4f). The double layer capacitance (C_{dl}) was found to be 12.0, 16.1, 15.6, 5.2, 8.8, and 8.4 mF cm^{-2} for B12C, B18C, B24C, Py12C, Py18C, and Py24C (Figures S74-S75, S76b). The ECSA of the COFs evaluated by C_{dl} were found to be 300, 403, 390, 130, 290, and 211 cm^2 for B12C, B18C, B24C, Py12C, Py18C, and Py24C (Figure S76d). The calculated Faradaic efficiency from gas chromatography for HER was found to be 90 % (Figure S77). The Faradaic efficiency for both OER and HER are 89 % and 90 % (below 100 %) possibly due to the surface oxidation and capacitive contribution of the catalyst B18C COF during electrolysis, leading to charge transfer without desirable product formation. The chronopotentiometry study was performed at 25 mA cm^{-2}

current density to check the long-term durability of the most efficient catalyst (B18C), which showed stability up to 30 h with a decrease in the potential of 0.004 V (Figure 4h). We have also performed the chronopotentiometry at 250 mA cm⁻² current density in HER condition, which showed 0.276 V change in potential after 10 h (Figure S88b). The LSV was carried out after 1000 CV cycles, and B18C showed a 17 % increase in overpotential (η_{20}) which possibly due to a decrease in crystallinity and surface oxidation of the B18C COF catalyst (Figure 4h). The post catalytic PXRD after HER revealed the retention of the peaks, but the crystallinity dropped significantly, and new peaks generated at around 18.2° and 20.1° (2 θ) which is for PVDF binder (Figure S98d). High-resolution XPS spectra showed a shift in N1s peaks to higher binding energy possibly due to the oxidation of the imine bonded nitrogen in the catalyst surface during electrocatalysis and the O1s spectra after HER revealed appearance of a new peak at ~ 531 eV indicating the -C=O formation during the electrocatalysis by oxidation of aromatic carbons (Figure S98c). Post-catalytic SEM analysis indicates the retention of morphology even after long CV cycling. The post-catalytic FT-IR spectra exhibited -C=O formation, which accounts for the oxidation of the anode by reactive oxygen species formed from the cathode (Figure S98a).^[21]

The highest K⁺ binding affinity of the B18C over B12C and B24C COFs was supported via UV-visible spectroscopy. This experiment was conducted by adding B12C, B18C, and B24C COFs in the KMnO₄ solution separately. A sharp decrease in absorption observed when B18C was added in the solution followed by B24C and then B12C (Figure 5h, Figure S91). The HR-MS of the 18-crown ether-based aldehyde from methanol solution in the presence of KOH showed an intense peak of potassium-bound 18-crown-6 ether aldehyde, which further indicates the strong potassium-ion binding ability of 18-crown-6 ether core (Figure 5h, Figure S97). The kinetics for alkali metal ion adsorption of B18C COF measured using ICP-MS showed a sharp decrease in concentration of K⁺ ion, followed by Cs⁺ and Li⁺ (Figure S92). After binding with the corresponding alkali metal ion by different crown ether COF, the binding energies of C1s and N1s spectra in high-resolution XPS remain almost the same, but the O1s spectra shift towards slightly higher binding energy (Figures S93-S95).

To further understand the alkali metal binding effect of crown-ether moiety on the electrocatalytic performance of the COFs, we have carried out OER and HER of all the COFs in 1 M LiOH and 1 M CsOH electrolyte. LSV polarization curve in 1 M CsOH exhibited the lowest overpotential (η_{20}) for B24C (280 mV for OER and 363 mV for HER), followed by B18C (with an overpotential (η_{20}) of 296 mV for OER and 371 mV for HER) and B12C (shows an overpotential (η_{20}) of 332 mV for OER and 411 mV for HER) (Figures 5a, 5d, 5c and 5f). This performance enhancement for B24C can be explained by the stronger interaction of Cs⁺ with a 24-crown-8 ether unit^[10a,21]. Py12C, Py18C, and Py24C follow a consistent trend with overpotential (η_{20}) values 444, 415, and 391 mV for OER and 630, 560, and 486 mV for HER in 1 M CsOH (Figures 5a, 5d, 5c and 5f). B12C, B18C, B24C, Py12C, Py18C, and Py24C displayed Tafel slopes of 123, 118, 116, 181, 175, and 149 mV dec⁻¹ for OER and 199, 177, 172, 347, 308, and 300 mV dec⁻¹ for HER in 1 M CsOH

electrolyte (Figure S78). In 1 M LiOH, the LSV measurement of both OER and HER displayed the lowest overpotential (η_{20}) and Tafel slope for B12C COF. This behavior can be attributed to the highest binding constant for Li⁺ ion with the 12-crown-4 ether backbone (as Li⁺ binding constant of 24-crown-8 < 18-crown-6 < 12-crown-4).^[22] The HR-MS of the 12-crown ether-based aldehyde from methanol solution in the presence of LiCl showed a peak of lithium-bound 12-crown-4 ether aldehyde, which indicates the lithium-ion binding ability of the 12-crown-4 ether core (Figure S96). The overpotential (η_{20}) obtained in 1 M LiOH from LSV curves were 424, 443, 465, 440, 470, and 472 mV for OER and 375, 386, 436, 582, 634, and 626 mV for HER corresponding to B12C, B18C, B24C, Py12C, Py18C and Py24C (Figures 5b, 5c, 5e and 5f). The Tafel slope obtained by B12C, B18C, B24C, Py12C, Py18C, and Py24C was 69, 75, 78, 183, 167, and 127 mV dec⁻¹ for OER and 182, 195, 185, 399, 328, and 348 mV dec⁻¹ for HER (Figure S79). We have also performed the electrocatalytic OER and HER in the neutral medium by using 1 M K₂SO₄ as an electrolyte. LSV polarization curve in 1 M K₂SO₄ also showed the lowest overpotential (η_{20}) for B18C COF with respect to B12C and B24C COF for both OER and HER processes. The overpotential (η_{20}) calculated from the LSV curve of B12C, B18C, and B24C was found to be 667, 471, and 535 mV with Tafel slope of 511, 264, and 338 mV dec⁻¹ for OER and > 800, 606, and 691 mV with Tafel slope of 303, 304, and 304 mV dec⁻¹ for HER (Figure 5g, Figure S80). The importance of crown-ether core has been established by the poor electrocatalytic performance of Tet-COF and Py-COF, synthesized with a benzene and pyrene aromatic core without a crown-ether unit. Tet-COF and Py-COF showed overpotential (η_{20}) of 355 and 381 mV and overpotential (η_{50}) of 429 and 487 mV respectively for OER in 1 M KOH (Figure S104). Inspired by the promising OER and HER performance of B18C COF- catalyst in an alkaline medium (1 M KOH), we have performed the overall water splitting where B18C coated carbon cloth served as both cathode and anode. The LSV measurement of full-cell (B18C || B18C) showcased a cell potential of 1.784 V to drive a current density of 20 mA cm⁻², which is comparable with most of the COF and POP based bifunctional catalysts reported till now (Figure 4i, Figure S81b, Table S17). To check the long-term stability, we have performed the chrono potentiometric measurement at 15 mA cm⁻² current density, which showed a small (0.005 V) decrease in potential after 27 h (Figure 4i, Figure S81c). The chronopotentiometry study of full-cell at 100 mA cm⁻² showed 0.17 V change in potential after 10 h (Figure S87c). The dynamic stability was assessed through 1000 CV cycles, and a minor change of cell potential has been observed at 20 mA cm⁻² current density.

To further validate our experimental observations, we employed density functional theory (DFT) using the Vienna ab initio simulation package (VASP).^[23] Computational details are provided in Text S1, Supporting Information. For molecular-level insights, we first modelled a single molecular unit of B12C, B18C, and B24C, along with their K⁺-bound counterparts (K-B12C, K-B18C, and K-B24C) by incorporating K⁺ ions into the crown ether pores, terminated by the methyl group. The optimized geometries of all pristine and K⁺-bound systems B12C, B18C, and B24C are provided in Figure S106. We simulate the OER and HER

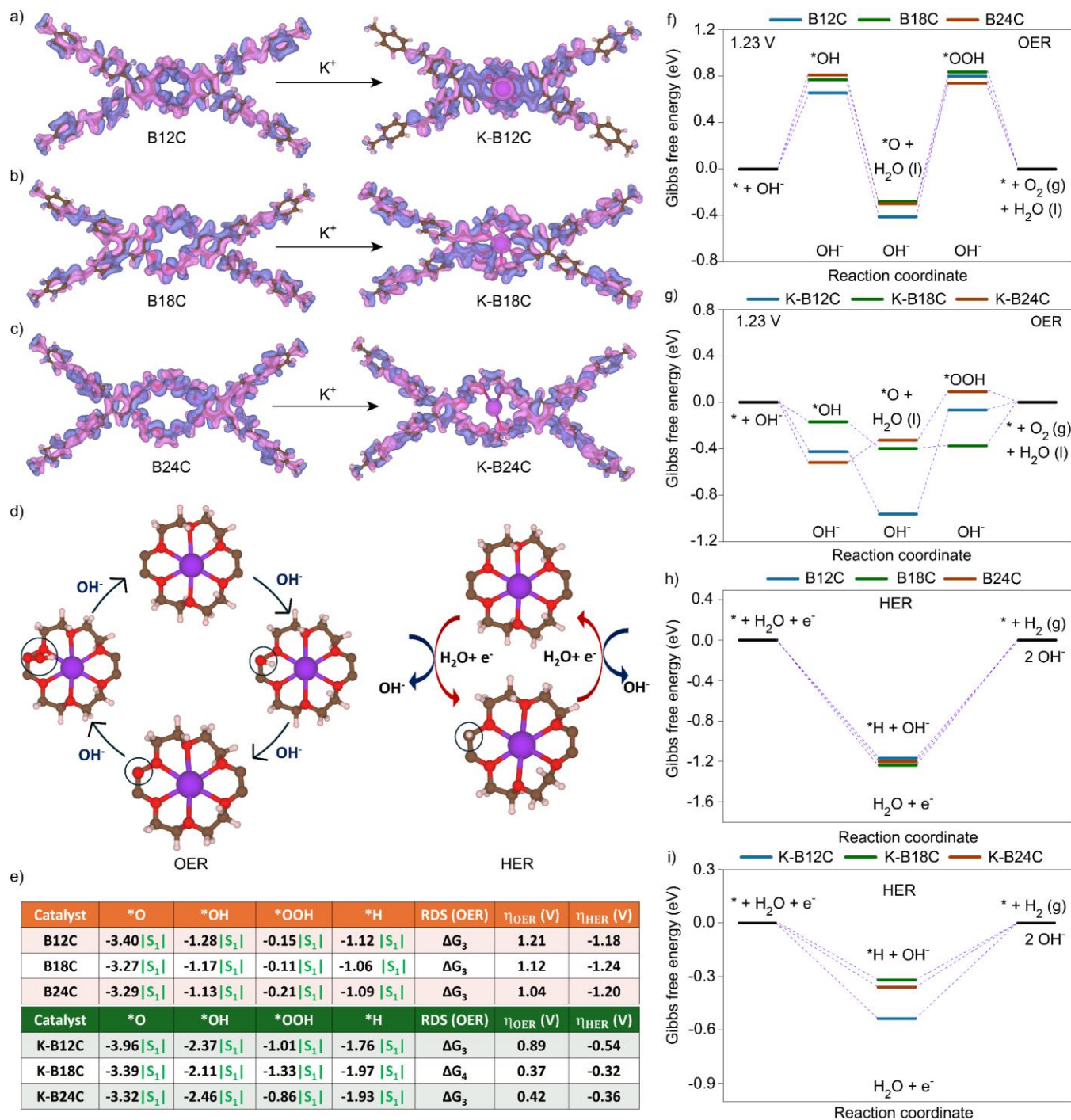


Figure 6: Mechanism investigation of electrochemical OER and HER activity using DFT. Charge density difference diagram of optimized molecular structures for pristine and K⁺-bound a) B12C, b) B18C, and c) B24C crown ethers. The pink and blue color gradients represent charge depletion and accumulation regions, respectively, with an isovalue of 0.004. d) Schematic illustration of the reaction pathways for the OER and HER mechanisms in an alkaline medium. The elementary steps are outlined in Text S2 of the Supporting Information. e) Adsorption energy of *O, *OH, and *OOH intermediate (* indicates adsorbed species) at the most stable adsorption site (S₂) in eV units. The RDS (rate-determining step) at 1.23 V, along with the OER and HER overpotential values (η_{OER} , and η_{HER}) in volts, are also included. Free energy diagrams at 1.23 V for OER of f) pristine and g) K⁺-bound B12C, B18C, and B24C, and for HER of h) pristine and i) K⁺-bound B12C, B18C, and B24C, with the black solid horizontal line representing the neutral surface. Note that the Gibbs Free energy change values for all elementary steps are tabulated in Tables S11-S14 of the Supporting Information.

pathways to compare their activity in an alkaline medium, considering the adsorption of *O, *OH, *OOH, and *H intermediates at different heterogeneous sites (Figure

S107, Table S9). Subsequently, the most stable configurations were selected for further analysis. Notably, there is strong competition between the S₁ and S₅ sites for a

few intermediate adsorptions in pristine B12C, B18C, and B24C, as reflected in their relative energies (Table S9). However, with the K⁺ ion incorporation into the crown ether pore, the S₁ site emerges as the most stable active site for all intermediates. This behavior is attributed to K⁺ induced charge accumulation near the crown ether pore, which activates adjacent sites and increases adsorption energies compared to pristine systems (Figure 6a-6c). Upon K⁺ incorporation the S₁ site in K-B12C, K-B18C, and K-B24C exhibits the highest charge accumulation of -0.13 |e|, -0.07 |e|, -0.07 |e|, respectively, relative to their pristine counterparts. This charge enrichment enhances S₁'s reactivity, leading to stronger intermediate adsorption in K⁺-bound systems (Table S10). Further, the density of states (DOS) analysis (Figure S108) revealed that with K⁺ ions incorporation, there are some C(p) states appearing at the Fermi energy, and the Fermi level (E_f) is also shifted towards the conduction band, indicating the activation of nearby S₁ active sites. This shift enhances the intermediate adsorption energy, further supporting the enhanced adsorption and catalytic performance. Using the computational hydrogen electrode (CHE) model, we calculated the thermodynamic overpotential values of OER and HER (η_{OER} , η_{HER}) by calculating the Gibbs-free energy change (ΔG) at 0 V and 1.23 V (equilibrium potential) following the adsorbate-evolution mechanism (AEM) via an associative pathway (Figure 6d, Text S2).^[24] The lower η_{OER} values observed in K⁺-bound crown ethers indicate significantly improved OER activity compared to pristine systems (B12C | K-B12C : 1.21 V | 0.89 V ; B18C | K-B18C : 1.12 V | 0.37 V ; B24C | K-B24C : 1.04 V | 0.42 V), represented in Figure 6e. The Gibbs free energy changes (ΔG) for all elementary steps at 0 V and 1.23 V are summarized in Table S11-S14, Figure S110. At 1.23 V, the potential-determining step (PDS) for OER predominantly involves *O → *OOH formation (ΔG_3), except in K-B18C, where *OOH → O₂ (g) (ΔG_4) formation is the PDS (Figure 6e-6g). Similarly, K⁺-bound crown ethers exhibit enhanced HER activity with lower η_{HER} values than their pristine counterparts (B12C | K-B12C: -1.18 V | -0.54 V; B18C | K-B18C: -1.24 V | -0.32 V; B24C | K-B24C: -1.20 V | -0.36 V) (Figures 6e, 6h, 6i). Among these, K-B18C emerged as the best bifunctional electrocatalyst with the lowest η_{OER} and η_{HER} values. We also analyzed the Cs-B18C and Li-B18C, which showed lower OER and HER activity than K-B18C, with η_{OER} = 0.51 V, η_{HER} = -0.54 V for Cs-B18C, and η_{OER} = 2.09 V, η_{HER} = 1.84 V for Li-B18C (Tables S13-S14). Among the alkali metal ion bound B18C systems, the K⁺-bound B18C exhibits the optimal binding adsorption energy for all key intermediates, as shown in Table S13, falling within the Sabatier principle^[25-26], leading to its highest catalytic activity among the studied systems in this work. These DFT-derived insights align well with experimental results, establishing K⁺-bound crown ethers as promising bifunctional catalysts for OER and HER.

CONCLUSIONS

In summary, we have developed a method to polarize and increase the hydrophilicity of the crown-ether based COFs by capturing the alkali metal ions from the electrolyte solution to improve the OER, HER, and water-splitting

performance. Through the tuning of crown ether unit (12-crown-4, 18-crown-6, and 24-crown-8) in the COFs and different electrolytes (LiOH, KOH, CsOH, and K₂SO₄), we have shown how the binding affinity of crown ether with different alkali metal affecting the OER and HER performance. We have achieved superior electrocatalytic performance for B18C which showed electrochemical stability (performance retention after 1000 CV cycles and 16 h chronoamperometry in both OER and HER conditions) and chemical robustness in basic medium. The post-catalytic study indicates the surface oxidation of the catalyst during electrocatalysis. We achieved the best OER and HER performance for 18-crown-6 functionalized COFs in KOH electrolyte, as the K⁺ ion most efficiently binds in this crown pore. The DFT studies confirm the greater stabilization of the OER intermediate after K⁺ ion binding with respect to the free 18-crown-6 ether core and the stabilization of intermediates aligns with the binding strength of K⁺ ion by different crown ether core. We acknowledge that further in-situ studies are required for the detailed understanding of the mechanism. We believe this strategy can be integrated into the other nanostructures as well to improve the OER, HER, and water-splitting performance.

ASSOCIATED CONTENT

Supporting Information. Synthesis, crystallography, and characterization details are provided in the Supporting Information file. This material is available free of charge via the Internet at:

<http://pubs.acs.org>.

Accession Codes. Deposition Number 2406662 and 2406663 contains the supporting crystallographic data for this paper. These data can be obtained free of charge via the Cambridge Crystallographic Data Centre (CCDC).

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Notes

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