The detrimental effect of combustion of fossil fuels to produce energy can be avoided by the implementation of renewable energy sources. In this regard, the sustainable electrochemical production of hydrogen from water is a key element in the transition toward carbon-neutral energy systems. Application at a global scale requires the discovery of precious metal-free electrocatalysts that unify high energetic efficiency, long-term stability and economic viability. Here we report the striking properties of noble metal-free, alkali-metal cobalt borophosphates acting as robust and efficient materials for bi-functional electrocatalytic water-splitting to give hydrogen and oxygen. Alkali-metal cobalt borophosphates are porous crystalline inorganic materials with chiral DNA-like helical structures bearing two chemically distinct types of water molecules, coordinated and strands of hydrate water associated via hydrogen bonds, located in the channels, which are predestined to possess superior catalytic performance. Depending on the applied electrode potential, they can be reversibly switched between catalysis of the hydrogen and oxygen evolution reactions, both at low overpotentials. This bifunctionality provides access to technologically simple overall water-splitting systems with energetic efficiencies exceeding the 75% level (above 90% based on a higher heating value) and uncompromised long-term stability, now verified with a two-and-a-half month period.

**Broader context**

The detrimental effect of combustion of fossil fuels to produce energy can be avoided by the implementation of renewable energy sources. In this regard, electrochemical water-splitting has been considered as an attractive strategy to generate clean and renewable energy, which comprises the hydrogen evolution reaction (HER) at the cathode and the oxygen evolution reaction at the anode (OER) to form molecular hydrogen and oxygen, respectively. Today, commercial electrolyzers to split water are operated at 1.8–2.0 V, substantially greater than the theoretical value of 1.23 V. Apart from the operational voltage, the long-lasting stability is a matter of great concern. Therefore, designing efficient, durable and robust multifunctional electrocatalyst systems to enhance water-splitting performance is highly desirable yet a prodigious challenge. At the same time, understanding the mechanism of water-splitting and describing the structure of the active catalyst is also crucial for the further development of this field. Here, we introduce borophosphates, a new class of chiral materials based on a transition metal for efficient and durable electrochemical water-splitting. Borophosphates are known for their capturing crystal chemistry with diverse structural architectures. Unexpectedly, this system can produce hydrogen and oxygen for months (at 1.53 V) under alkaline electrochemical conditions, thus offering a cost-effective and suitable earth abundant material system for practical implementation. We further describe the active catalyst structure during hydrogen and oxygen evolution and correlate the structure with the activity of the catalysts.

**Introduction**

With decreasing resources of fossil fuels and a rising demand for growth of a sustainable energy economy without net CO₂ emissions, it is essential to utilize renewable energy more effectively for production of non-fossil fuels.¹⁻⁴ One attractive way is the formation of hydrogen (H₂) and oxygen (O₂) through efficient and sustainable electrolysis of water.⁵ Use of novel low-overpotential and bi-functional catalyst materials for both the H₂ evolution reaction (HER) and the O₂ evolution reaction (OER) in a common reaction medium could make the complete system more energy efficient and robust for practical applications.⁶⁻⁹
Noble metal-based materials have shown promising catalytic activity for either the OER (ruthenium, iridium) or the HER (platinum), but scarcity and high costs remain a major impediment for their pervasive use.\textsuperscript{10,11} Pronounced progress has been achieved in the last few years in developing noble metal-free derived catalysts, especially with earth-abundant transition metals (TMs) for the OER and HER.\textsuperscript{12–18} Moreover, apart from attaining higher catalytic activity, special efforts have also been dedicated to the realization of long-term stable catalytic systems.\textsuperscript{19–21} Current technological systems for alkaline water electrolysis are often based on (initially) metallic nickel electrodes at the anode and the cathode that act as bifunctional catalysts for both the OER and HER. In spite of tremendous efforts dedicated to this perplexing area, a bifunctional, noble-metal free HER and OER catalyst that excels with high current densities at low overpotentials and is robust so that it can rival the performance of metallic nickel electrodes is still far from reality.\textsuperscript{22} Bifunctional electrodes with the same catalyst material for both the HER and OER could be beneficial with respect to their ease of production and applicability, e.g., single-step deposition of both catalysts by coating of anodes and cathodes in integrated systems for light-driven water-splitting. Unexpected progress along this line is reported herein.

Phosphates have attracted tremendous interest for the OER since the discovery of \textit{in situ} deposited cobalt interlayer (oxide) phosphate by Nocera and co-workers and the curiosity on such amorphous interlayer cobalt phosphate (including crystalline phosphate) materials has grown comprehensively over the past few years.\textsuperscript{23–31} Interestingly, Artero and co-workers were able to construct of complex BPO anions comprises isolated species, oligomers, rings, chains, layers and even 3D frameworks. Keeping this in mind, we aimed to explore a novel class of materials, \textit{i.e.}, two helical borophosphates LiCo[H$_2$O]$_2$[BP$_2$O$_8$]·2H$_2$O (LiCoBPO) and NaCo[H$_2$O]$_2$[BP$_2$O$_8$]·H$_2$O (NaCoBPO) for electrocatalytic overall water-splitting. We discovered that these materials are not only switchable bifunctional catalysts in the HER and OER but also combine outstanding performance and energetic efficiency with high durability (> 2.5 months) in alkaline water electrolysis. This and the structure–activity relationships of the materials, the nature of active species involved and the surface-structural arrangements in each half reaction are here reported.

**Results and discussion**

**Structural analysis**

Single crystals of both LiCoBPO and NaCoBPO are accessible by a mild hydrothermal technique (see Experimental). The phase purity of the products was proven by Rietveld refinement of the powder X-ray diffraction pattern (PXRD), and the corresponding lattice parameters of a hexagonal cell were determined to be $a = 9.4392(5)$ Å and $c = 15.7255(8)$ Å for LiCoBPO and $a = 9.4601(14)$ Å and $c = 15.8430(2)$ Å for NaCoBPO that are consistent with the single crystal structure refinements (Fig. S3, ESI\textsuperscript{†}).\textsuperscript{41} Optical and scanning electron microscopy (SEM) showed that the deep pink crystals have a hexagonal bipyramidal shape (Fig. 1a and Fig. S4, S5, ESI\textsuperscript{†}) and are porous (Fig. 1b and Fig. S6, ESI\textsuperscript{†}). Transmission electron microscopy (TEM) displayed preservation in morphology (Fig. S7, ESI\textsuperscript{†}) and the composition of materials was confirmed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and energy dispersive X-ray (EDX) analysis (Fig. S8 and Table S1, ESI\textsuperscript{†}). Furthermore, the presence of ligated as well as crystal water was determined by Fourier transform infrared (FT-IR) spectroscopy (Fig. S9, ESI\textsuperscript{†}). Notably, the flexibility of the helices through dehydroxylation was monitored by thermogravimetric analysis (TGA) and its differential (DTG) (Fig. S10, ESI\textsuperscript{†}). The chemical state, bonding situation and surface structure of the BPO single crystals were analyzed by X-ray photoelectron spectroscopy (XPS; and Fig. S11 and S12, ESI\textsuperscript{†}).

The helical BPOs crystallize in the chiral space groups $P6_122$ and $P6_322$, respectively. The main structural features are one-dimensional infinite loop-branched helical $\frac{1}{2}$[BP$_2$O$_8$]$^{3-}$ chains built of alternating borate and phosphate tetrahedra connected via common corners. The arrangement around a six-fold screw axis forms helices which are “left-handed” (6 5) or “right-handed” (6 1) (Fig. 1c).\textsuperscript{41} This fascinating chiral arrangement of tetrahedral building units is similar to $\alpha$-quartz (SiO$_2$) with 3 1 and 3 2 screw axes.\textsuperscript{42} The structure can also be compared with the molecule deoxyribonucleic acid (DNA), where double-strands form a helical structure and the handedness of DNA can be determined from the twisting direction of the two strands.\textsuperscript{43} The helices $\frac{1}{2}$[BP$_2$O$_8$]$^{3-}$ running along [001] are interconnected via CoO$_4$(OH)$_2$ coordination octahedra, and the free threads of helices are occupied by lithium or sodium ions which are in an irregular surrounding of oxygen atoms (Fig. 1d).\textsuperscript{44} The remaining crystal waters form hydrogen bonds.
with each other along the spiral and are located within the inner walls of helical channels (Fig. 1e) and play a key role in holding the structure together. Strikingly, this chiral architecture is closely related to the chiral zinc phosphate (CZP) topology. 45

Electrocatalytic OER and HER performance

We first investigated the electrocatalytic OER performance of BPOs, electrophoretically deposited on fluorine doped tin oxide (FTO) in 1 M KOH (Fig. 2a). The overpotential for the OER was determined to be 293 mV at a current density of 10 mA cm$^{-2}$ for LiCoBPO and 328 mV for NaCoBPO (Fig. S13, ESI†). Interestingly, the resulting overpotentials attained were some of the lowest compared to other cobalt-based materials as well as lower than most of the high-performance TM based catalysts (see Table S2, ESI†) reported so far on FTO (Table S4, ESI†).46,47 While cycling, prior to the OER, a reversible redox couple was attained which could be attributed to Co$^{2+}$/Co$^{3+}$, and is typical for first-row TM based materials giving strong indication of the formation of the M(OH)$_2$/MOOH phase (Fig. 1a, ESI†).48–50 The OER kinetics of BPOs was investigated using Tafel plots (Fig. S14, ESI†) where the Tafel slope of LiCoBPO (58 mV dec$^{-1}$) was superior to NaCoBPO (60 mV dec$^{-1}$). The Tafel slope is an inherent property of electrocatalytic materials which is indeed a valuable parameter of the rate-limiting step for reactions involving electron transfer. A Tafel slope close to 59 mV dec$^{-1}$ (attained in our case) corresponds to the OER mechanism involving a reversible one-electron transfer prior to a chemical turnover-limiting step.49,51–53 In order to gather more information on the intrinsic activity of the catalysts, the double-layer capacitances ($C_{dl}$) of the catalysts were determined. Fig S15c (ESI†) depicts the $C_{dl}$ of the electrodes measured from the capacitive currents as a function of the scan rate obtained from the corresponding CV curves (Fig. S15a and b, ESI†).47,54,55 The LiCoBPO exhibited highest $C_{dl}$ (0.72 mF cm$^{-2}$) which was almost twice higher than NaCoBPO (0.42 mF cm$^{-2}$). As the electrocatalytic active surface area (ECSA) is generally considered to be a crucial parameter for increasing electrochemical activity, the $C_{dl}$ were further converted into ECSA using the specific capacitance value for a standard with 1 cm$^2$ of exposed surface area (see Experimental).47,54 The calculated active ECSA of LiCoBPO was 18 cm$^2$ whereas a value of 10.5 cm$^2$ was attained for NaCoBPO. The improved ECSA of LiCoBPO implies the greater exposure of active sites by favoring efficient adsorption and transfer of reactants.9 Subsequently, electrochemical impedance spectroscopy (EIS) was performed to gain knowledge of the electron-transfer kinetics.9 As shown in Fig. S15d (ESI†), the Nyquist plots obtained by EIS measurement indicated a small charge transfer resistance ($R_{ct}$) for LiCoBPO compared to NaCoBPO.
signifying faster charge transport leading to higher catalytic activity. In addition to the presented BPOs, cobalt phosphate (Experimental; Fig. S16, ESI†) (430 mV) and state-of-the-art benchmarking catalysts RuO2 (354 mV), IrO2 (400 mV) and Pt were also electrophoretically deposited on FTO and measured for comparison at 10 mA cm\(^{-2}\), and the catalytic activities of BPOs were excellent (Fig. S17a, ESI†). Separately, to have a direct correlation with Co-based catalysts, the catalytic OER activity of Co\(_3\)O\(_4\) (360 mV), Co(OH)\(_2\) (382 mV), CoOOH (401 mV) and metallic Co (430 mV) was also measured in similar conditions (Experimental; Fig. S18 and S19a, ESI†) that underlined the superiority of the BPOs as well as the need of a core–shell structure to enhance catalytic activity. The chronoamperometry (CA) of LiCoBPO and NaCoBPO, at OER conditions, at 1.53 and 1.56 V maintaining 10 mA cm\(^{-2}\) produced constant current over 24 h (Fig. S20a, ESI†) for LiCoBPO.

The electrochemical HER performance of the catalysts was studied by linear sweep voltammetry (LSV) in 1 M KOH (Fig. 2b and Fig. 13b, ESI†). LiCoBPO proved to be a better catalyst with a 245 mV overpotential than NaCoBPO with 298 mV at −10 mA cm\(^{-2}\). The resulting overpotential obtained for LiCoBPO is superior in comparison to the highly HER active oxides or phosphates and pretty much in the range of high-performance TM based catalysts on FTO (Table S3, ESI†). The corresponding Tafel slope (Fig. S14, ESI†) of LiCoBPO was 98 mV dec\(^{-1}\), which is lower than that of NaCoBPO (124 mV dec\(^{-1}\)). The obtained Tafel slope here suggests that the HER reaction on the BPO surface favors the Volmer–Heyrovsky mechanism where the water discharge (Volmer step) reaction is the rate-limiting step.\(^{56,57}\) Additionally, the HER activity of BPOs was compared with noble metal catalysts Pt (42 mV) and IrO\(_2\) (430 mV) as well as with the Co\(_3\)(PO\(_4\))\(_2\)·8H\(_2\)O (358 mV), Co\(_3\)O\(_4\) (n/a), Co(OH)\(_2\) (n/a), CoOOH (n/a) and metallic Co (315 mV) catalysts at −10 mA cm\(^{-2}\) (Fig. S17–S19; ESI†). Except for Pt, the activity of other catalysts is significantly lower compared to BPOs. The CA responses of LiCoBPO and NaCoBPO for the HER were measured at 0.25 and 0.3 V maintaining the current at almost −10 mA cm\(^{-2}\) for 24 h (Fig. 20b, ESI†).

Reversible switchable properties

Notably, the color of the working electrodes was completely transformed from pink to black during water oxidation and from pink to light brown during the HER indicating significant surface-structural changes. These color changes are switchable, i.e., the black catalyst after the OER is transformed to light brown during the HER and vice versa under CV conditions. This illustrates that although the surface of the particles was transformed into active structures, the core of the particle still contained a substantial amount of LiCoBPO structure as indicated by the various experimental techniques (see GIXRD, TEM, XPS and in situ XAS results in the successive sections). The catalytic activities were also retained by the CA treatments (Fig. S21 and S22, ESI†). This type of switchable behavior of the catalysts has recently been reported for H\(_2\)-CoCat/O\(_2\)-CoCat (in phosphate buffer),\(^{32}\) its Ni analog (in borate buffer)\(^{34}\) and FeO\(_x\) (in KOH).\(^{58}\)

Fig. 2 Electrocatalytic performance of helical borophosphates (LiCoBPO and NaCoBPO) using a three-electrode system. (a) CV and (b) LSV on FTO, and (c) CV and (d) LSV on NF for the OER and HER in 1 M KOH electrolyte. The comparison with the state-of-the-art catalysts is presented in Fig. S17 and S40, ESI†.
but in all these catalysts associated with significantly lower catalytic activities and far less durability. In the case of LiCoBPO, the switchable property was achieved with excellent catalytic activities for both the OER and HER and the interconversion of these catalyst modifications was fully reversible.

**Ex situ post catalytic characterization**

The structural transformation and generation of the active sites during electrochemical operation were studied for LiCoBPO. Significant loss of Li from LiCoBPO was detected by ICP-AES measurements after operation at catalytic OER potentials suggesting lattice alterations leading to structural disorder with vacancies. However, the grazing incidence X-ray diffraction patterns (GIXRD) post OER and HER did not reveal any major structural differences when compared to the as-synthesized LiCoBPO (Fig. S23–S24; ESI†). Further, the FT-IR spectrum showed a sharp increase in the bands at 3320 cm⁻¹ after OER CA confirming substantial hydroxylation (Fig. S25, ESI†). The presence of Co and P was also identified from the EDX analysis (Fig. S26 and S27, ESI†). The TEM investigation of LiCoBPO after OER CV showed the formation of a thin amorphous shell (~2 nm) on the surface of the particles and the thickness of the shell was further increased after CA (~20 nm), indicating the formation of the hydroxylated phase as discussed for other TM based catalysts in the literature (Fig. S28, ESI†).48,49 However, this type of amorphous shell formation was not detected after HER LSV or CA, apart from the usual surface passivation to CoO (Fig. S29, ESI†).

The formation of the Co hydroxide-oxohydroxide species on the surface of the catalyst during OER was additionally proved by the Co 2p XPS spectra (Fig. S30, ESI†). Co(II) and Co(III) ions have almost similar 2p binding energies (BE) but can be distinguished by the Co 2p₁/₂–2p₃/₂ spin–orbit level energy difference, which is 16 eV for high-spin Co(II) and 15 eV for low-spin Co(III).59 The Co 2p₁/₂–2p₃/₂ spin–orbit spacing of 16 eV in the deposited catalyst was decreased to 15.6 eV after CV and 15.1 eV after CA. This result indicates that surface Co(II) species were oxidized to mixed Co(II/III) after CV and further oxidized during CA.59 In the case of HER LSV and CA, the resultant spin–orbit spacing was 16.0 and 15.8 eV, indicating that there was no change in the oxidation state during HER LSV but slight surface passivation during HER CA (Fig. S30, ESI†). The detailed deconvolution profiles and the resulting Co(II)/Co(III) ratio of the area of the Co 2p region are given in Fig. S31 and S32, and Tables S5 and S6 (ESI†). In the Li 1s region, both OER CV and HER LSV showed a peak at a BE of 55.5 eV but the surface composition revealed a significant loss of Li from the surface (~30%), and after CA, no Li was present on the surface designating total surface-structural rearrangements (Fig. S33).60 The XPS studies of P 2p and B 1s after the electrochemical HER and OER did not reveal any detectable change in the coordination environments of phosphate (PO₄³⁻) and borate (Fig. S34 and S35, ESI†).61,62 The O 1s spectra clearly show the formation of surface hydroxide species, especially after the electrochemical OER treatment while the peak between 529 and 530 eV indicates the formation of oxidic species (CoOₓ) on the surface (Fig. S36, ESI†).63,64 The surface composition acquired in XPS is also consistent with the results of ICP-AES and EDX. Four probe resistivity measurements were additionally carried out on the FTO substrates which confirmed significantly higher charge mobility for the post OER and HER treated materials compared to the as-synthesized LiCoBPO (Table S7, ESI†).

Note that a substantially lower amount of Na was expelled from the structure of NaCoBPO under OER conditions (ICP-AES) in comparison to Li (due to higher coordination modes of Na in the structure), which explains the superior activity of LiCoBPO over NaCoBPO. Apart from this, a structural transformation similar to that of LiCoBPO is likely expected to occur for the Na-analogue.

**In situ XAS characterization**

To shed light on the local atomic and electronic structure, extended X-ray absorption fine-structure (EXAFS) and near-edge structure (XANES) studies were carried out under quasi in situ conditions (Fig. 3 and 4). After applying oxidizing potentials (Fig. 3a), the structure transforms to the one of the CoOₓ catalyst (also known as CoCat).64 On the contrary, in Fig. 3b, there is a clear metallic contribution visible in the spectrum of the catalyst after CA at reducing potentials (HER). After deposition of the LiCoBPO powder on the electrode, a slight shift of the edge energy position towards lower energy was seen; this could correspond to a slight decrease of the Co oxidation state (see Table S8, ESI†). The oxidation state of Co clearly increases after exposure to oxidizing potentials (Fig. 3 and Table S8, ESI†). The estimation of the Co oxidation state based on the edge energy position is difficult when there is a metallic phase present. That is why instead we used the bond valence sum, determined from the EXAFS simulation of the Co edge EXAFS spectra (see Fig. 4 and Tables S8–S14, ESI†).64,65 The simulation shows that the LiCoBPO powder material corresponds well to the crystal structure (both with respect to coordination numbers and interatomic distances). After deposition on the electrode, there is a slight modification in the distances and coordination, but within the accuracy of the simulation parameters (Table S11, ESI†). The spectra of materials exposed to oxidizing potentials (OER) were simulated as a linear combination between the spectrum of the as-deposited material and the Co catalyst.66 For both spectra (after CV and CA) similar results were obtained indicating that after exposure to an oxidizing potential part of the material is converted to the CoOₓ structure. The CoOₓ is more ordered than the typical Co catalyst as seen from the resolvable ‘double’ Co-Co distance, which is not visible in the electrodeposited oxides. However, even long exposure to an oxidizing potential does not result in a full conversion of the material. The spectra of the materials exposed to reducing potentials (HER LSV and HER CA) were simulated as a linear combination of three spectra: (i) the simulated spectrum of metallic Co, (ii) the spectrum of the as-deposited material, and (iii) the CoOH phase (Table S9, ESI†). In the material after LSV, there is the formation of Co(OH) and no detectable metallic contribution. After CA, the metallic contribution increases to about 40% and the CoO amount does not change significantly.
Insights into the active catalytic structure

The above results indicate that the helical BPOs act as pre-catalysts for water-splitting that are transformed to the catalytically active structures under electrochemical conditions. The fascinating structure of borophosphates provides the required flexibility in the structural transformation and simultaneously facilitates efficient electron transport within the network. A large number of water molecules inside the helical channels and coordinated to cobalt octahedra assist the proton-coupled electron transfer similar to extensive hydrogen bonding in a water network around the oxygen-evolving Mn$_4$CaO$_5$ cluster of photosystem II.67 Interestingly, recent studies have also elucidated that solvation structures can greatly enhance the electron transfer rates.68 Apart from the structural aspects, the superior O$_2$ evolution at anodic bias is attributed to (i) surface reorganization leading to lattice vacancies and defects due to the loss of Li or Na, (ii) the presence of a large amount of structural hydroxides that helps to form Co-oxo/hydroxide/hydroxides at the surface, which is considered to be a prerequisite for active-site formation in OER catalysis, (iii) the pronounced increase in the oxidation state of Co(n) to the higher oxidation state of Co by generation of an amorphous shell consisting of Co(OH)$_2$/CoOOH species and CoO$_x$ (CoCat) at the particle surface, (iv) crystal water within the channels in the core of BPO that can further enhance the diffusion of ions and electrolytes exposing more active sites, and (v) a large electrochemically active surface area leading to more catalytically active reaction sites in the material and the faster charge transfer process at the electrode. Thus, the active species on the catalyst surface facilitate the adsorption of OH$^-$ ions and accelerate the transport of electrons for the recombination of two oxygen atoms to give efficient O$_2$ evolution. On the other hand, metallic Co coated with CoO and LiCoBPO has a strong affinity for H-adsorption thus promoting formation of active sites and thereby explaining the high HER efficiency.32

Activities on a conductive foam substrate

Encouraged by the robust performance of BPOs for the HER and OER on FTO supports, we further set out to explore their electrochemical performance on nickel foam (NF) which has a large working surface area with low ion transport resistance and effective gas diffusion (Fig. 2c and d).69-71 An impressive improvement in the catalytic OER performance was achieved where only 216 mV and 242 mV overpotentials are required to reach the current density of 10 mA cm$^{-2}$ for LiCoBPO and NaCoBPO, respectively (Fig. S37a, ESI†). A smaller Tafel slope (Fig. S38a, ESI†) of LiCoBPO (62 mV dec$^{-1}$) indicated more favorable reaction kinetics than NaCoBPO (99 mV dec$^{-1}$). The $C_\text{dl}$ of LiCoBPO (2.14 mF cm$^{-2}$) was twice as large as that of NaCoBPO (1.07 mF cm$^{-2}$) (Fig. S39, ESI†) and the calculated ECSA from $C_\text{dl}$ was 1.25 cm$^2$ for LiCoBPO and 0.62 cm$^2$ for NaCoBPO, suggesting more active sites of LiCoBPO are accessible which is due to the structural reorganization owing to faster release of Li than Na (as determined by ICP-AES).72-74 Further, the EIS measurement revealed that the charge transfer resistance $R_\text{ct}$ of LiCoBPO was slightly lower compared to NaCoBPO implying a rapid charge transfer process (Fig. S39d, ESI†). Similarly, for the HER, the overpotential acquired at $-10$ mA cm$^{-2}$ was 121 mV for LiCoBPO and 207 mV for its sodium analog (Fig. 37b, ESI†). Besides, LiCoBPO displayed a Tafel slope of 121 mV dec$^{-1}$ which was smaller compared to NaCoBPO (128 mV dec$^{-1}$) (Fig. S38b, ESI†). The overpotential of LiCoBPO in the OER (even at high catalytic currents of 10, 100 and 1000 mA cm$^{-2}$) was extremely low in comparison to the commercial noble metal-based catalysts or any established TM based catalyst system in alkaline media (Fig. S40, Tables S2, and S4, ESI†).46,75-77 The achieved catalytic HER activities are also some of the best in comparison to the recently known oxides, chalcogenides or pnictides but lesser than mono-functional NiFe-, NiMo- or CoMo-alloys (Table S3; ESI†). This superiority was further evidenced by measuring the active Co-based Co$_4$O$_9$, Co(OH)$_2$, CoOOH and metallic Co catalysts (see Fig. S41 for OER and HER overpotentials; ESI†). The CA measurements for the OER and HER established the excellent stability of the systems over 40 h (Fig. S42, ESI†). The closer view of the SEM images of the as-prepared and after OER CA materials further demonstrated the dramatic changes on the surface of the LiCoBPO crystallites (Fig. S43 and S44, ESI†) which influence the performance of the catalytic activity.
Alkaline water-splitting device

The aforementioned outstanding OER and HER catalytic performance on NF verified the bifunctionality of these electrocatalyst materials and applicability as an anodic and cathodic catalyst for overall water-splitting. As envisioned, employment of the BPOs on both electrodes indeed facilitated excellent performance of overall water-splitting in a two-electrode configuration \( \text{LiCoBPO}_8 \) and \( \text{NaCoBPO}_8 \) (Fig. 5a and Fig. S45, ESI†). A cell voltage of only 1.53 V was achieved at 10 mA cm\(^{-2}\) for \( \text{LiCoBPO}_8 \) whereas 1.58 V was attained for \( \text{NaCoBPO}_8 \), which are among the best values of current bifunctional electrocatalysts.\(^9,78,79\) Based on the minimal electrical potential difference to split water (close to 1.23 V, related to Gibbs energies), these overall potentials correspond to energetic efficiencies exceeding the 75% level (78% for \( \text{NaCoBPO}_8 \), and 80% for \( \text{LiCoBPO}_8 \)). Based on a higher heating value of H\(_2\) gas, which here is assumed to correspond to an electrical potential difference of 1.48 V, the energetic efficiencies exceed the 90% level (94% for \( \text{NaCoBPO}_8 \), and 97% for \( \text{LiCoBPO}_8 \)). Furthermore, the superior performance of BPOs for water electrolysis was compared to that of noble metal-based catalysts and is shown in Fig. S46 (ESI†).

For technological applications, long-term stability is required. Insufficient catalyst robustness indeed is a prominent problem and it is especially critical for catalyst materials based on non-noble metals.\(^{80-82}\) In reports of new catalyst materials, stability often has not been assessed for time periods of technological relevance. Here, the durability of the electrodes was assessed at a potential supporting a current density of 10 mA cm\(^{-2}\). The initial stable current over 90 h (inset, Fig. 5a) prompted us to explore \( \text{LiCoBPO}_8 \) for a longer-stability run. An unceasing stability of two-and-a-half months was acquired with continuous growth in the current (Fig. 5b) demonstrating the undying nature of the catalysts which indeed renders the BPOs as highly promising catalysts for implementation in an integrated low-cost electrolyzer. The ICP-AES analysis of the electrodes post electrolysis confirmed no additional iron contamination apart from the NF (Fig. S47, ESI†) and therefore, we hypothesis that the increase in current density over time results from the Co-enriched surface-active sites with severe structural modifications (see Note 1; ESI†) rather than the incorporation of iron from KOH (Table S15, ESI†). The possible contribution of nickel (from the NF) was also ruled out by performing a controlled water-splitting experiment on bare NF at a potential of 1.53 V (cell potential of \( \text{LiCoBPO}_8 \) at 10 mA cm\(^{-2}\)) as well as at 1.84 (cell potential of NF at 10 mA cm\(^{-2}\)) where only a decrease in the current density was attained (Fig. S48, ESI†). Moreover, the ICP-AES of the electrolyte after long-term measurements was measured, which disclosed negligible Ni leaching by further eliminating the possible incorporation of nickel in the structure or possible formation of Ni(OH)\(_2\). In addition, a faradaic efficiency of \( \sim 100\% \) for the HER and \( \sim 96\% \) for the OER was obtained.

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**Fig. 4** In situ EXAFS spectra collected at the Co K edge. (a) presents the Fourier transform of the EXAFS spectra and (b) depicts the original \( k^3 \)-weighted EXAFS spectra. For Fourier transformation a cosine window function, covering between 10% from the beginning and the end of the EXAFS range (3–14 Å\(^{-1}\)) was used. The experimental spectra are shown in magenta (non-treated compound), blue (after exposure to oxidizing potentials), green (after exposure to reducing potentials) and in black (the reference metallic Co and the Co oxide catalyst were taken from ref. 64). The simulated spectra are shown in red. The simulation parameters are given in Tables S9–S14 (ESI†). Vertical dotted lines indicate common structural motifs (interatomic distances) to guide the eye. For visibility, the amplitude of the spectrum of the metallic Co is reduced by a factor of 3.
Fig. 5 Alkaline electrolyzer using the two electrode configuration. (a) is the current–potential plot of an alkaline electrolyzer using LiCoBPO|LiCoBPO and NaCoBPO|NaCoBPO on NF as both the cathode and anode (bare NF is shown in brown) in 1 M KOH with a scan rate of 5 mV s⁻¹. The inset with the noble-metal system is shown in Fig. S46 (ESI†). The inset of (a) shows the stability of electrodes at an applied bias of 1.53 V (LiCoBPO) and 1.58 V (NaCoBPO) (CA). The CA of LiCoBPO was further investigated for ~73 days and yielded continuous growth in current demonstrating the undying nature of the catalysts. The inset of (b) shows the schematic view of an electrolyzer.

(Table S16, ESI†). An inverted electrochemical cell (graduated) was assembled to collect the evolved H₂ and O₂ at atmospheric pressure and the volumes and their ratios (~2:1) evolved were measured (Fig. S49 and S50, ESI†). Finally, a controlled two-electrode experiment of LiCoBPO was also performed on the FTO substrate that exhibited a cell potential of 1.94 V at a current density of 10 mA cm⁻². Strikingly, the long-term stability (at 1.95 V) test over 10 days also displayed continuous growth in current density over time demonstrating the fast and easy separation of Li and transformation of the material into a Co-rich surface as well as excluding the effect of the electrode substrate (Fig. S51, ESI†).

Conclusions

We have shown that helical metal borophosphates are not only aesthetically highly appealing materials. They also represent a new class of catalyst precursor material which is transformed under operation conditions into either OER or HER catalysts, both with excellent characteristics regarding energetic efficiency and long-term stability. The possibilities of tuning catalyst properties have been demonstrated by comparison of lithium and sodium as redox-inert metal ions in the helical borophosphate; further catalyst optimization could result from the exchange of cobalt ions against other redox-active metals. We consider that this material class may also provide new opportunities in other electrocatalytic applications, e.g., the reverse processes of oxygen reduction and hydrogen uptake reactions or the dark photosynthesis of fuels.

Experimental

Synthesis of LiCo(H₂O)₂[BPO₄]·H₂O (LiCoBPO)

Single crystals of LiCo(H₂O)₂[BPO₄]·H₂O were prepared by mild hydrothermal synthesis. For LiCo(H₂O)₂[BPO₄]·H₂O, a mixture of 2.002 g of Co(CH₃COO)₂·4H₂O, and 2.715 g Li₂B₄O₇ was placed in 20 mL of distilled water. Subsequently, 5.554 g of H₃PO₄ (85%) was added to the mixture and the pH was adjusted to 1 by addition of 2 mL HCl (37%). The mixture was then transferred into a 50 mL Teflon-lined autoclave (filling degree ~30%), treated under autogenous pressure at 180 °C for three days, and cooled down naturally to ambient temperature. The reaction product was separated by centrifugation, washed with distilled water and acetone several times and dried overnight in air at 60 °C. The product consisted of pink hexagonal bipyramid crystals with dimensions ranging from 0.1 mm to 0.5 mm.

Synthesis of NaCo(H₂O)₂[BPO₄]·H₂O (NaCoBPO)

For NaCo(H₂O)₂[BPO₄]·H₂O, a mixture of 2.005 g of Co(CH₃COO)₂·4H₂O, and 3.221 g Na₂B₄O₇ was placed in 20 mL of distilled water. Subsequently, 5.554 g of H₃PO₄ (85%) was added to the mixture and the pH was adjusted to 1 by addition of 2 mL HCl (37%). The further experimental procedure was continued as used for LiCo(H₂O)₂[BPO₄]·H₂O. The separated pink crystals were washed thoroughly and dried overnight in air at 60 °C. The dimensions of the crystals obtained here were also in a similar range as observed for LiCo(H₂O)₂[BPO₄]·H₂O.

Synthesis of Co₃(PO₄)₂·8H₂O

In a typical synthesis, 0.5 g of Na₃PO₄·12H₂O was first dissolved in 20 mL of H₂O. To this solution, a second solution, which was formed by previously dissolving 0.5 g of Co(CH₃COO)₂·4H₂O in 10 mL H₂O, was added dropwise. Immediate violet precipitation was observed, and the solution was further stirred for 3 hours. The final product was separated by centrifugation, washed with distilled water and ethanol several times and dried overnight in air.

Synthesis of CoOOH

Commercially available Co(OH)₂ was dispersed in 30 mL 4 M KOH solution which was then heated slowly up to 45 °C. 2 mL of 30% H₂O₂ solution was then added dropwise and was kept at the same temperature for 18 h. The final brown precipitate was
filtered and washed with deionized water three times, then
dried at 65 °C overnight in air.

Instrument details

X-ray diffraction. Identification of the sample phases was
determined using PXRD on a Bruker AXS D8 advanced automatic
diffractometer equipped with a position sensitive detector (PSD)
and a curved germanium (111) primary monochromator. Cu-K\(\alpha\)
(\(\lambda = 1.5418 \text{ Å}\)) radiation was used and the XRD profiles recorded
were in the range of 5° < 2\(\theta\) < 80°. The diffraction pattern fitting
was conducted using the program FullProof where a theoretical
line profile is calculated from a structural model that is refined
using a least-squares approach until it matches the discrete data.
The identified final structural models were drawn with the
DIAMOND program version 3.0. GIXRD was recorded in the
Bragg–Brentano geometry, using a Bruker AXS (D8 Advance)
diffractometer with Cu-K\(\alpha\) radiation.

Elemental analysis. The chemical composition of the
as-synthesized lithium or sodium cobalt borophosphates, as
well as the dissolution of metal ions in the electrolyte during
electrochemical conditions, was confirmed by ICP-AES on a
Thermo Jarrell Ash Trace Scan analyzer. The as-synthesized
materials were dissolved in acid solutions (aqua regia) whereas
the electrolytes after the electrochemistry were taken directly
for analysis. The results of three independent measurements
were averaged. The composition of the as-synthesized materials
showed good agreement with the chemical formulae.

Electron microscopy. SEM was carried out to examine
texture, morphology and surface details of the crystals under investigation whereas EDX analyses were used to semi-
quantitatively evaluate the presence of cobalt and phosphorous
present on the sample surfaces. The elements with lower
atomic numbers such as lithium and boron were not determined
due to the detection limits. The samples were placed on a
silicon wafer and the measurements were carried out on an
LEO DSM 982 microscope integrated with EDX (EDAX, Appollo
XPP). Data handling and analysis were conducted with the software package EDAX. The SEM images of the material on
nickel foam electrode were taken on a Helios NanoLab G3 UC
DualBeam (FIB/SEM system) from the company FEI operated at
an accelerating voltage of 5 kV.

The microstructure investigations of the as-synthesized materials and the materials after electrochemical investigations
were carried out using TEM analysis. A small amount of the
powder was placed on a TEM-grid (carbon film on a 300 mesh
Cu-grid, Plano GmbH, Wetzlar, Germany). The microstructure
particle size, morphology, crystallinity, and phase composition
of the materials was studied using an FEI Tecnai G² 20
S-TWIN transmission electron microscope (FEI Company, Eindh-
oven, Netherlands) equipped with a LaB\(_6\)-source at a 200 kV
acceleration voltage. The EDX analysis was performed with an
EDAX r-TEM SUTW detector (Si (Li)-detector). Images were
recorded with a GATAN MS794 P CCD-camera. Both SEM and TEM experiments were carried out at the Zentrum
für Elektronenmikroskopie (ZELMI) of the TU Berlin.

Thermal analysis. In order to understand the information on
decompositions, phase transitions and recrystallization events,
simultaneous constant rate TGA and DTG analyses of the well
ground as-synthesized materials were performed on a Rubotherm
setup. The materials were first dried at 80 °C and were then
placed in an open alumina crucible and heated at 5 K min\(^{-1}\)
to 800 °C in a continuous nitrogen gas flow and cooled down to
room temperature. The TG curves were corrected by subtraction
of a blank run.

FT-IR spectroscopy. The presence of different modes of vibrations of the as-synthesized materials was studied using a
BIORAD FTS 6000 FTIR spectrometer under attenuated total
reflection (ATR) conditions. The data were recorded in the range of
400–4000 cm\(^{-1}\) with an average of 32 scans at 4 cm\(^{-1}\) resolution.
Further, the presence of –OH groups and H\(_2\)O in the crystal
structures of the investigated borophosphates was directly com-
pared with the literature known examples.

Brunauer–Emmett–Teller (BET) surface area. The surface areas and the pore size distributions of the materials were
determined on a Quantachrome Autosorb1 apparatus. Nitrogen
desorption/desorption isotherms were measured at ~19°C
after degassing the sample at 120 °C overnight. The BET surface
areas (\(S_{\text{BET}}\)) were calculated from the adsorption data in a
relative pressure ranging from 0.01 to 0.1.

Four-point probe resistivity measurements. The resistivity
was measured using a Signature Pro4 system with a Keithley
2400 source-measure unit (SP4-40045TBY) using a four-point
probe resistivity technique. The spacing between tungsten
carbide tips was 1.016 mm with a radius of 0.245 mm and
the spring pressure was 45 grams. The borophosphates were
electrophoretically deposited on FTO to estimate the specific
resistivity of each synthesized material and the average results
are presented.

XPS measurements. The XPS measurements were conducted
using a Kratos Axis Ultra X-ray photoelectron spectrometer
(Kratos Analytical Ltd, Manchester, UK) with an Al K\(\alpha\) (1486.7 eV)
monochromatic radiation source with a 90° takeoff angle (normal
to the analyzer). The vacuum pressure in the analyzing chamber
was kept at 2 × 10\(^{-9}\) Torr. The high-resolution XPS spectra were
collected for C 1s, O 1s and Co 2p levels with pass energy 20 eV and
step size 0.1 eV. The binding energies were then calibrated relative
to the C 1s peak energy position at 285.0 eV. Analyses of the data
were carried out using Casa XPS (Casa Software Ltd) and Vision
data processing programs (Kratos Analytical Ltd).

In situ X-ray absorption spectroscopy (XAS). The in situ X-ray
absorption spectra (XANES/EXAFS) were collected at the BESSY
synchrotron radiation source operated by the Helmholtz-
Zentrum Berlin.\(^{83}\) The measurements were conducted at the
KMC-3 bending-magnet beamline at 20 K in a helium-flow
cryostat (Oxford-Danysfik). The incident beam energy was
selected by a Si(111) double-crystal monochromator. The mea-
measurements at the cobalt K-edge were performed in transmission
mode with an ionization chamber and in fluorescence mode
using a 13-element energy-resolving Ge detector (Canberra).
The extracted spectrum was weighted by \(k^3\) and simulated in
\(k\)-space (\(E_0 = 6547 \text{ eV}\)). All EXAFS simulations were performed
using in-house software (SimX) after calculation of the phase functions with the FEFF program (version 8.4, self-consistent field option activated).\textsuperscript{65,66} The data range used in the simulation of the EXAFS spectra was $20–1000$ eV ($3–16$ Å$^{-1}$). The EXAFS simulation was optimized by a minimization of the error sum obtained by summation of the squared deviations between measured and simulated values (least-squares fit). The fit was performed using the Levenberg-Marquardt method with numerical derivatives. The error ranges of the fit parameters were estimated from the covariance matrix of the fit. Further details are given elsewhere.\textsuperscript{65,66,83}

LiCoBPO samples for XAS experiments were prepared on fluorinated tin oxide substrates in analogy to the electrochemical experiments. The samples were electrochemically treated for OER CV (3 cycles), HER LSV (3 cycles) and OER CA (25 h) at 1.53 V vs. RHE and HER CA (25 h) at $-0.25$ V vs. RHE (maintaining a current density of 10 and $-10$ mA cm$^{-2}$) for 24 hours in 1 M KOH solutions. After the desired electrochemical treatment, the samples were immediately freeze-quenched using liquid N$_2$ under vigorous N$_2$ gas flow and stored in liquid N$_2$ until XAS measurements were conducted.

**Gas chromatography.** An Agilent 7890A gas chromatograph (GC) was used to determine the hydrogen and oxygen contents in the headspace. The GC was equipped with a carboxen-1000 column and a thermal conductivity detector (TCD). The carrier gas was argon (Ar). The catalysts were first immersed in the 53 mL closed electrolyzer set-up and bubbled with Ar for 1 h. Subsequently, the gas in the headspace was taken with a syringe and injected into the GC. After the experiment, the amount of H$_2$ and O$_2$ collected in the head-space was determined. The O$_2$ contribution during sampling was corrected by estimating O$_2$ before and after the electrochemical reaction.

**Electrochemical measurements**

First of all, the single crystals of LiCoBPO and NaCoBPO were placed in a mortar and thoroughly ground for 5 minutes using a pestle ($S_{\text{eff}}$ is 1.30 m$^2$ g$^{-1}$ and 2.45 m$^2$ g$^{-1}$). The electrodes used for electrochemical measurements were prepared by electrophoretic deposition (EPD) with a potential difference of 10 V in a mixture of a minimum amount of iodine (for 50 mg of catalyst, 3 mg of iodine) and acetone on a $1 \times 1$ cm$^2$ area of fluorinated tin oxide coated glass (FTO, Sigma Aldrich, resistivity 8–12 $\Omega$ sq.$^{-1}$). The EPD was carried out for 3 minutes for each FTO electrode. The loading of the deposited materials on each electrode was weighed and the amount obtained was $\sim 1$ mg cm$^{-2}$. The catalytic activity of the materials was then measured in 1 M KOH solution at room temperature using a single-compartment three-electrode electrochemical cell (material deposited on FTO-glass as a working electrode, Pt wire as a counter electrode and Hg/Hg$_2$SO$_4$ (CH instruments) as a reference electrode) with a potentiosstat (SP-200, BioLogic Science Instruments) controlled by the EC-Lab v10.20 software package.

Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were conducted with the typical electrolyte resistance and an IR compensation of 80% was applied. The electrolyte was not stirred during the electrochemical experiments. The potentials reported in the presented work were referenced to the reversible hydrogen electrode (RHE) through RHE calibration, and in 1 M KOH at pH 14, $E$(RHE) = $E$(Hg/Hg$_2$SO$_4$) + 0.64 + (0.0591 × pH) V. The Tafel slopes were derived from OER and HER polarization curves obtained at 1 mA s$^{-1}$. The active ECSA was assessed from the electrochemical double-layer capacitance ($C_{dl}$) of the catalytic surface and the electrochemical capacitance was obtained by measuring the non-faradaic capacitive current related to double-layer charging from the scan-rate dependence of CVs. The $C_{dl}$ values of the materials were converted into ECSA according to the equation $ECSA = C_{dl}/C_s$ where $C_s$ is the specific capacitance of the material for a standard with 1 cm$^2$ of real surface area under identical electrolyte conditions. For measuring the ECSA, the general specific capacitances $C_s = 0.040$ mF cm$^{-2}$ for FTO and $C_s = 1.7$ mF cm$^{-2}$ for NF in 1 M KOH electrolyte were used based on typical reported values.\textsuperscript{47,74} To evaluate the electron transfer resistance at the catalyst/electrolyte interface, EIS was conducted. EIS was performed at 1.5 V (vs. RHE). A sinusoidal voltage with an amplitude of 5 mV and scanning frequency ranging from 100 kHz to 1 Hz was applied to carry out the measurements. The impedance spectra were fitted using a simplified Randles equivalent circuit. The chronogramperometric measurements were performed in 1 M KOH at selected constant potentials (at a current density of 10 mA cm$^{-2}$) vs. RHE to reveal the long-term stability of the materials.

In addition to the FTO, the deposition of the materials on nickel foam (NF, Racemat BV) electrodes was also realized by EPD and the obtained loading of the material on the NF electrode was $\sim 3$ mg cm$^{-2}$. CV, LSV, ECSA, EIS, and long-term chronogramperometric measurements were also performed on NF similarly to the FTO electrodes. The overall water-splitting reaction was performed in a two-electrode system on materials deposited on NF or FTO and subsequently, the long-term durability was also tested at a selected potential, when the current reached 10 mA cm$^{-2}$.

**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**

69 X. Y. Lu and C. A. Zhao, Nat. Commun., 2015, 6, 6616.