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Polybenzoxazine-Derived N-doped Carbon as Matrix for Powder-Based Electrocatalysts

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In addition to catalytic activity, intrinsic stability, tight immobilization on a suitable electrode surface, and sufficient electronic conductivity are fundamental prerequisites for the long-term operation of particle- and especially powder-based electrocatalysts. We present a novel approach to concurrently address these challenges by using the unique properties of polynbenzoxazine (pBO) polymers, namely near-zero shrinkage and high residual- char yield even after pyrolysis at high temperatures. Pyrolysis of a nanocubic prussian blue analogue precursor (K$_{x}$Mn$_{y}$[Co(CN)$_6$]$_z$·nH$_2$O) embedded in a bisphenol A and aniline-based pBO led to the formation of an N-doped carbon matrix modified with Mn$_2$Co$_3$O$_7$ nanocubes. The obtained electrocatalyst exhibits high efficiency toward the oxygen evolution reaction (OER) and more importantly a stable performance for at least 65 h.

Introduction

Electrocatalytic splitting of water into hydrogen and oxygen is limited by high overpotentials of the oxygen evolution reaction (OER).[1] Low-cost, non-precious, earth-abundant metals are typically catalyst powders, which have to be brought in contact with the electrode surface maintaining fast electron transfer pathways especially among the powder particles as well as stable fixation under vigorous gas evolution at high current densities. The lack of strategies for the fixation of powder catalysts leads to suboptimal catalyst performance especially with respect to stability during operation at high current densities. Organic polymers are typically used as binder materials, although they might be insulating if used in too high concentrations, thus blocking catalytically active sites and decreasing the intrinsic activity of the catalyst.[2] Even in alkaline electrolytes, in which abundant transition metal-based catalysts can be used, Nafton is often used as binder material, which can be considered unsuitable under these conditions due to covering surface active sites and its intrinsic insulating properties. Evidently, it is important to enhance the intrinsic conductivity of electrocatalysts, especially when poorly conducting materials are used or poorly conducting binder materials are added. The addition of carbon nanomaterials such as carbon black, carbon nanotubes, or graphene oxide/ reduced graphene oxide is commonly used to enhance the conductivity of related slurry electrodes.[4] However, mixtures of carbon additives with powder-based electrocatalysts do not overcome limitations imposed by the poor adhesion on the electrode surface and typically an unsuitable binder material such as Nafton is used to glue the catalyst/carbon composite powder to the electrode surface.

We present the first application of polybenzoxazines (pBO), a class of high-performance thermosets, as new binder matrices in electrocatalysis to concurrently address the aforementioned issues in powder-catalyst fixation. pBos consist of highly crosslinked networks of benzoxazine (BO) monomers or oligomers.[5] They arise from Mannich-type reactions of primary amines, aldehydes, and phenol derivatives.[5] Especially, two unique features of this specific polymer class make pBos highly suitable as precursors for electrocatalyst matrices: i) near-zero shrinkage with respect to the deposited monomer film during polymerization, which allows for maintaining a homogeneous electrode coating after polymerization whereas other types of polymers shrink upon solvent evaporation...
hence weakening the catalyst film adhesion on electrode surfaces. ii) Highly crosslinked pBO networks are well known as flame-retardant materials providing high residual char yields after pyrolysis, an important prerequisite for the formation of a stable carbon-based binder matrix.\(^\text{10}\) Thus, subsequent polymerization and pyrolysis transform the insulating organic pBO matrix into a conducting carbon matrix\(^\text{11}\) with incorporated electrically interconnected catalyst powder particles exhibiting high physical stability.

Our strategy is to embed the prussian blue analogue (PBA) potassium manganese hexacyanocobaltate \((\text{K}_x\text{Mn}_y\text{[Co(CN)]}_n)\times n\text{H}_2\text{O}\) as a model catalyst precursor into a benzoxazine-based precursor matrix. A sequence of polymerization and pyrolysis converts the composite into Mn- and Co-containing nanocubes embedded into a pBO-derived carbon matrix forming a highly stable OER active film on the electrode.

Results and Discussion

Three-step electrode preparation

Catalyst particles embedded in a porous N-doped carbon matrix were prepared according to the three-step procedure shown in Scheme 1 and described in detail in the Experimental Section. Thermally induced polymerization of a mixed film of a bisphenol A and aniline-based BO monomer and \(\text{K}_x\text{Mn}_y\text{[Co(CN)]}_n\) drop-coated on a glassy carbon electrode surface led to a polymer layer with incorporated PBA particles. Subsequent pyrolysis transformed the deposited pBO/PBA film into a conducting N-doped carbon matrix incorporating mildly oxidized Mn and Co nanocubes (carbon–Mn\(\text{O}_x\); Scheme 1).

The unique near-zero shrinkage property of pB0s led to a homogenously distributed carbon matrix over the electrode surface even after pyrolysis (Figure S1 in the Supporting Information). The modified electrode was entirely covered with Mn\(_x\)Co\(_y\)O\(_z\), nanocubes and with relatively larger particles representing agglomerates of the nanocubes (Figure S1). Polymerization and pyrolysis were performed under Ar flow to prevent complete degradation of pBO. However, although the thermal treatment was performed under inert gas atmosphere, Mn was oxidized by traces of oxygen at higher temperatures. This was also observed after pyrolysis of the pure PBA precursor. The Mn core-level XPS spectrum shows a Mn\(_{2p_3/2}\) peak with a binding energy of 641.48 eV, representing an oxidized manganese \((\text{Mn}^{4+}/\text{Mn}^{3+})\) species (Figure S2). Thermogravimetric analysis (TGA) of the two precursors (PBA and pBO) was employed to gain further insight into the influence of the temperature during the polymerization and pyrolysis processes on the decomposition behavior (Figure 1). In a first step, the tempera-

![Scheme 1. Electrode preparation procedure and transformation of the precursor materials into the final catalyst.](image)

**Figure 1.** TGA of Araldite (red line), \(\text{K}_x\text{Mn}_y\text{[Co(CN)]}_n\times n\text{H}_2\text{O}\) (blue line), and a 1:1 mixture of Araldite and \(\text{K}_x\text{Mn}_y\text{[Co(CN)]}_n\times n\text{H}_2\text{O}\) (purple line).

Influence of the PBA-to-pBO ratio

The influence of the pBO content on the OER activity of the PBA-derived electrocatalyst was investigated by means of hydrodynamic cyclic voltammetry using electrodes prepared with 0, 2, 10, 17, 28, or 50 wt% pBO with respect to the overall solid content in the drop-coated ink (Figure 2a,b). The voltam-
stability (Figures S3–S5). Mn superconductivity and on the other hand a matrix of improved efficiency amount of graphitic carbon providing on the one hand (TEM) of the pretreated samples revealed the presence of a sufficient amount of graphitic carbon particles. However, consecutive potential cycling (50 cycles, scan rate 50 mV s⁻¹) substantially activates the catalytic activity of the modified electrodes prepared with 28 and 50 wt% pBO whereas all other electrodes lost activity because of insufficient catalyst fixation on the electrode surface caused by the low amount of pBO during film formation (Figure 2b). Samples before and after electrochemical cycling are referred to as “as-prepared” and “pretreated”, respectively. The pretreatment process apparently eliminates amorphous carbon layers, thus exposing more highly active sites to the electrolyte, concomitantly reducing the required overpotential for OER. The carbon removal can be considered as self-limiting. After activation, the catalysts with a pBO content of 50 wt% showed the highest activity. The activation effect explains the different surface morphologies seen in the SEM images of the as-prepared and pretreated electrodes with 50 wt% pBO (Figure 2d and 2e).

The SEM image of the as-prepared electrode shows the Mn₃O₇ nanocubes covered with an additional layer, whereas the image of the pretreated electrode reveals uncovered and porous Mn₃Co₇O₇ nanocubes. Transmission electron microscopy (TEM) of the pretreated samples revealed the presence of a sufficient amount of graphitic carbon providing on the one hand high conductivity and on the other hand a matrix of improved stability (Figures S3–S5). Mn₃Co₇O₇ nanocubes obtained without any addition of pBO showed an initial high activity during the first voltammogram, however, the catalyst detached easily from the electrode surface leading to drastic activity loss (Figure 2a,b). Stabilization of the Mn₃Co₇O₇ nanocubes using Nafion as a binder leads to a substantially less active and less stable film (Figure S6) compared to the activated sample containing a PBA/pBO ratio of 1:1, thus clearly confirming the benefit of using pBO-derived carbon networks for incorporating catalyst particles compared to the most commonly used binder. SEM revealed the preservation of the cubic structure of the precursor material during the heat-treatment processes (Figure 2c–e).

Catalyst characterization
A sample containing 50 wt% pBO was investigated by means of SEM, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and TEM-related techniques such as high-resolution TEM (HRTEM), scanning TEM (STEM) in the high-angle annular dark field mode (HAADF), and STEM-electron energy loss spectroscopy (EELS). The edge length of the cubic catalyst particles varied between 120 and 270 nm and was independent of the preparation step (Figure S7). Energy dispersive X-ray spectroscopy (EDX) and XPS revealed the presence of the expected components Mn, Co, O, and C (Figures S8 and S9) in the catalyst layer. HRTEM micrographs revealed a mixed amorphous/graphitic carbon layer covering the whole structure, confirming the results from the SEM images (Figure 2c). The existence of mixed amorphous/graphitic carbon was further confirmed by Raman spectroscopy (Figure S15), XPS (Figure 4), and XRD (Figure 5). HAADF STEM micrographs show the presence of small nanoparticles and the presence of flake-like regions em-

Figure 2. RDE cyclic voltammograms (scan rate 5 mV s⁻¹, 0.1 m KOH, O₂-saturated, 1600 rpm) of GCEs modified with different amounts pBO in the drop-coating solutions (0, 2, 10, 17, 28, and 50 wt% of solid content in solution) before (a) and after potential cycling (b). SEM images of as-prepared KₓMnₓ[Co(CN)₆]ₓ·ₙH₂O (c), carbon–MnₓCoₓO₇ before (d) and after (e) potentiodynamic activation.
bedded in a graphitic carbon matrix (Figures 3 a, b, S12–S14). Moreover, Co is shown to partly remain as metallic Co (Figures 3 e, S5, S10, and S11), whereas Mn is only present in its oxide forms and could not be observed in its metallic state, supporting the earlier statement of its tendency to be oxidized. Furthermore, a Mn-, Co-, and C-containing phase seems to exist (Figure 3 e).

Additional STEM EELS maps also show a partial segregation of Mn and Co, Mn-rich oxides and Co/MnCoO core–shell particles (Figures S5, S10, and S11). Furthermore, XRD and XPS revealed the existence of metal carbide phases (Figures 5 and 4), which are in good agreement with the literature about pyrolysis of PBA in inert atmosphere at 600 °C.[8] The C 1s spectrum (Figure 4 c) was deconvoluted into five peaks with binding energies at 283.52, 284.22, 285.36, 288, and 291.57 eV corresponding to metallic carbides, sp2 C–C, C–O–C/C–N, O–C–O, and a shake-up feature, respectively.[9] The peak at 283.52 eV can be safely assigned to carbides of Co and Mn owing to its good conformance to the C 1s energies of other transition metal carbides, and is therefore in accordance with the MnCoC phase in Figure 3 e.[10] Deconvolution of the N 1s spectrum revealed the presence of pyridinic N (399.09 eV) and pyrrolic N (401.06 eV) groups (Figure 4 e), and hence the formation of N-doped carbon as described previously by Zhang et al. for the pyrolysis of the used pBO.[11] The presence of Co2+ is difficult to conclude from the binding energies of the Co2p1/2 and Co2p3/2 peaks (Figure 4 b).[12] However, both Co2p peaks have characteristic satellite features at higher binding energies, supporting the presence of Co2+ ions.[13] The absence of satellite features in the Mn2p (Figure 4 a) spectrum and the peak splitting of 5.5 eV in the binding energy of the Mn3s spectrum (Figure 4 f) confirms the presence of oxidized Mn species.[12, 14]

XRD revealed the existence of three crystalline phases with different compositions (Figure 5). The reflection at 25.8° is assigned to both graphitic and amorphous carbon. The second dominant reflection for graphitic carbon at 44° cannot be observed because it is hidden underneath other signals. Therefore, a clear assignment of the carbon nature is not possible.

Figure 3. TEM analysis of as-prepared carbon–Mn$_x$Co$_y$O$_z$. HAADF STEM (a, b) and HRTEM (c, d) micrographs of the carbon–Mn$_x$Co$_y$O$_z$ composite showing several nanoparticles with a flake-like structure and the C matrix. EELS mapping was obtained from the white squared area. Individual EELS composition maps of Mn (red), Co (green), O (blue), and C (turquoise) along with the composites maps of Mn–Co–O, Mn–Co, Mn–O, and Co–O (e).

Figure 4. XPS analysis of the as-prepared carbon–Mn$_x$Co$_y$O$_z$ composite. High-resolution XPS spectra of Mn 2p (a), Co 2p (b), C 1s (c), O 1s (d), N 1s (e), and Mn 3s (f).

Figure 5. XRD patterns of carbon–Mn$_x$Co$_y$O$_z$ and reference patterns of Mn$_2$Co$_2$C, MnO, and Mn$_3$C$_2$. 
based just on the XRD data. The reflections at 35.12° and 58.85° originate from the (111) and (220) planes, respectively, of cubic MnO (JCPDS 75-0625) with the space group *Fm*3*m*, whereas the most intense reflection at 41.20° and the additional two at 47.93° and 70.16° correspond to the (111), (002) (200), and (220) (202) planes of tetragonal Mn$_2$Co$_2$C (JCPDS 89-3688) with the space group *P4/mmm*. The remaining intense reflection at 44.28° was assigned to the (511) plane of the cubic Mn$_2$C$_6$ phase (JCPDS 80-1701) with the space group *Fm*3*m*. The cubic crystal system of two of the phases is reflected in the highly cubic particle shape. The formation of carbides is in good agreement with previous reports on the heat treatment of PBA up to 600°C in an inert gas atmosphere. The presence of MnO confirms the results of the TGA data regarding the observed weight increase during the cooling step. Although the XRD pattern was difficult to analyze and does therefore not preponderate, it confirms the clear results obtained by TEM and XPS, despite the CoMn$_2$O$_4$ spinel structure as seen in TEM not being observed in XRD, likely due to its very small size (~10 nm).

**Electrochemical characterization**

A PBA/PBO ratio of 1:1 revealed the highest activity. Therefore, this ratio was chosen for a detailed study of the electrochemical performance of MnCo nanocubes embedded in a PBO-derived N-doped carbon matrix with respect to activity and stability towards OER. Carbon–Mn$_2$Co$_2$C showed high OER activity affording a current density of 1 mA cm$^{-2}$ at 1.54 V versus RHE, and a current density of 10 mA cm$^{-2}$ at 1.60 V versus RHE (Figure 6a), whereas the pure pyrolyzed PBO does not exhibit significant OER activity. The overpotential of 0.37 V required to reach a current density of 10 mA cm$^{-2}$ is significantly lower than other Co$_x$Mn$_{3-x}$O$_2$-based catalysts, which have overpotentials in the range of 0.39–0.63 V. The Tafel slope of carbon–Mn$_2$Co$_2$C was 59 mV dec$^{-1}$ (Figure 3b), which indicates very fast kinetics and a charge transfer coefficient (α) very close to 1 (α = 2.303RT/nF, please check equation, I changed α to n and added definitions with R the universal gas constant, T the temperature, n the number of electrons transferred, and F the Faraday constant). According to the Tafel slope, the discharge of OH$^-$ is the rate determining step. In situ Raman spectroscopy (Figure S16) indicates that the transition metal oxides are mainly responsible for catalyzing the OER whereas the N-doped carbon matrix facilitates electrical interparticle connection. A recently developed stability assessment methodology[17] was applied to evaluate the carbon–Mn$_2$Co$_2$C catalyst and showed a negligible change in activity at current densities of 1.4 and 10 mA cm$^{-2}$ (Figure 6c). Additional stability measurements were conducted using carbon–Mn$_2$Co$_2$C-modified Ni foam in a custom-built flow-through cell. During the accelerated galvanostatic stability test with an applied current density of 10 mA cm$^{-2}$ (with respect to the exposed surface of ø = 8 mm), the corresponding potential increased from an initial value of 1.61 to 1.68 V versus RHE after 67 h (Figure 6d). After the first 19 h, the potential remained constant without any visible change until the end of the measurement indicating a stable state of the catalyst layer. Taking into account that Ni foam is by itself active for catalyzing the OER, analogous measurements were performed with pure Ni.

![Figure 6](image-url)

**Figure 6.** a) LSV (5 mVs$^{-1}$, 0.1 M KOH, O$_2$-saturated, 1600 rpm) of an activated carbon–Mn$_2$Co$_2$C electrode prepared with a PBO/PBA ratio of 1:1 in comparison with pure pyrolyzed PBO. b) Tafel plot derived from the LSV in (a). c) E vs. t curves at current densities of 1.4 and 10 mA cm$^{-2}$, respectively, extracted from stability measurement cycles. d) E vs. t curves of carbon–Mn$_2$Co$_2$C on Ni foam (white), and pure Ni foam (black) recorded in 0.1 M KOH, O$_2$-saturated at a current density of 10 mA cm$^{-2}$ extracted from the stability measurement cycles.

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foam as control. The activity of pure Ni foam increased at the beginning of the measurement owing to the formation of NIO/NiOOH, however, it later remained constant at an overpotential of about 0.17 V higher than the carbon–Mn₃Co₄O₉-modified Ni foam electrode (Figure 6d). The observed activity and stability can hence safely be attributed to the properties of the suggested carbon–Mn₃Co₄O₉ catalyst.

Conclusions

We suggest a novel approach for the preparation of highly active and stable catalyst-modified electrodes for the oxygen evolution reaction (OER). Benzoxazine (BO) monomers were deposited together with the prussian blue analogue (PBA) \( K_{\text{Mn}}[\text{Co(CN)}_6]_3 \cdot n \text{H}_2\text{O} \) on an electrode surface followed by temperature-induced polymerization, leading to the formation of a homogeneous polymer/PBA composite film owing to the near-zero shrinkage property of polybenzoxazine (pBO). Subsequent pyrolysis formed an N-doped carbon matrix embedding cataytically active Mn₃Co₄O₉ nanocubes. The pBO content showed a significant impact on the catalytic activity. Owing to the intrinsic stability of the pBO, only 5% loss in activity during accelerated galvanostatic stability tests at 10 mA cm⁻² on carbon–Mn₃Co₄O₉ sprayed on Ni foam after 67 h was observed.

Experimental Section

Electrode preparation

Carbon–Mn₃Co₄O₉ modified glassy carbon electrodes were prepared according to the following procedure: a glassy carbon rod \((\text{Ø}=3 \text{ mm}, \text{L} \approx 1 \text{ cm}; \text{HTW, Germany})\) was polished successively with polishing pastes of decreasing particle sizes \((3 \mu \text{m diamond paste, } 1 \mu \text{m and } 0.3 \mu \text{m Al₂O₃ paste; Leco, USA})\) to obtain a mirror-like surface. The polished electrodes were immersed in a 1:1 mixture of ethanol and ultra-pure water and sonicated for 15 min. The dried electrodes were drop-coated with an ink \((7.2 \mu \text{l})\) containing \(K_{\text{Mn}}[\text{Co(CN)}_6]_3 \cdot n \text{H}_2\text{O} \) and Araldite 35600 CH \((900 \text{ s}). \quad [17] \) The measurements were done either with a RDE (GCE, 1600 rpm) or an electrochemical flow-through cell (Ni foam electrode) in oxygen-saturated KOH \((0.1 \text{ M}, \text{ flow rate: } 30 \text{ mL min}^{-1})\). The measurements were done either with a RDE (GCE, 1600 rpm) or an electrochemical flow-through cell (Ni foam electrode) in oxygen-saturated KOH \((0.1 \text{ M}, \text{ flow rate: } 30 \text{ mL min}^{-1})\).

In situ Raman spectra were recorded during chronoamperometric measurements at different potentials in KOH \((0.1 \text{ M})\). All potentials are referred to the reversible hydrogen electrode (RHE) and converted according to \(E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 \text{ V}, \text{ pH} = 14 \log \text{OH}^- - 1.059 \text{ pH} \).

Physical characterization

XRD measurements were performed using a PANalytical theta-20 theta diffractometer equipped with a CuKα radiation source. Scans were run from 5 to 80° with a step width of 0.01°, Raman spectra were recorded using a Jobin–Yvon iHR550 spectrometer (Germany) equipped with a TE cooled charge coupled device. Excitation was done with a laser MIP 6000, Model Ignis 660 (Laser Quantum, UK) at a wavelength of 661 nm (in situ) or 532 nm (D and G band). The typical laser power was 11 mW and the spectra were acquired for 10 s. To focus the laser in solution, an immersible objective (Olympus, Japan) with a 60 times magnification was employed. SEM images and EDX were performed using a Quanta 3 D FEG SEM (FEI, USA) operated at 20.0 kV for SEM imaging and at 30 kV for EDX analysis and mapping. XPS spectra were recorded on a K-Alpha instrument (Thermo Scientific, USA) equipped with a monochromatic AlKα source \((1486.6 \text{ eV})\). The measurements were performed at a base pressure of \(2 \times 10^{-9} \text{ mbar} \) with pass energies of 200 and 20 eV for survey and high-resolution spectra, respectively. Deconvolution of the C 1s and N 1s peaks was performed after subtraction of Smart background. TGA curves were recorded on a Q500 (TA Instruments, USA). A combination of non-isothermal and isothermal steps were run under a nitrogen atmosphere, following a similar heating program like the one used for the electrode preparation: \(10 \text{ °C min}^{-1} \) ramp from 20 to 160 °C, isothermal for 2 h at 160 °C, \(10 \text{ °C min}^{-1} \) ramp from 160 to 180 °C, isothermal for 2 h at 180 °C, \(10 \text{ °C min}^{-1} \) ramp from 180 to 200 °C, isothermal for 2 h at 200 °C, \(10 \text{ °C min}^{-1} \) ramp from 200 to 220 °C, isothermal for 1 h at 220 °C, \(10 \text{ °C min}^{-1} \) ramp from 220 to 240 °C, isothermal for 1 h at 240 °C, \(10 \text{ °C min}^{-1} \) ramp from 240 to 600 °C, isothermal for 2 h at 600 °C, cooling at \(1 \text{ °C min}^{-1} \) from 600 to 190 °C. TEM studies were conducted using a field-emission gun FEI.
Manganese hexacyanocobaltate synthesis

K₃Mn[Co(CN)₆]·nH₂O was synthesized using a co-precipitation reaction adapted from Ref. [19]. Mn(CH₃COO)₂·4H₂O (1.219 mmol, Sigma–Aldrich, Germany) and PVP (2.445 g (K:30) were dissolved in a mixture of ethanol (tech.) and ultrapure water (325 mL, 3:1) (solution A, 3.75 mM Mn²⁺). K₃[Co(CN)₆] (0.652 mmol, Sigma–Aldrich, Germany) was dissolved in ultrapure water (163 mL) (4 mM Co²⁺, solution B). Solution B was added into the stirred solution A using a peristaltic pump with a volume flow of 1.5 mL·min⁻¹. Precipitation started immediately. The reaction mixture was stirred for 1 h at room temperature and then allowed to stand for 24 h. The precipitate was collected by centrifuging the reaction mixture in 50 mL Falcon tubes (4000 rpm, 50 min) and washed 2 times with absolute ethanol (each 10 mL). The solid was dried overnight at 60°C yielding 284 mg of the product.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: catalyst stability · electrocatalysis · oxygen evolution reaction · polybenzoxazine · prussian blue analogue

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FULL PAPERS

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Polybenzoxazine-Derived N-doped Carbon as Matrix for Powder-Based Electro catalysts

Matrix reloaded: Powder oxygen evolution reaction (OER) catalysts are commonly immobilized on electrodes by means of embedding in a Nafion matrix, even in alkaline environment. We present an alternative approach using the unique properties of benzoxazine polymers. Polymerization and pyrolysis of a benzoxazine/prussian blue analogue powder composite leads to highly stable immobilized OER active electrocatalyst particles on the electrode surface.

A new matrix for powder-based electrocatalysts based on polybenzoxazine @ruhrunibochum @icn2nano @icrea community

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