Supporting Information (SI)

Double perovskite cobaltites integrated in a monolithic and noble metal-free photoelectrochemical device for efficient water splitting

Authors
Junjie Zhu, 1 Jónína B. Guðmundsdóttir, 2 Ragnar Strandbakke, 2 Kevin G. Both, 2 Thomas Aarholt, 3 Patricia A. Carvalho, 4 Magnus H. Sørby, 5 Ingvild J. T. Jensen, 4 Matylda N. Guzik, 6 Truls Norby, 2 Halvard Haug, 1 Athanasios Chatzitakis 2*

Affiliations
1 Institute for Energy Technology (IFE), Instituttveien 18, NO-2007 Kjeller, Norway
2 Centre for Materials Science and Nanotechnology, Department of Chemistry, University of Oslo, FERMiO, Gaustadalléen 21, NO-0349 Oslo, Norway
3 Department of Physics, University of Oslo, POB 1048 Blindern, NO-0316 Oslo, Norway
4 SINTEF Materials Physics, Forskningsveien 1, NO-0373 Oslo, Norway
5 Institutt for Energiteknikk (IFE), Department for Neutron Materials Characterization, POB 40, NO-2027 Kjeller, Norway
6 Department of Technology Systems, University of Oslo, POB 70, NO-2027 Kjeller, Norway

*Corresponding author: a.e.chatzitakis@smn.uio.no
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**Table S1:** Sum spectrum EDS compositions for the pre- and post-operation (48 h) BGLC587 catalyst.

| Element | Atomic fraction (%) | Atomic error (%) | TEM region |
|---------|---------------------|------------------|------------|
| **Pre-operation** | | | |
| Co | 52.89 | 5.46 | |
| Ba | 18.94 | 2.56 | |
| La | 11.6 | 1.57 | |
| Gd | 16.56 | 2.25 | |
| **Post-operation** | | | |
| Co | 57.96 | 6.15 | |
| Ba | 4.53 | 0.62 | |
| La | 21.65 | 2.98 | |
| Gd | 15.86 | 2.19 | |

**Table S2:** XPS compositions for pre-operation BGLC587 catalyst.

| XPS region | Atomic fraction (%) |
|------------|---------------------|
| Co 3p | 39 |
| Ba 4d | 13 |
| La 3d | 26 |
| Gd 4d | 22 |

**Table S3:** Relative XPS compositions based on Co 3p and Ba 4d for the pre- and post-operation BGLC587 catalyst, compared to results from Table S1.

| Atomic fraction (%) | XPS | EELS (from Table S1) |
|---------------------|-----|-----------------------|
|                     | Ba  | Co | Ba | Co |
| Pre-operation | 25  | 75 | 26 | 74 |
| Post-operation | 9   | 91 | 7  | 93 |

**Table S4:** Electrochemical parameters as extracted by the EIS measurements at potentials for 10 mA cm$^{-2}$. The parameters are coupled to the fitted data of Fig. 9b.

| Catalyst | $R_\text{s}$ (Ω) | $R_\text{d}$ (Ω) | $Y(0)_\text{d}$ (F) | n_d | $R_\text{int}$ (Ω) | $Y(0)_\text{int}$ (F) | n_int |
|----------|------------------|------------------|---------------------|-----|------------------|---------------------|------|
| BGLC587 | 7.1              | 19.7             | $2.48 \times 10^4$ | 0.83| 3.2              | $3.59 \times 10^4$ | 0.74 |
| BGLC82  | 7.2              | 23.4             | $1.94 \times 10^4$ | 0.83| 1.8              | $2.94 \times 10^4$ | 0.81 |
| BGLC37  | 8.0              | 24.0             | $3.95 \times 10^4$ | 0.82| 1.7              | $3.19 \times 10^4$ | 0.82 |
| IrO$_2$ | 7.1              | 41.0             | $0.47 \times 10^4$ | 0.87| 0.9              | $0.36 \times 10^4$ | 1.0  |

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Table S5: Electrochemical parameters as extracted by the EIS measurements at the onset potentials for 0.3 mA cm$^{-2}$. The parameters are coupled to the fitted data of Fig. 9c.

| Catalyst | $R_s$ (Ω) | $R_d$ (Ω) | $Y(0)_d$ (F) | $n_d$ | $R_{int}$ (Ω) | $Y(0)_{int}$ (F) | $n_{int}$ |
|----------|----------|----------|--------------|-------|--------------|-----------------|-----------|
| BGLC587 | 6.6      | 37.3     | 0.00287      | 0.52  | 563          | 3.3 $10^{-4}$   | 0.87      |
| BGLC82  | 6.8      | 32.5     | 0.0022       | 0.58  | 576          | 2.6 $10^{-4}$   | 0.88      |
| BGLC37  | 7.4      | 52.9     | 0.0069       | 0.47  | 717          | 4.8 $10^{-4}$   | 0.828     |
| IrO$_2$ | 6.4      | 3.9      | 0.0022       | 0.57  | 587          | 0.9 $10^{-4}$   | 0.91      |

The exponential value of the CPE$_d$ parameter is approx. 0.5, which clearly indicates this constant phase element has a Warburg behaviour, consistent with a purely diffusive process. Therefore, the C$_d$ parameter in the onset potentials was found by the interfacial CPE element alone. In fact, even if the effective capacitance is extracted, it is so large that it does not contribute to the total effective capacitance of the double layer.

Table S6: Electrochemical parameters as extracted by the EIS measurements at non-faradaic current regions. The parameters are coupled to the fitted data of Fig. 9d.

| Catalyst | $R_s$ (Ω) | $R_d$ (Ω) | $Y(0)_d$ (F) | $n_d$ | $R_{int}$ (Ω) | $Y(0)_{int}$ (F) | $n_{int}$ |
|----------|----------|----------|--------------|-------|--------------|-----------------|-----------|
| BGLC587 | 6.9      | 8.8      | 6.7 $10^{-4}$ | 0.74  | 79072        | 1.0 $10^{-4}$   | 0.78      |
| BGLC82  | 7.0      | 6.9      | 8.7 $10^{-4}$ | 0.73  | 59741        | 1.0 $10^{-4}$   | 0.79      |
| BGLC37  | 7.7      | 10       | 7.0 $10^{-4}$ | 0.71  | 120300       | 1.7 $10^{-4}$   | 0.77      |
| IrO$_2$ | 8.4      | -        | -             | -     | 58002        | 0.6 $10^{-4}$   | 0.87      |

Using this approach as $R_{ct} = R_d + R_{int}$ and after the CPEs are transformed into capacitances. The effective capacitance was determined by $C_i = \left[Y_R^{-1}R_i^{1-n_i}\right]^{1/n_i}$. Thereafter, $C_{dl} = \frac{1}{C_d + C_{int}}$. It should be noted that a simple Randles circuit was used in the case of IrO$_x$, where it provided much better fitting results.

Table S7: Comparison between capacitance values as obtained by cyclic voltammetry at the potential range 1.0-1.1 V vs. NHE, and capacitance values as extracted by EIS at two potential regions. $R_{ct}C_{dl}$ parameter

| Catalyst | Capacitance from CV scanning (µF) | Capacitance from the CV scanning potentials (µF) | Capacitance from EIS at onsets (µF) | Capacitance at 10 mA cm$^{-2}$ (OER region) (µF) | Relative decrease from non-faradaic to OER regions |
|----------|----------------------------------|-----------------------------------------------|-----------------------------------|--------------------------------------------------|-----------------------------------------------|
| BGLC587 | 35.8                             | 70                                            | 148                               | 24                                               | 66%                                           |
| BGLC82  | 36.3                             | 75                                            | 124                               | 28                                               | 63%                                           |
| BGLC37  | 60.7                             | 80                                            | 350                               | 42                                               | 47%                                           |
| IrO$_2$ | 15.1                             | 55                                            | 18                                | 17                                               | 69%                                           |
Table S8: Performances of previously reported state-of-the-art perovskite catalysts supported on glassy carbon disc electrode for the OER in alkaline media.

| Catalyst | Overpotential (mV) | Tafel (mV dec\(^{-1}\)) | Stability | Amount | Ref |
|----------|-------------------|--------------------------|-----------|--------|-----|
| SrFeO\(_3\) | 400 | 65-70 | 24, some degradation | - | 3 |
| Ba\(_{0.5}\)Sr\(_{0.5}\)Co\(_{0.8}\)Fe\(_{0.2}\)O\(_{3-\delta}\) | 500 | 129 | N/A | 0.64 mg cm\(^{-2}\) | 4 |
| (Pr\(_{0.5}\)Ba\(_{0.5}\))CoO\(_3-\delta\) | 350 (@ 5 mA cm\(^{-2}\)) | 60 | 2 h, some degradation | 0.25 mg cm\(^{-2}\) | 5 |
| PrBa\(_{0.5}\)Sr\(_{0.5}\)Co\(_{1.5}\)Fe\(_{0.5}\)O\(_{3+\delta}\) | 358 | 52 | 12 h, some degradation | 0.20 mg cm\(^{-2}\) | 1 |
| (PrBa\(_{0.85}\)Ca\(_{0.15}\))\(_{0.5}\)MnFe\(_{0.5}\)O\(_{3-\delta}\) | 410 | 86 | N/A | 0.28 mg cm\(^{-2}\) | 6 |
| RP-LaSr\(_3\)Co\(_{1.5}\)Fe\(_{1.5}\)O\(_{10-\delta}\)/La\(_{0.25}\)Sr\(_{0.75}\)Co\(_{0.5}\)Fe\(_{0.5}\)O\(_{3-\delta}\) | 324 | 58 | 2.7 h, 5% degradation | 0.25 mg cm\(^{-2}\) | 7 |
| Cs\(_{0.4}\)La\(_{0.8}\)Mn\(_{0.25}\)Co\(_{0.75}\)O\(_3\) | 400 | 101 | 12 h, 2% degradation | 0.45 mg cm\(^{-2}\) | 8 |
| BaGdCo\(_{1.8}\)Fe\(_{0.2}\)O\(_3\) | 477 | 60 | 48 h, 3% degradation | 4.00 mg cm\(^{-2}\) | 9 |
| CaCu\(_3\)Fe\(_4\)O\(_{12}\) | 380 | 51 | N/A | 0.25 mg cm\(^{-2}\) | 10 |
| RP-La\(_{0.5}\)Sr\(_{1.5}\)Ni\(_{1-x}\)Fe\(_{x}\)O\(_{4-\delta}\) | 360 | 44 | N/A | 15.3 μg cm\(^{-2}\) | 11 |
| SrCo\(_{0.5}\)Sr\(_{0.5}\)O\(_{3-\delta}\) | 417 | 66 | N/A | 0.255 mg cm\(^{-2}\) | 12 |
| Ba\(_{0.5}\)Gd\(_{0.8}\)La\(_{0.7}\)Co\(_{0.6}\)O\(_{6-\delta}\) | 470 | 78 | 48 h no degradation from \(j-t\) some degradation from STEM | 0.28 mg cm\(^{-2}\) | This work |
Table S9: EDS quantification of the NiMo layers from Fig. S19 obtained from the selected areas in each sample

| Sample                                    | Ni  | Mo  | Ti  | Ni:Mo |
|-------------------------------------------|-----|-----|-----|-------|
| Fresh NiMo layer (b from Fig. S14)       | 85.26 | 10.07 | 4.67 | 8.5   |
| Post operation NiMo layer (e from Fig. S14) | 41.58 | 3.93 | 54.33 | 10.6  |
Table S10: Configurations and performances of previously reported bias-free photoelectrochemical water electrolysis cells.

| Device configuration (Anode||Cathode) | Device configuration | Monolithic (M), Wired (W), Monolithic but Wired (MW) | All earth-abundant catalysts, Device size | Electrolyte, Illumination conditions | STH efficiency (%) | Stability, Notes | Work, Date |
|---------------------------------------|----------------------|------------------------------------------------------|-------------------------------------------|------------------------------------|-------------------|----------------|------------|
| BGLC587/FTO|| Si mini module/Ti-foil/NiMo, PV “buried” in tandem | Monolithic (M), Wired (W), Monolithic but Wired (MW) | Yes, Mini module: 4 cm² Electrodes: 4 cm² | 1 M NaOH, 1 Sun | 6.64 | 71 h, No degradation | This work |
| Pt||GaInP(p)/GaAS(n)/Pt | Wired (W) | No, - | 3 M H₂SO₄, 0.01 M Triton X, 11 Suns | 12.4 | 20 h, 20% drop in current | 13, 1998 |
| RuO₂||Al₀.₁₅Ga₀.₈₅As(pn)/Si(pn)/Pt | Wired (W) | No, Illuminated: 0.22 cm² Electrolysis: 10 cm² | 1 M HClO₄, 135 mW cm⁻² | 18.3 | 14 h | 14, 2000 |
| CoPi/BiVO₄/a-Si:H(pin)/nc-Si:H(pin)||Pt wire | Wired (W) | Partially, 0.283 cm² | Neutral pH 1 Sun | 5.2 | 1 h, Less than 5% drop in current | 15, 2014 |
| WO₃/FTO/pn-Si||np-Si/Ti/TiO₂/Pt | Monolithic (M), Wired (W) | Partially, 2 x 7.04 cm² | 1 M HClO₄, Nafion membrane, 2 Suns | 0.24 | 20 h, Stable H₂ generation | 16, 2015 |
| Pt||GaInP(pn)/InGaAs(pn)/Ge(pn)/Pt | Wired (W) | No, Illuminated: 1 cm² Electrolysis: 4 cm² | Neutral pH 10 Suns | 15 | 1 h, 3 solar cells and 2 PEM electrolyzers | 17, 2013 |
| FTO/a-Si(pin)/ a-Si(pin)/ a-Si(pin)||Pt | Partially, 1 cm² | 5 M KOH, 1 Sun | 6.2 | 31 days, Stable current density | 18, 2006 |
| Pt||Pt connected to CIGS 3 cells wired side by side | Monolithic (M), Wired (W) | No, - | 3 M H₂SO₄, 1 Sun | 10 | 27 h | 19, 2013 |
| NiFe||NiFe connected to 2 halide perovskites (Pb co/containing) | Wired (W) | Yes, Perovskite: 0.159 cm² Electrodes: 1 cm² | 1 M NaOH, 1 Sun | 12.3 | 2 h, Stable photocurrent | 20, 2014 |
| NiFeO₅/BiVO₄||CIGS/CdS/Pt | Wired (W) | Partially, Buffer pH 6.8, 3.7 | 10 min | 21, | | |


| System                                      | M | 0.1 cm² | 1 Sun | 20% degradation | Year |
|---------------------------------------------|---|---------|-------|-----------------|------|
| Ni/TiO₂/GaInP₂/GaAs/NiMo                    | M | Yes, 1 cm² | 1 M KOH, 1 Sun | 8.6 | 4 h, 10% degradation | 2018 |
| IrO₂||FTO/Al/CuSCN/Cu₂O/Ga₂O₃/TiO₂/RuOₓ wired to a Pb-based perovskite | W | No, - | Buffer pH 5, 1 Sun | 4.55 | 10 h, 9% degradation | 2015 |
| NiFeO₂/H, Mo:BiVO₄||FTO/Al/Sb₂Se₃/CdS/TiO₂/Pt | W | Partially, 0.32 cm² | Buffer pH 7, 1 Sun | 1.5 | 10 h, 25% | 2020 |
| NiFeO₂/Mo:BiVO₄||Glass/Al/Cu₂O/Ga₂O₃/TiO₂/RuOₓ | W | Partially, - | Buffer pH 9, 1 Sun | 3 | 12h | 2018 |
| CoOₓ-NiOₓ/BiVO₄||Ti-foil/CIGS/ZnSe/Pt series connected anode and cathode | M | Partially, Photoanode: 0.88 cm² Photocathode: 0.33 cm² | Buffer pH 9.5, 1 Sun | 1.1 | 20 h, 28% degradation | 2017 |
| FeNiOOH/Fe₂TiO₅/Fe₂O₅/ITO||a-Si:H/µc-Si:H/ µc-Si:H/Ni foam | M | Yes, 1 cm² | NaOH, 3 Suns | 1.75 | >24 h | 2019 |
| IrO₂(DSA)||ITO/ETM/Perovskite/MoO₃/HTM/IZO/Au-pnn-Si/Ti/Pt | W | No, 0.3 cm² | 1 M H₂SO₄, 1 Sun | 17.4 | 0.11 h | 2020 |
Supplementary Note 1

XPS analysis of the pre- and post-operation BGLC587

Figure S7 shows XPS spectra for BGLC587 pre- and post-operation. The pre-operation survey spectrum shows the presence of Gd, La, Co and Ba together with C and O, while the post-operation survey is dominated by Na, F, O and C (Figure S7a). The La 3d and O 1s spectra pre-operation (Figure S7b and c) are similar to spectra reported for the LaCoO$_3$ phase. The I$_O$ component of O 1s can unambiguously be assigned to perovskite lattice oxygen, e.g., LaCoO$_3$, while the II$_O$ component can be assigned to other oxide phases, under-coordinated oxygen and/or adsorbed O$_2$ or OH species. The Gd 4d spectrum (Figure S7e), which contains multiple components due to final state interactions with the 4f$^7$ valence band electrons, was fitted by the procedure used by Thiede et al. Although only one set of Gd components was necessary to obtain a good fit, the presence of more than one Gd phase cannot be completely ruled out.

The Ba 4d spectrum Figure S7f shows clear indications of two different Ba 4d states. This was also seen in the Ba 3d spectrum (Figure S7d), where the two components labelled I$_{Ba}$ and II$_{Ba}$ are consistent with previous reports for similar materials. The fact that the I$_{Ba}$ and II$_{Ba}$ components in the Ba 3d$_{5/2}$ region are repeated with 2/3 of the peak area in the Ba 3d$_{3/2}$ region verifies the identification as Ba 3d$_{5/2}$ components.

The Co 2p spectrum is complicated, as the main peak is accompanied by several plasmon loss peaks, which vary in separation and intensity depending on the chemical state of Co. To obtain a good fit of the spectrum in Figure S7d, the two components I$_{Co}$ and II$_{Co}$ had to be added. These components are repeated with 1/2 of the peak area in the Co 2p$_{1/2}$ region, demonstrating the presence of both Ba and Co in the sample. Due to the overlap between Ba 3d and Co 2p, however, a detailed description of the Co phase(s) was not possible. The Co 3p region is less described in the literature, but a doublet splitting of 1.1 eV is assumed. The Co 3p spectrum in Figure S7g was fitted with 3p doublet components at a fixed distance of 1.1 eV. In addition, a second doublet set is added to the high BE region. As for Co 2p, it is unclear whether these secondary components are an indication of Co in a different state, or if it is just part of the satellite structure of the main component.

A complete determination of the composition of the post-operation powder based on the XPS spectra was challenging due to low sample amounts. However, certain observations can be made:

Post-operation, the Co 2p/Ba 3d region is dominated by a component that is repeated with a 2:1 ratio between the 3/2 and 1/2 level, indicative of Co and thus suggesting a loss of Ba. The Co 2p component corresponds with the position of the weakest Co component in the pristine powder (II$_{Co}$). The component labelled as I$_{Ba}$ in pre-operation is still present, repeating with a 3:2 ratio between the 5/2 and 3/2 levels. In the Ba 4d spectrum, the I$_{Ba}$ components were also present, while the II$_{Ba}$ region appeared broader, possibly indicating a mix of several Ba phases. To estimate the relative content of Ba before and after cycling, quantification was done based on two regions not affected by peak overlap: Ba 4d and Co 3d, which confirms that the Ba content decreases relative to Co (Table S3). For the post-operation powder the La 3d and Gd 4d peaks overlapped with F KLL and Si 2s, which means that a reliable quantification of the relative content of Co, Ba, Gd and La could not be obtained.

The Gd 4d peak is broadened in a way that can be fitted by assuming Gd in two different chemical states, with identical multiplet splitting. Co 3p is also broadened, and can be fitted by increasing the intensity of the weak peak found in the pristine powder. This could be consistent with the relative change in peak intensity observed for Co 2p, but a more extensive XPS investigation, including pure reference samples of the different candidate compositions, is needed to fully understand the chemical decomposition of the BGLC system upon cycling.
Supplementary Note 2

Performance of the PV-PEC with IrO$_2$ as the anode electrode

The STH begins at 8.4% (Figure S25), which is lower than the expected efficiency of 9.3% according to the fitted $j$-$V$ curve of the mini module and the $j$-$E$ curves of IrO$_2$ and NiMo (Figure S26a). This discrepancy is again attributed to ohmic losses in the electrolyte, but possibly due to the series connected potentiostat. In this case the evaporation of the electrolyte reduces the photocurrent density, but unlike the ea-PV-PEC, the efficiency of the device was constantly decreasing. After 24 h of continuous operation the efficiency was reduced to approx. 7.5% (Figure S25). The loss is mainly attributed to dissolution of IrO$_2$ as preliminary monolithic devices retrieved their efficiency after IrO$_2$ is electrodeposited again (see Figure S27). We took this device for outdoor operation as well and as expected by the laboratory performance, as well as the $j$-$E$ curves of the HER and OER catalysts, an STH fluctuating around 7% was achieved (Figure S28). It can be seen that the sunlight intensity was significantly fluctuating due to passing clouds during the first hour of operation. It is also interesting to notice that under light intensities of around 0.4 and 0.2 Suns, the STH was well above 8%, reaching even 9%. Fittings of the $j$-$V$ curves of the mini-PV module under different light intensities (0.2 to 0.8 Suns) to the $j$-$E$ curves of IrO$_2$ and NiMo further confirm the performance range of the PV-PEC device (Figure S26b-e). The discrepancies observed may be attributed to different performance of the solar cells under natural sunlight and laboratory emulation. Finally, the IrO$_2$-coated FTO shows over 75% of the transmittance in the visible region, where the EQE has an excellent response (Figure S29).
Supplementary Note 3

Synthesis of BGLC-based double perovskites by sol-gel citrate method

Precursors

- Barium(II)carbonate (Alfa Cesar 99.8%) – 197.35 g mol\(^{-1}\)
- Gd(III)nitrate hexahydrate (Sigma-Aldrich 99.9%) – 451.36 g mol\(^{-1}\)
- La(III)nitrate hexahydrate (Sigma-Aldrich 99.99%) – 433.01 g mol\(^{-1}\)
- Co(II)nitrate hexahydrate (Sigma-Aldrich ≥ 98%) – 291.03 g mol\(^{-1}\)
- Citric acid monohydrate, (Sigma-Aldrich ≥ 99.0%) – 210.14 g mol\(^{-1}\)
- Ammonia 28% (AnalaR NORMAPUR®)

Citric acid (CA) was dissolved in water in an 1 L beaker on a hotplate using a 1:1 ratio of CA and moles of cations. A stoichiometric amount of BaCO\(_3\) was slowly added until fully dissolution. Subsequently, the nitrates were added and dissolved. The pH was adjusted with concentrated ammonia until the solution became clear – pH below 6-7 will make the solution bleak and precipitate.

The water was evaporated on the hotplate at 150 °C under continuous magnetic stirring until a very viscous gel was formed. At this point the beaker was covered with a watch glass and put in a ventilated heating cabinet at 250 °C to obtain a more homogeneous heat distribution. The beaker was left in the heating cabinet for 2 hours for the combustion reaction to complete.

The xerogel/ash obtained from the combustion was crushed thoroughly in a mortar inside a fume hood. The powder was put in a crucible and covered with perforated heat resistant alumina foil to prevent contamination of furnace. The powder was fired at 450 °C for 2 h with a ramp rate of 300 °C/h to burn off most of the organic compounds. When done, the powder was crushed thoroughly a second time in a mortar and calcined at of 1100 °C for 5 h with a ramp rate of 250 °C/h.
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