Supporting Information

Enhanced water oxidation performances of birnessite and magnetic birnessite nanocomposites by transition metal ion doping

Gökhan Elmacı¹*, Gökhan Özgenç², Philipp Kurz³*, Birgül Karan²

¹Department of Chemistry, Faculty of Science, Adıyaman University, 02040 Adıyaman, Turkey

²Department of Chemistry, Faculty of Science, Hacettepe University, 06800 Ankara, Turkey

Experimental Section

Preparation of the Paste

The paste was prepared using the method of Lee et al.¹ by thoroughly mixing 100mg of the catalyst with 30mg of polymer binder (PEO), 0.1mL of acetyl acetone, 0.1mL of surfactant (Triton© X-100) and 1mL of deionized water.

Preparation of the Electrodes

MnOx@MnFe₂O₄ electrodes were prepared using the drop-coating method similar to that reported by Lee et al. ¹. 1.1 μ L of a homogeneous suspension of paste was drop-coated onto clean 1 cm² FTO to cover the electrode surface. The coated electrode was then dried at 60°C in oven for 30 min and then sintered at 450°C for 60 min.

Tafel plots

Tafel plots were determined using staircase-type chronoamperometry program. The potential of the working electrode was increased with 100 mV from 0.9V to 1.3V step by step and then back again to 0.9V in the same way. The applied potential was kept constant at each step for 300 s.

Evaluation of the chemical WOC performances of the catalysts with Gas Chromatography method

The method used refers to a previously developed procedure ². Precisely weighed catalyst samples (about 5 mg of each) and 685 mg (1.25 mmol) of $(NH_4)_2Ce(NO_3)_6$, were filled into 20 mL septum vials. After addition of 5 mL of air-saturated water, the vials were capped using gas-tight septa and sonicated for 20 s. The reaction containers were now kept at 40°C in a water bath and headspace gas samples (100 µL each) were taken from the vials at 10 min intervals using a gas-tight syringe (Hamilton). The gas

samples were injected into a PerkinElmer Clarus 480 gas chromatograph equipped with a 12 ft. x 1/8 in. molecular sieve column (5 Å, Restek) and a thermal conductivity detector. Six injections at 10 min intervals were carried out.

The amount of evolved oxygen was then calculated for each headspace extraction from the detected $O_2:N_2$ signal ratios. To do so, the amount of oxygen from air (corresponding to the detected nitrogen peak) was calculated and subtracted, leaving the excess O_2 generated by the water-oxidation reaction. Further details on measurement methods and additional details are included in the ref³.



Characterization Section:

Fig. S1 XRD patterns of birnessite (KB), CoB and NiB



Fig. S2 FT-IR spectra of KB, TMB and TMB@MF catalysts.



Fig. S3 TGA curves of KB, CoB and NiB samples.



Fig. S4 TGA curves of TMB@MF samples.



Fig. S5 SEM image of NiB powder.



Fig. S6 SEM image of CoB powder.



Fig. S7 SEM images of ZnB@MF powder



Fig. S8 SEM image of CaB@MF powder



Fig. S9 Magnetization curve of CoB@MF (a), SEM image of CoB@MF powder (b).



Fig. S10 Cross section SEM images of CoB@MF coated electrode at four different magnifications before EC.



Fig. S11 Cyclic voltammetry (CV) curves of CuB@MF,CrB@MF, ZnB@MF samples.



Fig. S12 Tafel measurements for TMB@MF, bare and doped birnessite electrodes of types.



Fig. S13 SEM image of CoB@MF on FTO substrate after 1h EC at a constant potential of +1.73V vs RHE in pH7 electrolyte.



Fig. S14 SEM image of ZnB@MF on FTO substrate after 1h EC at a constant potential of +1.73V vs RHE in pH7 electrolyte.



Fig. S15 Oxygen evolution curves for reactions of TMB, TMB@MF with Ce⁴⁺. The amount of evolved oxygen was normalized per gram of catalyst. Reaction conditions: aqueous suspensions with 1 mg of oxide mL⁻¹; $[Ce^{4+}] = 250$ mM; T = 40 °C. The estimated experimental error of the entire measurement procedure is ~±10%.

Metal oxide anode	Overpotential	Tafel slope	pН	Reference
	η: [mV]	[mV decade ⁻¹]		
	(For 1 mAcm ⁻²)			
ZnB@MF	680	253	7	this work
CrB@MF	650	200	7	this work
CuB@MF	620	158	7	this work
NiB@MF	495	87	7	this work
CoB@MF	490	94	7	this work
СоВ	475	80	7	this work
NiB	460	76	7	this work
KB	480	92	7	this work
1D MnO ₂ nanowires	460	105	7	4
MnO ₂ @mpg-C ₃ N ₄	420	90	7	4
MnO _x	590	60-80	7	5
MnO _x	600	120	7	6
MnO _x /C	450	150	7	7
CaMnxOy	550	_a	7	8
a-Mn ₂ O ₃	440	_a	7	9

Table S1. Comparison of overpotentials and tafel slopes between TMB and TMB@MF metal

 oxide anodes and literature data

^a; data not available

References

- 1. S. Y. Lee, D. Gonzalez-Flores, J. Ohms, T. Trost, H. Dau, I. Zaharieva and P. Kurz, *ChemSusChem*, 2014, 7, 3442-3451.
- 2. G. Elmacı, C. E. Frey, P. Kurz and B. Zümreoğlu-Karan, J. Mater. Chem. A , 2016, 4, 8812-8821.
- 3. C. E. Frey and P. Kurz, *Chem. Eur. J.*, 2015, **21**, 14958-14968.
- 4. G. Elmacı, A. S. Ertürk, M. Sevim and Ö. Metin, *Int. J. Hydrogen Energy*, 2019, **44**, 17995-18006.
- 5. I. Zaharieva, P. Chernev, M. Risch, K. Klingan, M. Kohlhoff, A. Fischer and H. Dau, Energy Environ. Sci., 2012, **5**, 7081-7089.
- 6. A. Indra, P. W. Menezes, I. Zaharieva, E. Baktash, J. Pfrommer, M. Schwarze, H. Dau and M. Driess, *Angew. Chem.*, 2013, **125**, 13447-13451.
- 7. J. Melder, W. L. Kwong, D. Shevela, J. Messinger and P. Kurz, *ChemSusChem*, 2017, **10**, 4491-4502.
- 8. H. Simchi, K. A. Cooley, J. Ohms, L. Huang, P. Kurz and S. E. Mohney, *Inorg chem*, 2017, **57**, 785-792.
- 9. Z. N. Zahran, E. A. Mohamed, T. Ohta and Y. Naruta, *ChemCatChem*, 2016, **8**, 532-535.