Reviewer 4

Subject: Submission of the revised version of sustainability-2439014

Title: *Recent Trends in transition metal phosphides TMPs-based seawater electrolysis for hydrogen evolution*

Dear Reviewer,

Thank you very much for the time and effort you spend to evaluate this manuscript. Your expert opinion was very objective and helped us to improve the manuscript. We have thoroughly revised the manuscript and tried our level best to address all the recommendations in the revised version.

Below is the point-by-point response to your comments with detailed reference to the main file/manuscript. Please find hereafter our answers (**in red**).

We once again appreciate and are thankful to you for these useful suggestions.

Sincerely,

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Response to reviewer's comments

Hydrogen is possible the most promising fuel of the future. Hydrogen could be obtained from water electrolysis, which is a known, but still crucial subject, because of the technology. Because seawater is the largest resource of water on earth, and a good electrolyte, it becomes one of the most interesting subjects of study. The competitive chloride evolution, anodic oxygen evolution, and cathodic hydrogen evolution push the research in area of catalytic electrodes. This paper is a review on electrocatalytic electrodes for seawater electrolysis and focus on the main subject, the chemical nature (type) of electrode, namely the phosphides (TMPs). The authors discussed about the structure of phosphides (TMPs) and made a classification based on their performance. Seawater electrolysis reaction were explained in relation with seawater chemical composition with or without other additives as NaOH and the emergent technologies which could use this, are presented. Characteristics of the catalytic electrodes, as element doping, Structure of bimetal

phosphide phases, Compounds of TMPs were discussed, with examples of results obtained different investigations methods as: SEM, TEM, HRTEM, SEAD, polarization and chronopotentiometric curves. The conclusions are very well presented. This paper could be a good instrument for researchers who wants to who want to deepen the research and knowledge in phosphides (TMPs) electrodes for application of seawater electrolysis. I do have 2 observations, one major:

R. Thank you for your encouraging remarks. We have comprehensively revised the manuscript and updated it with some latest findings. We have also included some more details to present a summarized picture of the subject area.

pointing this out. We agree with this comment. Therefore, we have added more details providing the necessary explanation after revision exploring extra data illustrated in Table 2 and Table 7.

Table.2 A brief review of the latest and most recent advanced methods for synthesizing transition metal phosphide-based catalysts.

Method of TMPs synthesis	Advantages	Disadvantages	References
Metal Organic Framework (MOF) derived methods	Control morphology High surface area Composition control Doped carbon layer formation	Two steps with lab-scale synthesis methods	[38]
Wet chemical methods	Monodispersed particles Composition control Single-step methods	Difficult to control the reaction condition at high volatile solvent required	
Bulk conversion	Large scale-synthesis Composition control	Bulk microstructure Poisonous byproducts gas formation	
Phytic acid derived methods	Large scale synthesis Composition control Doped carbon layer formation	Microstructure optimization	

Table.7 Main highlight of the HER performance of the electrocatalysts that have been reported.

Catalyst	Tafel Slope (mV dec^{-1})	Overpotential @10mA cm^{-2} (mV)	Electrolytes	Electrodes	References
VS2@V2C	37	148 (20 mA cm^{-2})	seawater (PH = 0)	GCE	[127]
h-MoN@ BNCNT	128	-	seawater	GCE	[128]
NiCoP/NF	-	287	Seawater artificial	NF	[96]
PSS-PPy/ Ni-Co-P	-	144	Seawater	CF	[129]
C-Co2P	-	30	1 M KOH,	GCE	[130]
C-Co2P	-	192 (1000 mA cm^{-2})	1 M KOH, 0.5 M NaCl, 41.2 × 10^{-3} M $MgCl_2$ and 12.5 × 10^{-3} M CaCl	GCE	[130]
Ru-CoOx	-	630 (100 mA cm^{-2})	1 M KOH + Seawater	NF	[131]
Mo5N6	-	94	1.0 M KOH	GCE	[31]
Ni-SN@C	-	28	1 M KOH	GCE	[132]
Ni-SN@C	-	23	1 M KOH	GCE	[132]
NiCoN|NixP| NiCoN	-	165	Seawater	NF	[81]
Ni5P4/ $Ni_{2+\delta}O_{\delta}(OH)_{2-\delta}$	-	144	Seawater	CC	[40]
Pt-Ru-Cr	45.7	256	Seawater	Ti mesh	[133]
Pt	45.8	285	Seawater	Ti mesh	[133]
Pt-Ru-Fe	46	248	Seawater	Ti mesh	[133]
Pt-Ru-Co	44.8	222	Seawater	Ti mesh	[133]
Pt-Ru-Ni	44.5	206	Seawater	Ti mesh	[133]

Pt-Ru-Mo	44.0	196	Seawater	Ti mesh	[133]
Pt/C	59	-	Seawater	GCE	[134]
PtNi5	119	-	Seawater	GCE	[134]
Pt-Ru-$Cr_{0.1}$	-	283.8	Seawater	Ti mesh	[135]
Pt-Ru-$Fe_{0.1}$	-	275.2	Seawater	Ti mesh	[135]
Pt-Ru-$Co_{0.1}$	-	266.5	Seawater	Ti mesh	[135]
Pt-Ru-$Ni_{0.1}$	-	263.3	Seawater	Ti mesh	[135]
Pt-Ru-$Mo_{0.1}$	-	254.6	Seawater	Ti mesh	[135]
Ti/NiPt	111	-	Seawater	Ti foil	[136]
Ti/NiAu	170	-	Seawater	Ti foil	[136]
Ru/Co	107	-	Sweater	Ti foil	[69]
Ru/Mo_1	137	-	Seawater	Ti foil	[69]
0.5Rh-G1000	-	340	Seawater	GCE	[137]
Pt@mh-3D MXene	-	280	Seawater	GCE	[138]

Q. Correct the references, everywhere is needed, with the standard abbreviation of the journal's names. Most of the references are not written correctly: in the instructions for authors, it is written that the name of the Journal should be abbreviated. Yes, but that means a standard abbreviation, so anyone reading the reference could identify the journal.

For example, reference no.2:

„Tian, X.; Lu, X. F.; Xia, B. Y.; Lou, X. W. D. J. J., Advanced electrocatalysts for the oxygen reduction reaction in energy 448 conversion technologies. 2020, 4, (1), 45-68."

Which is the Journal?!?! Searching on google, I found the journal „Joule" , In this case, the name is short, you can't write an abbreviation!

Another example, reference 3:

Yang, Y.; Yu, Y.; Li, J.; Chen, Q.; Du, Y.; Rao, P.; Li, R.; Jia, C.; Kang, Z.; Deng, P. J. N.-M. L., Engineering ruthenium-based electrocatalysts for effective hydrogen evolution reaction. 2021, 13, 1-20. Which is the Journal?!?!

Search for the article, find in this case: https://pubmed.ncbi.nlm.nih.gov/34302536/

If you look on the right side , at „Cite" – you will find the abbreviated name Nanomicro Lett

-you may go on journal sites, where you can find „cite" or „cite as" and you will find the abbreviated name of journal.

Hints: If you search on google, you could find the standard abbreviations for any journal.

R. thank you very much for your valuable advice. We have revised the complete bibliography and corrected all the mistakes, especially the abbreviation of the journal name.

The correct reference 2

Tian, X.; Lu, X. F.; Xia, B. Y.; Lou, X. W. D. Advanced electrocatalysts for the oxygen reduction reaction in energy conversion technologies. Joule, **2020,** 4, (1), 45-68.

Ref. 3

Yang, Y.; Yu, Y.; Li, J.; Chen, Q.; Du, Y.; Rao, P.; Li, R.; Jia, C.; Kang, Z.; Deng, P. Engineering ruthenium-based electrocatalysts for effective hydrogen evolution reaction. Nanomicro Lett, **2021,** 13, 1-20.

Q. It is a review, and the number of references could be enough, but there are also some recent reviews (2022, 2023) on seawater electrolysis from mdpi which might be taken into consideration. Please add a statement, where you consider (introduction or conclusion), a comparison or underline what it is the original point of view of this paper comparing with the other reviews.

R. Thank you very much for your insightful comment. We have addressed this weakness properly in the revised version. Some newly published reviews have been added with comparative analysis.

We have also illuminated the comparative strength of this manuscript. The principal change made in this respect is added on page 5 lines 100 to 117 as;

Some recently published reviews have summarized the progress in water splitting and H_2 evolution reactions. The literature summarized by Shah et al.,[32] discussed the structure, mechanism, and potential of Transition Metal Tellurides (TMTs) and Phosphides (TMPs) for HER. This article comprehensively reviewed the progress till 2022 with emphasis on TMTs and HERs. Ding et al [33] summarized the potential of Asymmetrically Coordinated Atoms for HERs. Fe, Ni, and Co are excellent materials with low cost, availability, and improved water-splitting efficiency. The work summarized by Li et al., [34] focused on the fabrication advances in layered double hydroxides (LDH) two-dimensional (2D) materials using these economical materials. Experts are emphasizing the in-situ evaluation of various exciting parameters and the impact of the reaction environment on water splitting efficiency. The incorporation of simulation techniques with the experimental investigation can help to improve the process efficiency and H_2 yield. Although some reviews have been published focusing the water splitting and HERs, still there is no critical discussion about the application of TMPs in seawater splitting. Therefore, this review was designed to give a quick overview of current developments regarding seawater electrolysis for H_2 production and the progress of HER electrocatalysts based on transition metal phosphide (TMPs).