Developing Abundant Metals-Based Anion-tailored Catalysts for Energy-efficient Hydrogen Generation via Electrochemical Water Splitting

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1. 研究課題 (Research Subject): Nanomaterials for Energy-efficient H_2 Production:

Hydrogen is expected to be the future fuel amidst the ongoing rapid depletion of fossil fuels and the negative environmental impacts thereof. However, a sustainable way of producing hydrogen depend largely on the electrolysis of water. Electrolysis of water is an energy intensive process that must be catalyzed with catalysts of appropriate structure and property to ensure energy efficiency while also ensuring that they are abundant. Here, we propose to develop non-precious metals-based anion-tailored chalcogenide and phosphide catalysts supported on respective metal foils for both water reduction and oxidation electrocatalysis. This is to be achieved by our in-house methodologies (chemical anion pre-oxidation of metal chalcogenides and phosphides and electrochemical hydroxylation with concurrent anion oxidation and surface amorphization). Prospective metals to be used include Ni, Co, Fe, Mo,

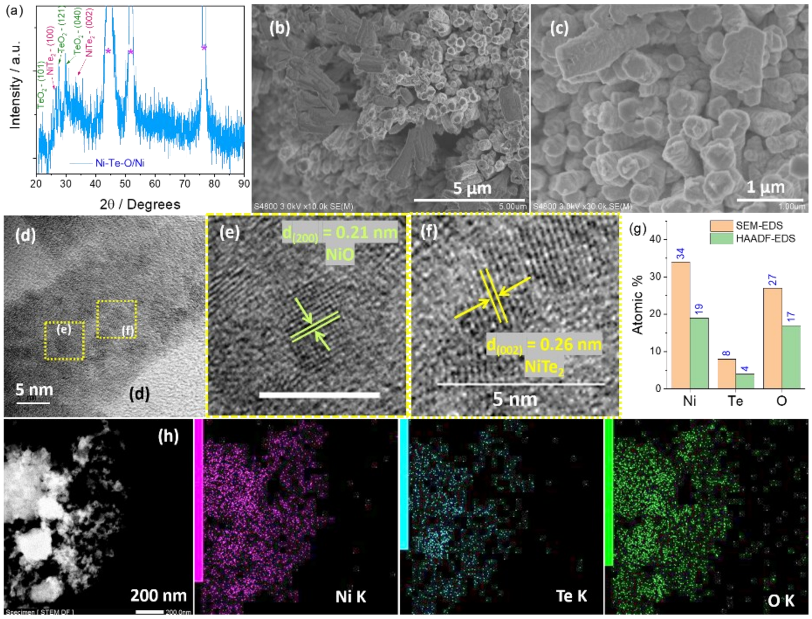

Figure 1: Material characterization results of aged $NiTe_2$/Ni. (a) XRD pattern, (b-c) SEM images, (d-f) TEM images, (g) Atomic ratio as per SEM-EDS and STEM-EDS results, (h) EDS-color maps, respectively.

Cu and W and the catalysts of interest will be sulphide, selenide, telluride, and phosphide of all the above said metal. With this, we intend to lower the potentials of water oxidation and reduction reactions closer to 1.48 and 0.00 V vs. RHE, respectively.

2. **主な研究成果 (Main Research Results):** As proposed above, we began with Ni as the substrate metal of choice to make NiS and $NiTe_2$ precatalysts on Ni foam substrates via hydrothermal chalcogenization. Then the pre-oxidation of anion was performed differently with these precatalysts. $NiTe_2$ grown on Ni foam was let to undergo anion oxidation by letting it age in air that resulted in nanocrystalline heterostructures comprising of NiO-$NiTe_2$, $NiTe_2$-$NiTeO_3$, and $NiTe_2$-TeO_2 which imparted numerous vacancies and defects in nanoscale that eventually led to highly enhanced OER, HER, and MOR activities in alkaline medium. As a result of combining the MOR half-cell with that HER half-cell, the same catalyst after aging in air witnessed a reduction of 260 mV in overvoltage for a current density of 100 mA cm^{-2} when compared to the conventional water electrolyzer built using the same catalyst (Figure 1a-h and Figure 2a-d). Inspired by the results that oxygen

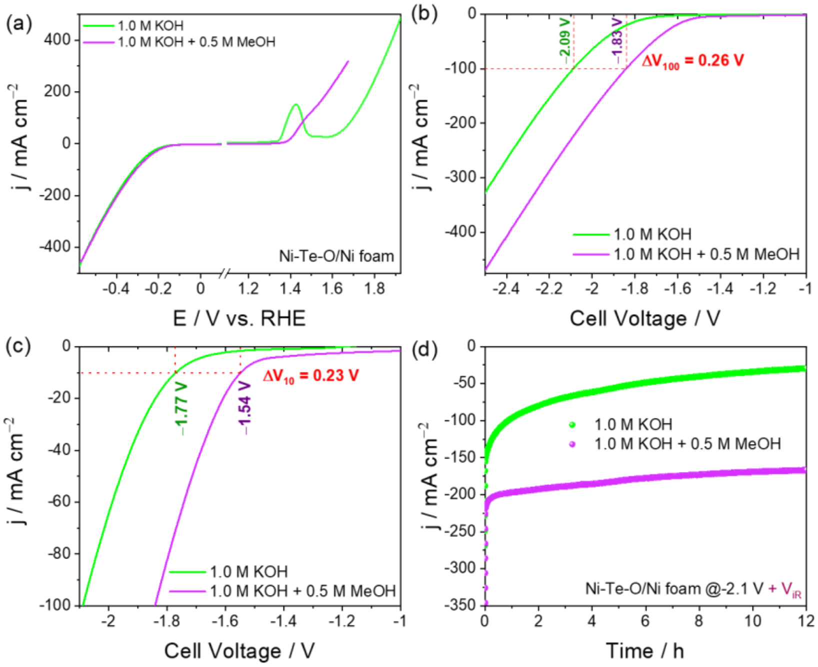

Figure 3: (a) LSVs showing HER performance of NiTe2/Ni after aging in the presence of absence of MeOH. (b-c) Full-cell polarization curves showing the reduction in cell voltage in the presence of MeOH. (d) CP responses of the same with and with MeoH.

impregnation could bring out via anodic CV cycling in KOH that resulted in the formation of NiS-OH/Ni foam, we were intrigued to find out what happens when oxygen impregnation is performed prior to sulphidation. To do that, we performed hydrothermal activation of Ni foam taking 0.1 M NaCl in 1.0 M KOH and used the same to treat the Ni foam substrates that resulted in the formation of $Ni(OH)_2$. Then the same was sulphidized using the conventional hydrothermal sulphidation. As a result, we were able to get a nickel hydroxysulphide superstructures on Ni foam (Ni-O-S/Ni) that performed exceptionally well towards both OER and HER.

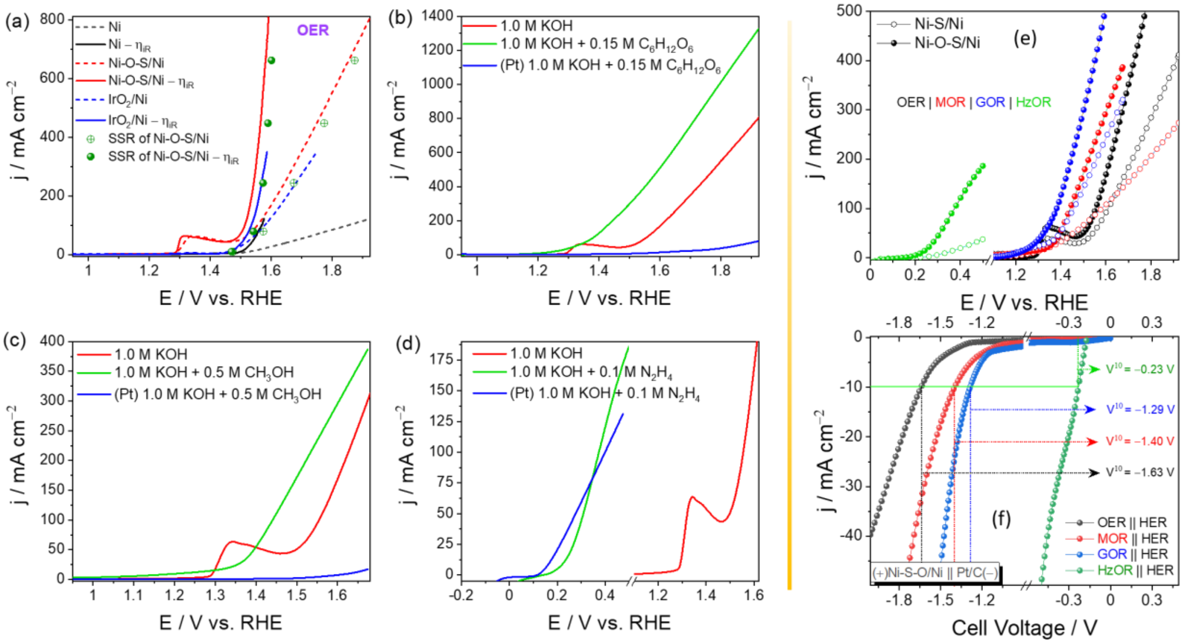

Figure 3: (a-d) Polarization curves of Ni-O-S/Ni showing the OER, GOR, MOR, and HzOR activities, respectively. (e) Polarization curves of Ni-O-S/Ni and Ni-S/Ni for all the studied small molecule oxidations. (f) Reduction in cell voltage witnessed with all these small molecule oxidations when coupled with a Pt electrode in a full-cell.

To our surprise, when screened for the oxidation of other small molecules such as hydrazine (HzOR), methanol (MOR), and glucose (GOR), we found that it performed equally well to that of the many state-of-the-art catalysts made from precious metals. When OER is replaced by the oxidation of these small molecules, extreme reduction in the cell voltages for H_2 production were witnessed (Figure 3a-f). The first catalyst is now communicated for publication ACS Applied Materials and Interfaces and the manuscript for Ni-O-S/Ni is under preparation. In addition to these two directly related works, we have carried out several fundamental electroanalytical research works concerning the accuracy of screening methods, electrochemical anodization of metal substrates, and wrote several reviews and perspectives in the previous year from April 2021 to March 2022. Please refer to the Research Achievements Section for details.

3. **共同研究者（Collaborators）**：

Prof. Sungchul Yi (Hanyang University, Seoul, South Korea)

Prof. Sudhagar Pitchaimuthu (Heriot-Watt University, UK)

Prof. Mathias Driess (TU Berlin, Germany)

Dr. Prashanth W. Menezes (Helmholtz-Zentrum, Berlin, Germany)

4. **研究業績（Research Achievements）**： The previous academic year was very successful for us in terms of academic publications as we were able to publish four original research works and six reviews and perspectives that are directly related to the development of the proposed projects which are listed below.

4.1. **学術論文(Academic Papers)**：

4.1.1. **S. Anantharaj***, S. Kundu, and S. Noda, Worrisome exaggeration of activity of electrocatalysts destined for steady-state water electrolysis by polarization curves from transient techniques. *Journal of The Electrochemical Society* 2022, 169, 014508. (I.F: 4.316, Ranking Q1). Know more about the media mentions of this work here.

4.1.2. **S. Anantharaj***, T. Nagamatsu, S. Yamaoka, S. Noda*, Efficient methanol electrooxidation catalyzed by potentiostatically grown Cu-O/OH(Ni) nanowires: Role of inherent Ni impurity. *ACS Applied Energy Materials* 2021, 5, 419-429. (I.F: 6.024, Ranking Q2)

4.1.3. **S. Anantharaj***, H. Sugime, S. Noda*, Why Shouldn't Double-Layer Capacitance (C_{dl}) Be Always Trusted to Justify Faradaic Electrocatalytic Activity Differences? *Journal of Electroanalytical Chemistry* 2021, 115842. (I.F: 4.464, Ranking Q1)

4.1.4. **S. Anantharaj***, Suguru Noda*, Mathiass Driess, Prashanth. W. Menezes*, The Pitfalls of Using Potentiodynamic Polarization Curves for Tafel Analysis in Electrocatalytic Water Splitting. *ACS Energy Letters*. 2021, 6, 1607-1611. (I.F: 23.101, Ranking Q1)

4.2. 総説・著書（Reviews and Book）

4.2.1. **S. Anantharaj*** and S. Noda, iR drop compensation in electrocatalysis: everything one needs to know!, *Journal of Materials Chemistry A*, 2022, 10, 9348-9354. (I.F: 12.732, Ranking Q1)

4.2.2. **S. Anantharaj*** and S. Noda, Layered 2D PtX_2 (X= S, Se, Te) for Electrocatalytic HER in Comparison with Mo/WX_2 and Pt/C: Are We Missing the Bigger Picture?, *Energy and Environmental Science*, 2022, 15, 1641-1478. (I.F: 38.532, Ranking Q1)

4.2.3. **S. Anantharaj***, Hydrogen Evolution Reaction on Pt and Ru in Alkali with Volmer-step Promotors and Electronic Structure Modulators, *Current Opinion in Electrochemistry*, 2022, 100961. (I.F: 7.271, Ranking Q1) *Invited Article*

4.2.4. P. E. Karthik*, V. R. Jothi, P. Sudhagar*, S. Yi*, and **S. Anantharaj***, Alternating Techniques for a Better Understanding of Photoelectrocatalysts. *ACS Catalysis* 2021, 11, 12763-12776. (I.F: 13.084, Ranking Q1)

4.2.5. **S. Anantharaj***, P. E. Karthik, and Suguru Noda, The Significances of Properly

Reporting Turnover Frequency in Electrocatalysis Research. *Angewandte Chemie Int. Ed.* 2021, 60, 23051-23067. (I.F: 15.336, Ranking Q1)

4.2.6. K. R. Davies, Y. Cherif, G. P. Pazhani, **S. Anantharaj**, H. Azzi, C. Terashima, A. Fujishima, and P. Sudhagar*, The Upsurge of Photocatalysts in Antibiotic Micropollutants Treatment: Materials Design, Recovery, Toxicity and Bioanalysis. *Journal of Photochemistry & Photobiology, C: Photochemistry Reviews.* 2021, 48, 100437. (I.F: 12.927, Ranking Q1)

4.3. 招待講演（Invited Lectures）:

4.3.1. Invited talk on **"Electrochemists: The Future Coders of Energy Conversion Science and Technology"** hosted by the Department of Chemistry, KMG College of Arts and Science, Gudiyatham, Vellore, TN, India. (02-07-2021)

4.3.2. Invited talk on "**7+ Years of Chasing Better Efficiency inn Electrocatalytic Water Splitting for H_2 Generation**" hosted by the Inorganic and Physical Chemistry Department, Indian Institute of Science, Bengaluru, India (10-11-2021).

4.3.3. Invited talk on "**Advances in Anodization of Cu to Access 1D Nanostructures for Methanol Electrooxidation**" hosted by the CIPET, Odisha, India (18-02-2022).

4.3.4. Invited talk on "**Significances of Having a Stronghold on Accurate Measurements and Analysis in Electrochemical Water Splitting**" hosted by the IIT Roorkee, Uttarkhand, India (01-03-2022).

4.3.5. Invited talk on "**Anion Engineering Strategies to Boost OER and HER Activities**" hosted by the Bishop Heber College, Trichy, India (12-05-2022).

4.3.6. Invited talk on "**A few unusual ways of enhancing OER and HER and activities of non-oxide/hydroxide electrocatalysts**" hosted by the IIT Mandi, HP, India (05-02-2022).

4.4. 受賞・表彰（Awards and Honors）:

4.4.1. Ramanujan Fellow, SERB, India - 2022

4.5. 学会および社会的活動 （Academic Societies and Activities）

4.5.1. A member of American Chemical Society, USA

5. **研究活動の課題と展望（Challenges and Prospects）：** As of now, the proposed project has no apparent challenge that may impede the progress. Hence, we aim to achieve the targets we proposed within the specified timeline. The promises shown by these approaches in lowering OER and HER overpotentials are of high importance which will eventually help us to achieve desired energy-efficiency with non-noble metal catalysts. Moreover, our research is directly related to the recent interest of the Japanese government in hydrogen generation from water and will aid them to achieve their goals of large scale production by 2030 and cost-efficient production by 2050. Hence, the proposed research plan is highly likely to be continued beyond the tenure of WRISE position by securing further funding from both public and private agencies and industries.