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

Principal Investigator: Anantharaj Sengeni

(Junior Researcher (Assistant Professor), WRISE, Waseda University)

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, Cu and W and the catalysts of interest will be sulphide, selenide, telluride, and phosphide of all the above said

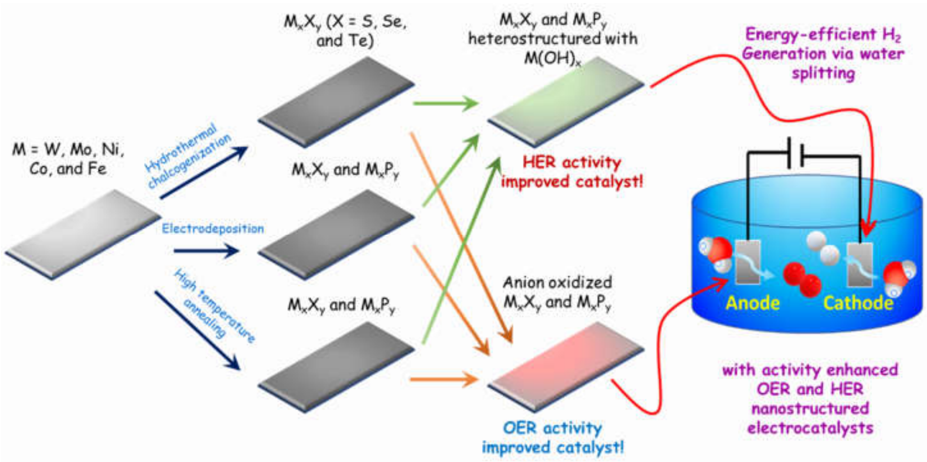

Figure 1: Schematic depiction of proposed research plan.

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)：** In the previous academic year, we have developed the following two multifunctional catalysts following the strategies proposed in **Figure 1** which are namely NiTeO/Ni foam (for the oxidation of water and methanol and the reduction of water to H_2) and Ni-O-S/Ni foam (for the oxidation of water, methanol, glucose, and hydrazine). This year, these catalysts were studied in depth for checking their reproducibility by repeating both the fabrication and the electrochemical characterizations. In addition, these catalysts were also studied in a bipolar membrane-partitioned and a proton exchange membrane partitioned full cells. With NiTeO/Ni, the same electrode is used as both cathode and the anode in the full cell configuration while a Pt/C cathode was used with the Ni-O-S/Ni anode as an asymmetric electrolyzer producing H_2 in an energy-efficient manner (**Figure 2**a-b). These works are now under consideration for publication in the ACS Applied Materials & Interfaces (Ni-O-S/Ni) and ACS Applied Energy Materials (NiTeO/Ni) and are expected to accepted for publication sooner. The highlights of results with these catalysts are listed below.

With NiTeO/Ni:

- Post-synthesis aging oxidized ditelluride dianion into TeO3- which improved the electrochemical accessibility
- As a result, NiTeO/Ni outperformed both Ni and NiTe2/Ni control electrodes
- NiTeO/Ni is also found to be an efficient electrocatalyst for methanol oxidation for the very first time in alkali.
- The full-cell featuring methanol oxidation required 260 mV lesser cell voltage at -100 mA cm^{-2} when compared to the conventional featuring only water oxidation and reduction.

With Ni-O-S/Ni:

- The peroxidation of Ni foam before sulfidation led to the unique formation of NiO/Ni_3S_2 heterostructure
- NiO-NiS heterointerphases led to improved electrochemical accessibility of Ni sites and thus improved the electrocatalytic activity.
- Ni-O-S/Ni outperformed IrO2 (in OER) and Pt (in the oxidation of glucose, methanol, and hydrazine)
- The Asymmetric full-cell featuring Pt/C cathode and Ni-O-S/Ni anode delivered H_2 evolving current density of -10 mA cm^{-2} with 0.23, 1.29, 1.40 and 1.63 as cell voltages when HzOR, GOR, MOR, and OER were the anode reactions.

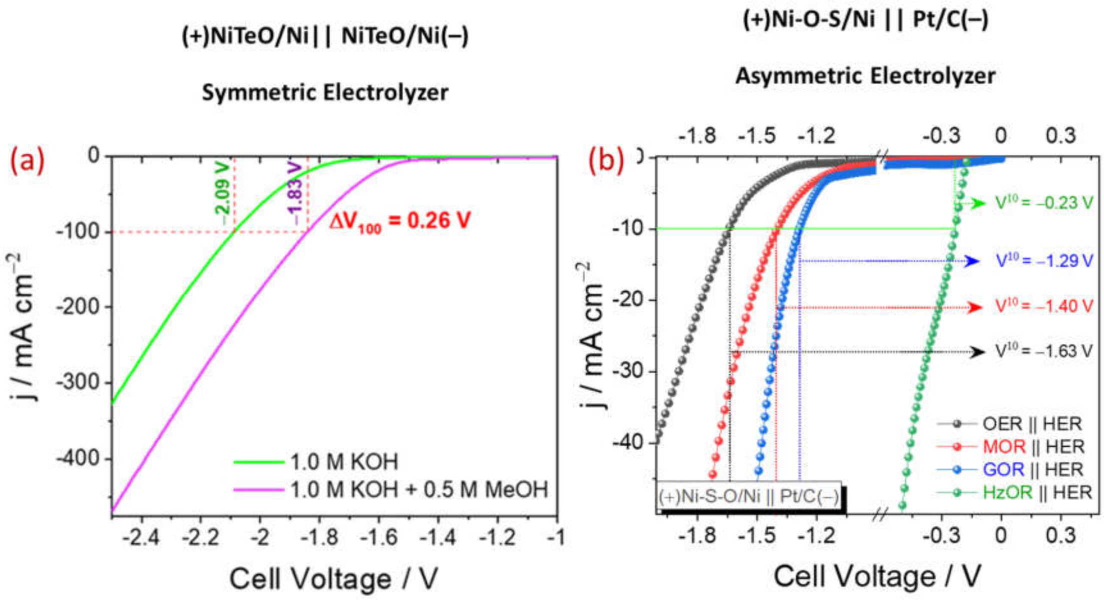

Figure 2: (a) Full-cell polarization curves of NiTeO/Ni with and without methanol for H2 generation in alkali. (b) Full-cell polarization curves of Ni-O-S/Ni in an asymmetric configuration with Pt/C cathode with OER, MOR, GOR, and HzOR as anode reactions.

In addition to these studies focused on the proposed research plan, we have also carried out a couple of important electrochemical screening works concerned about the accurate determination of activity by a newly-developed sampled-current-voltammetry (SCV) and established the roles of importance of vertex potentials of hydrogen underpotential deposition analysis for the determination of electrochemical surface area of various type of Pt electrodes and have also extended its scope recently to gold, silver, and palladium foil electrodes as these electrodes are found used in many energy conversion reactions including water electrolyzers and fuel cells. Our SCV method of determining the activity of electrocatalysts (**Figure 3**a-b) have gained widespread media coverage and is being well read and well cited. The HUPD work (Figure 3c) is also one of the most downloaded papers in Materials Today Energy and is expected to reach broader audience in the near future. Besides, these, we have also published several perspectives and reviews in high impact journals.

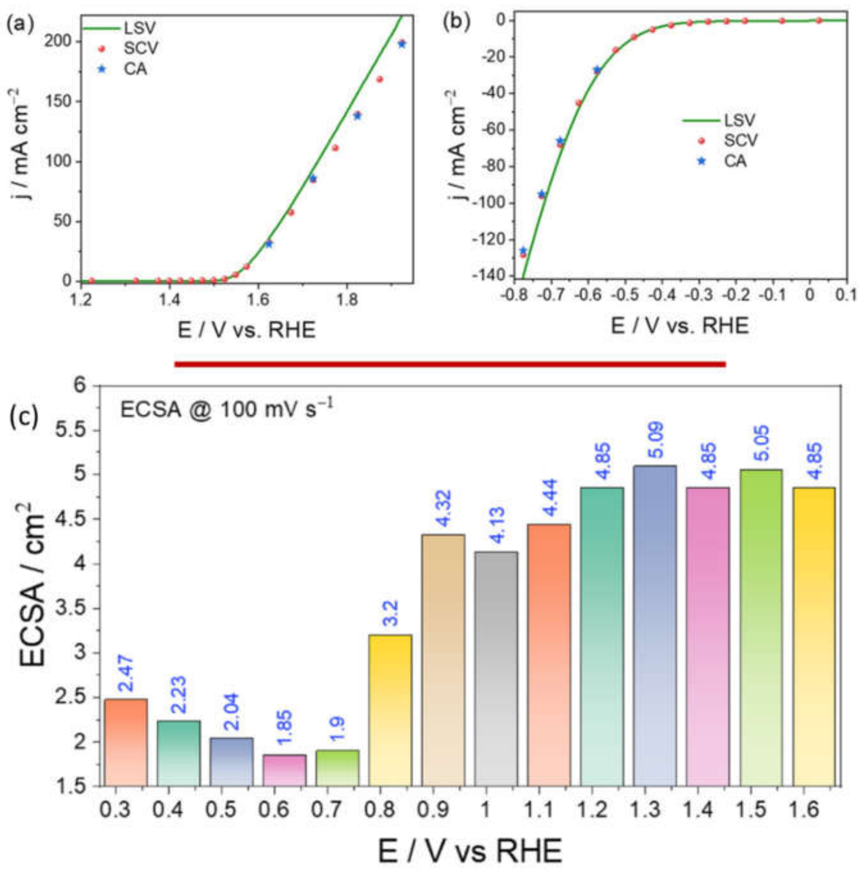

Figure 3: (a-b) OER and HER polarization curves of stainless steel foil with LSV, SCV, and CA responses in 1.0 M KOH. (c) Dependence of ECSA of Pt foil electrode with the increasing anodic vertex potentials in HUPD analysis.

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)

Dr. Sekar Karthikeyan (SRM IST, India)

4. **研究業績（Research Achievements）：** Just like the previous academic year, this academic year was a success for us in terms of academic paper publications, invited talks delivered, and the awards received.

4.1. **学術論文(Academic Papers)：**

4.1.1. **S. Anantharaj*** and S. Noda, The Importance of Carefully Choosing the Vertex Potentials of Hydrogen Underpotential Deposition, *Materials Today Energy*, 2023, 101234. (I.F: 9.257, Ranking Q1)

4.1.2. **S. Anantharaj***, P. E. Karthik and S. Noda, Ambiguities and Best Practices in the Determination of Active Sites and Real Surface Area of Monometallic Electrocatalytic Interfaces, *Journal of Colloids and Interface Science*, 2023, 634, 169-175. (I.F: 9.965, Ranking Q1)

4.1.3. P. Sudhagar*, K. Sridharan, S. Nagarajan, **S. Anantharaj**, P. Robertson, M. F. Kuehnel, A. Irebian, and M. Maroto-Valer, Solar Hydrogen Fuel Generation from Wastewater—Beyond Photoelectrochemical Water Splitting: A Perspective, *Energies*, **2022**, 15(19), 7399. (I.F: 3.252, Ranking Q2)

4.1.4. **S. Anantharaj*** and S. Noda, How Properly Are We Interpreting Tafel Lines in Energy Conversion Electrocatalysis?, *Materials Today Energy*, 2022, 101123. (I.F: 9.257, Ranking Q1)

4.1.5. **S. Anantharaj*** and S. Noda, Dos and Don'ts in Screening Water Splitting Electrocatalysts, *Energy Advances*, 2022, 1, 511-523. *Invited Article* (I.F: N/A, Ranking N/A)

4.1.6. **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: 14.551, Ranking Q1)

4.1.7. **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: 39.714, Ranking Q1)

4.1.8. **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: 7.664, Ranking Q1) *Invited Article*

4.1.9. **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: 4.386, Ranking Q1). Know more about the media mentions of this work here.

4.2. 招待講演（Invited Lectures）:

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

4.2.2. 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).

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

4.2.4. 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).

4.2.5. An in-person talk at SRMIST, Chennai on '**Appropriate Use of Electroanalytical Tools in Energy Conversion Reactions**' (14-08-2022)

4.2.6. An in-person talk at VIT-Vellore on '**An Introduction of Oxygen Electrochemistry**' (15-08-2022)

4.2.7. An in-person talk at VIT-Chennai on '**Two-Electron Oxygen Electrochemistry**' (18-08-2022)

4.2.8. An in-person talk at The Presidency College, Chennai on '**The Significance of Oxygen Electrocatalysis in Energy Storage and Conversion**' (19-08-2022)

4.3. 受賞・表彰（Awards and Honors）:

4.3.1. Most Downloaded author of Materials Today Energy – 2022 (Elsevier, UK)

4.3.2. Highly cited author – 2022 (TOP 5% category in Japan from RSC, UK)

4.3.3. Waseda Research Award – 2022 (High-Impact Publication)

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

4.4.1. A member of American Chemical Society, USA

4.4.2. A Member of The Electrochemical Society of Japan

5. 研究活動の課題と展望（Challenges and Prospects）: The remaining challenges with the proposed plans remain the successful scale-up of the synthesized catalysts to a 25 W electrolyzer (proto-type) and the assessing their activity accurately. Since, I am relieving from WRISE this year, I am planning to continue the progress in the new organization I am going to work while maintaining the close collaborative relationship with Prof. Suguru Noda at Waseda University.