Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Electrocatalytic OER behavior of Bi-Fe-O system: An understanding from the perspective of the presence of oxygen vacancies

Shaswati Jyoti[a], Aditi Vijay[a], Umberto Terranova[b], Santosh K Gupta[c], Kathi Sudarshan[c], Sonalika Vaidya[a]*

[a]Institute of Nano Science and Technology, Knowledge City, Sector 81, SahibzadaAjit Singh Nagar, Punjab 140306, India

[b]Faculty of Medicine and Health Science, Crewe Campus, University of Buckingham, Crewe, CW1 5DU, United Kingdom

[c]Radiochemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India

Corresponding Author: svaidya@inst.ac.in

## Supporting Information

### Calculation of Overpotential:

The potential obtained w.r.t Ag/AgCl was converted w.r.t RHE by using the following equation:

$$E_{(RHE)}=E_{(Ag/AgCl)}+E^{0}_{(Ag/AgCl)}+0.059\ pH \quad \text{---------} \quad (1)$$

where, $E^{0}_{(Ag/AgCl)}$=0.197V and pH=13. The effect of pH was considered here.

For the calculation of overpotential, we follow

$$\text{Overpotential} = E_{(RHE)}-1.23\ (\text{in V}) \quad \text{----------} \quad (2)$$

1.23 V is the equilibrium potential, which is independent of pH and is defined at p = 1 bar and T = 298.15 K (Q. Liang, G. Brocks and A. Bieberle-Hütter, *J. Phys. Energy*, 2021, **3**, 026001; I. C. Man, H.-Y. Su, F. C.-Vallejo, H. A. Hansen, J. I. Martnez, N. G. Inoglu, J. Kitchin, T. F. Jaramillo, J. K. Nørskov, and J. Rossmeisl, *ChemCatChem*, 2011, **3**, 1159.)

**Measurement of Open Circuit Voltage (OCV)**

The OCV represents the electrical potential difference between two terminals of an electronic device when it is isolated from any external circuit. At this juncture, no external load is attached to the device. It gives an idea about the loads that can be attached to the system. It is not a constant value and is a circuit-dependent property that would also change with the electrode material (N.H. Kwon, M. Kim, X. Jin, J. Lim, Y. Kim, N.-S. Lee, H. Kim and S.-J. Hwang, *NPG Asia Mater*, 2018, **10**, 659; D. Oh, K. Virwani, L. Tadesse, M. Jurich, N. Aetukuri, L. E. Thompson, H.-C. Kim, and D. S. Bethune, *J. Phys. Chem. C*, 2017, **121**, 1404; L. Sivasankaran, S. C. Pradhan, R. K Mishra, S. Soman, A. Ajayaghosh, *Solar Energy*, 2022, **236,** 182.)

The open-circuit voltage (OCV) measured for our system is $BiFeO_3$: 1.207 V; $Bi_2Fe_4O_9$: 1.208 V; $Bi_{25}FeO_{40}$: 1.349 V.

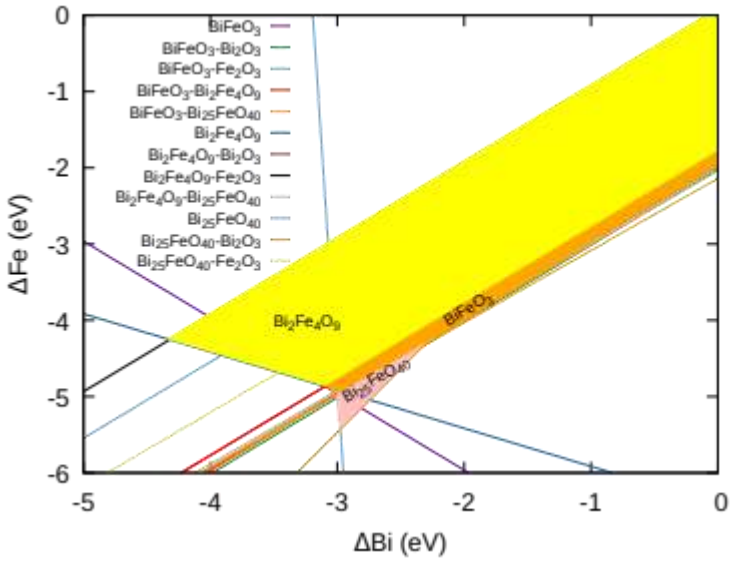


*Figure S1: Stability phase diagram of bismuth ferrite.*

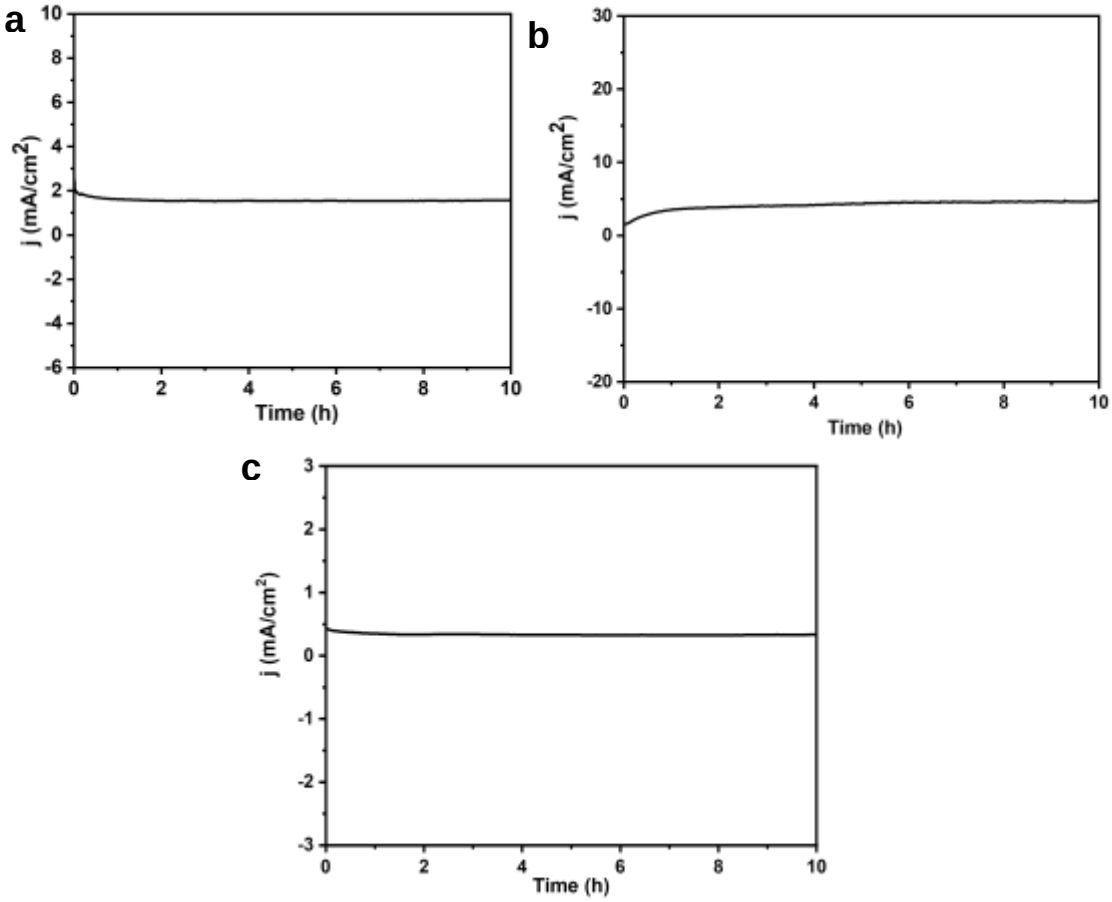


*Figure S2: Stability studies of (a) $BiFeO_3$, (b) $Bi_2Fe_4O_9$ and (c) $Bi_{25}FeO_{40}$ during electrochemical OER*

*Table S1: Allowed range of the oxygen chemical potentials in the three bismuth ferrite phases investigated.*

| | **$\Delta\mu_O$ (eV)** | |
|---|---|---|
| **Sample** | **O-poor** | **O-rich** |
| **$BiFeO_3$** | -2.02 | 0.00 |
| **$Bi_2Fe_4O_9$** | -2.85 | 0.00 |
| **$Bi_{25}FeO_{40}$** | -0.44 | 0.00 |