Electronic Supplementary Material (ESI) for Catalysis Science & Technology. This journal is © The Royal Society of Chemistry 2023

Supporting information



Fig. S1 Bode of 0.1mol/L KOH solution containing 10mmol/L HMF at a potential of 0.5V at NiO<sub>x</sub>/NF electrode.



Fig. S2 (a) EIS and (b)Bode of  $NiO_x/NF$  electrode in 0.1mol/L KOH solution at open circuit potential.



Fig. S3 Concentrations of productions in the first 3 hours during galvanostatic

electrolysis.



Fig.S4 Double-layer capacitance measurements for determining electrochemically active surface area for  $NiO_x/NF$  voltammetry in 0.1mol/L KOH, original electrode (a), after 1<sup>st</sup> electrolyse (b), after 2<sup>nd</sup> electrolyse (c), after 3<sup>rd</sup> electrolyse (d), after 4<sup>th</sup> electrolyse (e).



Fig. S5 Digital photo of the electrode after the accelerated life test. The notch was cut out during the test.



Fig. S6 (a) CV test of SECM probe in bulk solution with scan speed of 50 mV/s, (b) probe approximation curve of ASLT initial electrode and (c) probe approximation curve of the electrode after ASLT process.



Fig. S7 Cyclic voltammetry curve in Fig. 4 of the main article.



Fig. S8 (a) Fine XPS spectra of  $NiO_x/NF$  electrode at different periods of the ASLT process of Ni 2p and (b)O 1s, and (c) full XPS spectra before and after ASLT process.

In the Ni fine spectrum (Fig. S8a), the characteristic peaks at 852-859 eV are relatively broad before the ASLT, which result from the overlapping of Ni(II) and Ni(III) peaks. Among them, the Ni(II) peak at 854.5 eV is attributed to NiO. The Ni(III) peak at 856 eV belong to  $Ni_2O_3$ .<sup>1,2</sup> At the end of the accelerated life, the 2P peak of Ni gradually narrows and moves towards the higher binding energy. This means that the valence state of Ni-containing material increases due to oxygen embedding, and the proportion of Ni(II) on the catalyst surface gradually decreases, and a part of Ni(II) is transformed into high-priced Ni-containing material NiOOH.

From the high-resolution O1s fine spectrum (Fig. S8b), we fitted the line into three peaks. The small peak at 532.6  $\pm$  0.2 eV was attributed to the hydroxyl oxygen (O<sub>ad</sub>) (6.56%) in the surface adsorbed H<sub>2</sub>O<sup>3,4</sup>. The component at 529.7 eV is lattice oxygen species (OL), which is directly bonded to the metal and is attributed to the oxygen in the NiO lattice. After calculation by CasaXPS software, this component at accounts for 46.37% of the total area of the O1s peak.<sup>2,3,5,6</sup> The other component at

530.9 accounts for 47.07%, which is close to lattice oxygen, but the binding energy is higher. This is because the oxygen atom of this component is combined with highvalent nickel, and it is judged that this peak belongs to  $Ni_2O_3$ .<sup>7</sup> With the progress of electrolysis, the peak at 530.9 becomes narrower and stronger, and this peak is attributed to NiOOH transformed by Ni(OH)<sub>2</sub>, which finally accounts for 81.58%. At the same time, the XPS survey in Fig.S8c shows that the atomic ratio of initial O : Ni is about 1, and the atomic ratio after the accelerated lifetime test is 2.54. It proves that the species remaining on the electrode surface after the active substance falls off is NiOOH. This is closely related to the fine spectrum of Ni.



Fig. S9 Morphology changes of  $NiO_x/NF$  electrode during ASLT process, (a) initial electrode, (b) after the first electrolysis, (c) after the second electrolysis, and (d) after the third electrolysis. SEM instrument: ZEISS-Sigma 300 Field Emission Scanning electron microscope (FEG-SEM).



Fig.S10 (a,b) HRTEM images of as-prepared NiO and (c,d) the catalyst γ-NiOOH after galvanostatic oxidation. HRTEM instrument: Philips FEI Tecnai G2S-Twin microscope equipped with a field emission gun operating at 200 kV.

High-resolution transmission electron microscopy (HRTEM) images (Fig. S10(a)) reveal that the as-prepared electrocatalysts exhibit interplanar spacing d of 0.41 nm, 0.21 nm, and 0.15 nm, corresponding to the (111), (200), and (220) lattice planes of NiO (JCPDS:47-1049), respectively. After undergoing ASLT, the electrocatalysts show interplanar spacing d of 0.34 nm and 0.24 nm, corresponding to the (006) and (200) lattice planes of  $\gamma$ -NiOOH (JCPDS:06-0075).



Fig.S11 (a) Raman spectra of NiO/NF at each stage during ASLT process and (b) the

corresponding normalized Raman spectra.

According to the Raman spectra of the electrodes at different stages of ASLT (Fig. S11), the region below 600 cm<sup>-1</sup> is attributed to the one-phonon (1P) Ni-O mode (TO and LO) of NiO, while the Raman shifts between 600 cm<sup>-1</sup> and 1200 cm<sup>-1</sup> are the two-phonon (2P) mode (2TO, TO + LO, and 2LO) of NiO [8]. Therefore, we can identify the NiO structure of the as-prepared catalyst from Fig. S11(a). Previous studies have shown that the peak at 800 cm<sup>-1</sup> position is attributed to the transition metal u (OOH\*) [9]. To obtain the clear change of the Raman spectrum, we normalized Fig.S11(a) to obtain Fig. S11(b). It can be seen that a distinct peak appears at 800 cm<sup>-1</sup> after the fourth electrolysis, indicating that the structure has transformed into NiOOH at this point.

## Reference

- [1] Mansour A N. Characterization of NiO by XPS[J]. Surface Science Spectra, 1994, 3(3): 231-238.
- [2] Biesinger M C, Payne B P, Lau L W M, et al. X-ray photoelectron spectroscopic chemical state quantification of mixed nickel metal, oxide and hydroxide systems[J]. Surface and Interface Analysis: An International Journal devoted to the development and application of techniques for the analysis of surfaces, interfaces and thin films, 2009, 41(4): 324-332.
- [3] Bediako, D. K.; Lassalle-Kaiser, B.; Surendranath, Y.; Yano, J.; Yachandra, V. K.; Nocera, D. G. Structure–Activity Correlations in a Nickel–Borate Oxygen Evolution Catalyst J. Am. Chem. Soc. 2012, 134, 6801– 6809.
- [4] Nardi, K.L., Yang, N., Dickens, C.F., Strickler, A.L., Bent, S.F. Creating Highly Active Atomic Layer Deposited NiO Electrocatalysts for the Oxygen Evolution Reaction. Advanced Energy Materials.2015, 5, 1500412.
- [5] Wei C, Sun S, Mandler D, et al. Approaches for measuring the surface areas of metal oxide electrocatalysts for determining their photoelectron electrocatalytic activity[J]. Chemical Society Reviews, 2019, 48(9): 2518-2534.
- [6] Diaz-Morales, O.; Ferrus-Suspedra, D.; Koper, M. T. M. The Importance of Nickel Oxyhydroxide Deprotonation on Its Activity Towards Electrochemical Water Oxidation Chemical Science 2016, 7, 2639–2645.
- [7] Lian K, Thorpe S J, Kirk D W. Electrochemical and surface characterization of electrocatalytically active amorphous Ni<sup>®</sup> Co alloys[J]. Electrochimica acta, 1992, 37(11): 2029-2041.
- [8] Qiu Z, Ma Y, Edvinsson T. In operando Raman investigation of Fe doping influence on catalytic NiO intermediates for enhanced overall water splitting[J]. Nano Energy, 2019, 66: 104118.
- [9] Xu Y, Li N, Wang R, et al. Synergetic design of N-doped defect-enriched porous carbon matrix with Co-CoO. 85Se loading for water splitting[J]. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2022, 637: 128243.