Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

# Supporting information for

## Industrial-Scale Efficient Alkaline Water Electrolysis Achieved with Sputtered NiFeV-Oxide Thin-Film Electrodes for Green Hydrogen Production

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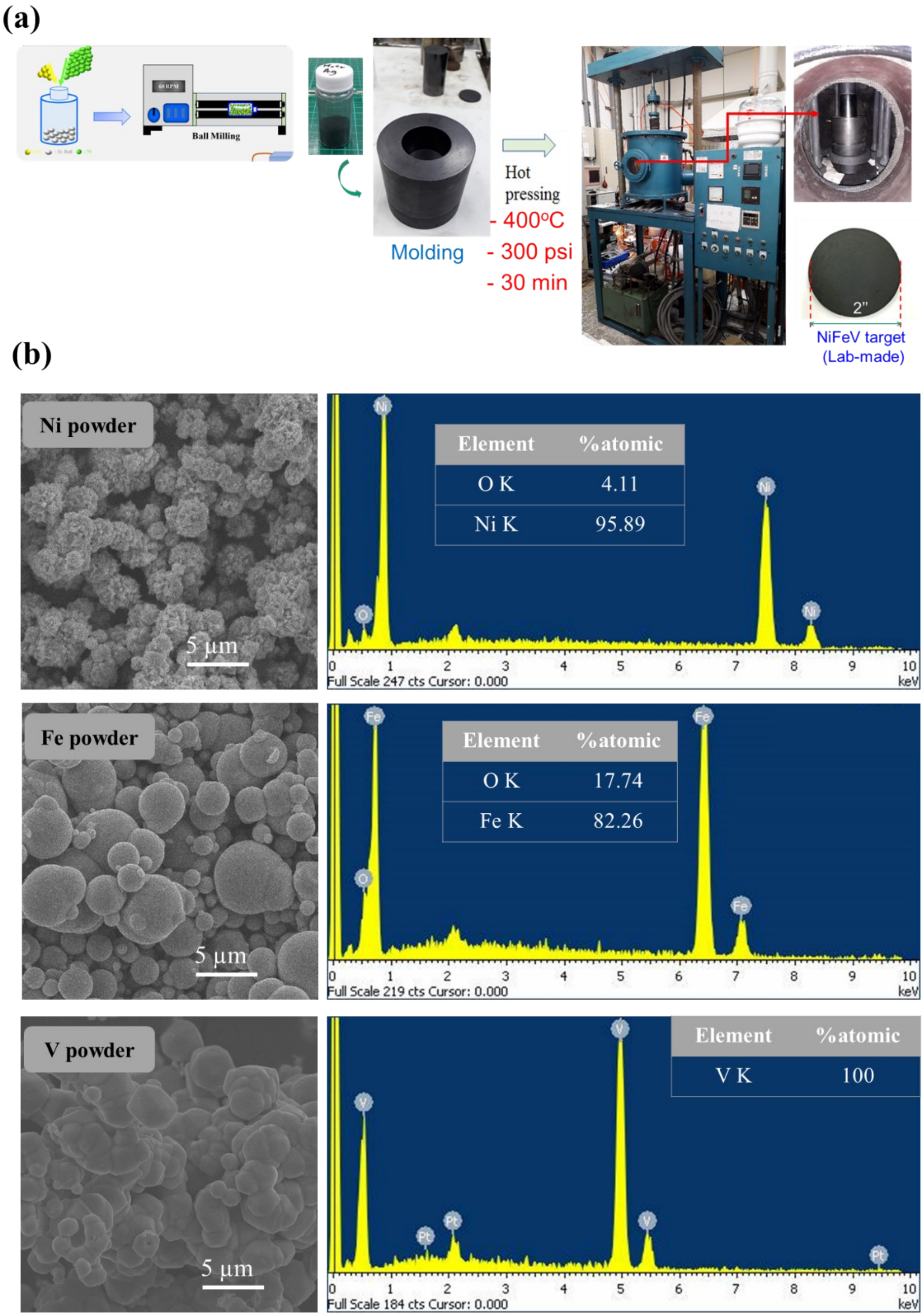

| Element | %atomic |
|---|---|
| O K | 4.11 |
| Ni K | 95.89 |

| Element | %atomic |
|---|---|
| O K | 17.74 |
| Fe K | 82.26 |

| Element | %atomic |
|---|---|
| V K | 100 |

**Figure S1.** (a) Fabrication procedure of NiFeV target by using our home-built hot press machine. (b) SEM and EDS results of Ni, Fe, and V powder for target fabrication.

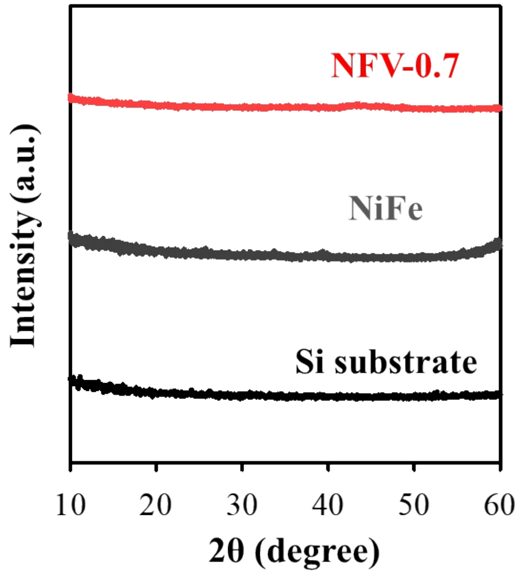

**Figure S2**. XRD patterns of substrate, NiFe, and NFV-0.7.

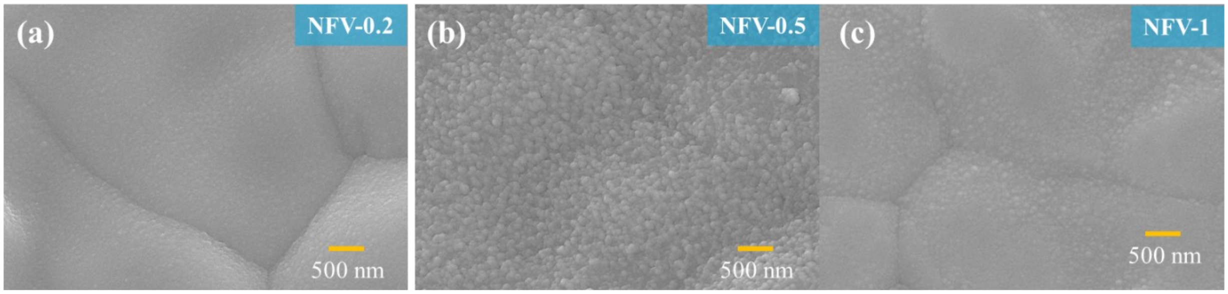

**Figure S3**. FE-SEM images of (a) NFV-0.2, (b) NFV-0.5, and (c) NFV-1.

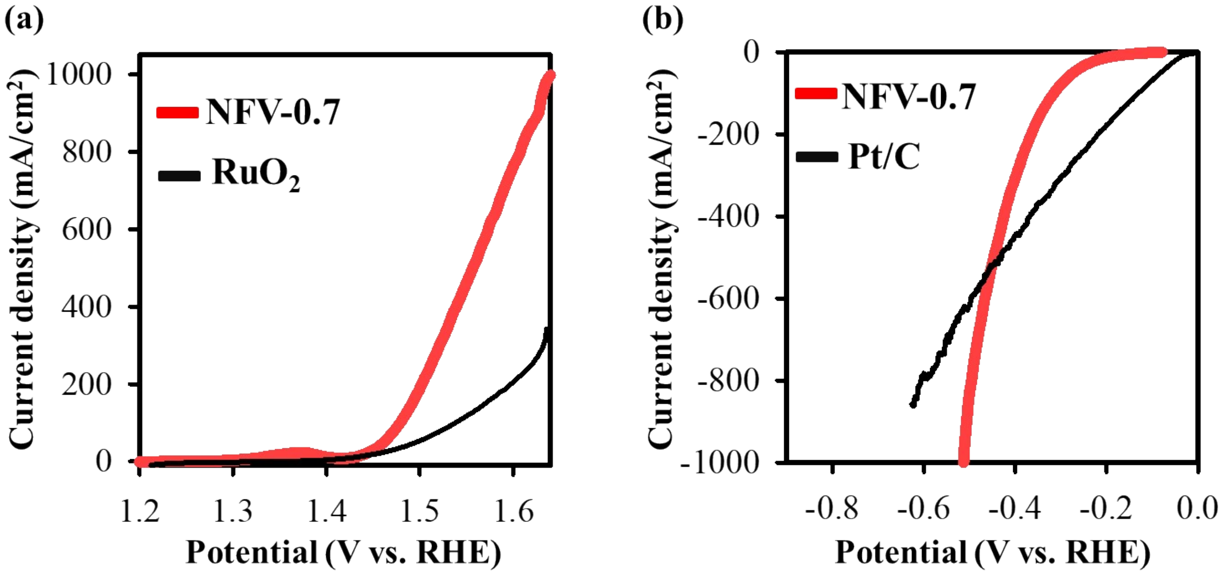

**Figure S4.** (a) The electrocatalytic performance comparison between our NFV-0.7 and $RuO_2$ for OER and (b) NFV-0.7 and Pt/C for HER.

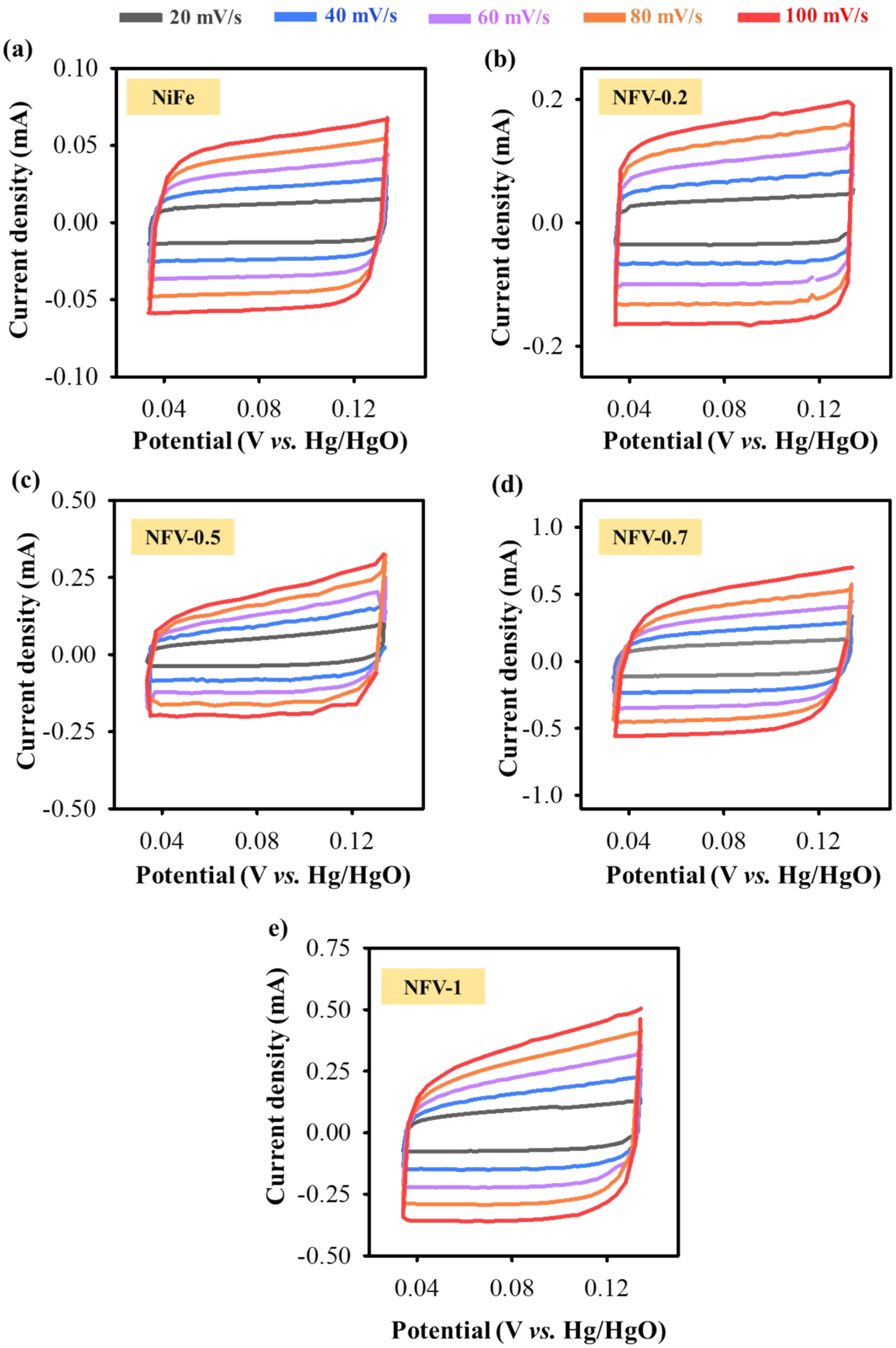

**Figure S5**. CV curves of (a) NiFe, (b) NFV-0.2, (c) NFV-0.5, (d) NFV-0.7, and (e) NFV-1 at different scan rates.

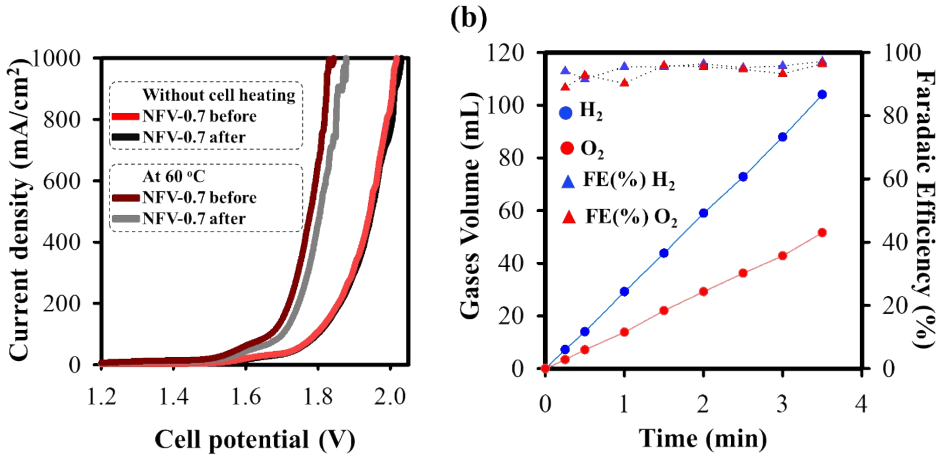

**Figure S6.** (a) LSV curves of NFV-0.7 electrolyzer before and after stability tests. (b) Experimental gas production measurement vs. time at 1000 mA/cm$^2$, accompanied by their corresponding Faradaic efficiencies.

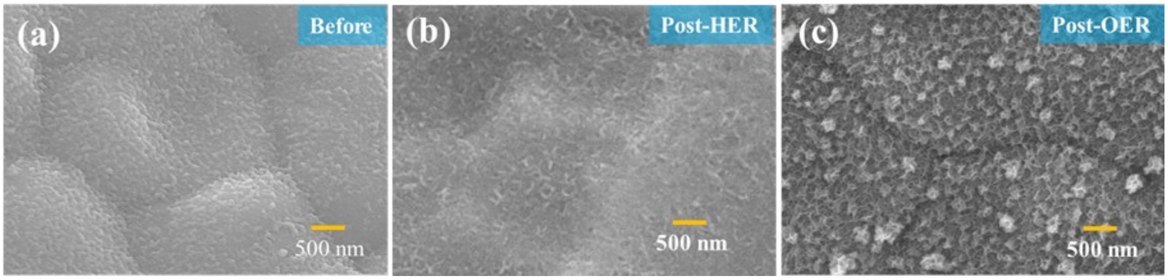

**Figure S7**. SEM images of NFV-7 (a) before the stability test, (b) after HER, and (c) after OER.

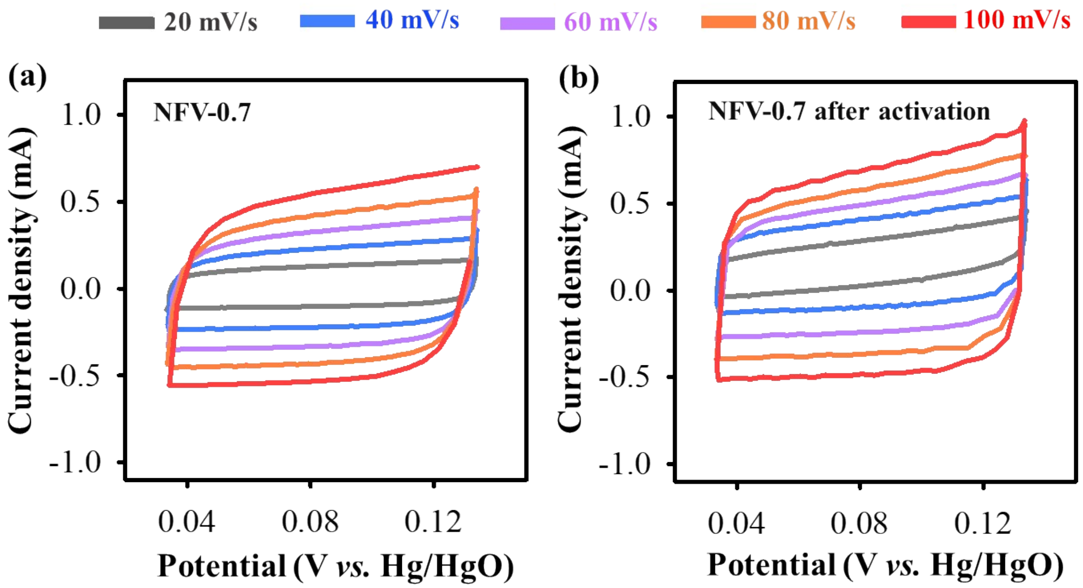

**Figure S8.** CV curves of NFV-0.7 (a) before and (b) after activation for 200 CV cycles.

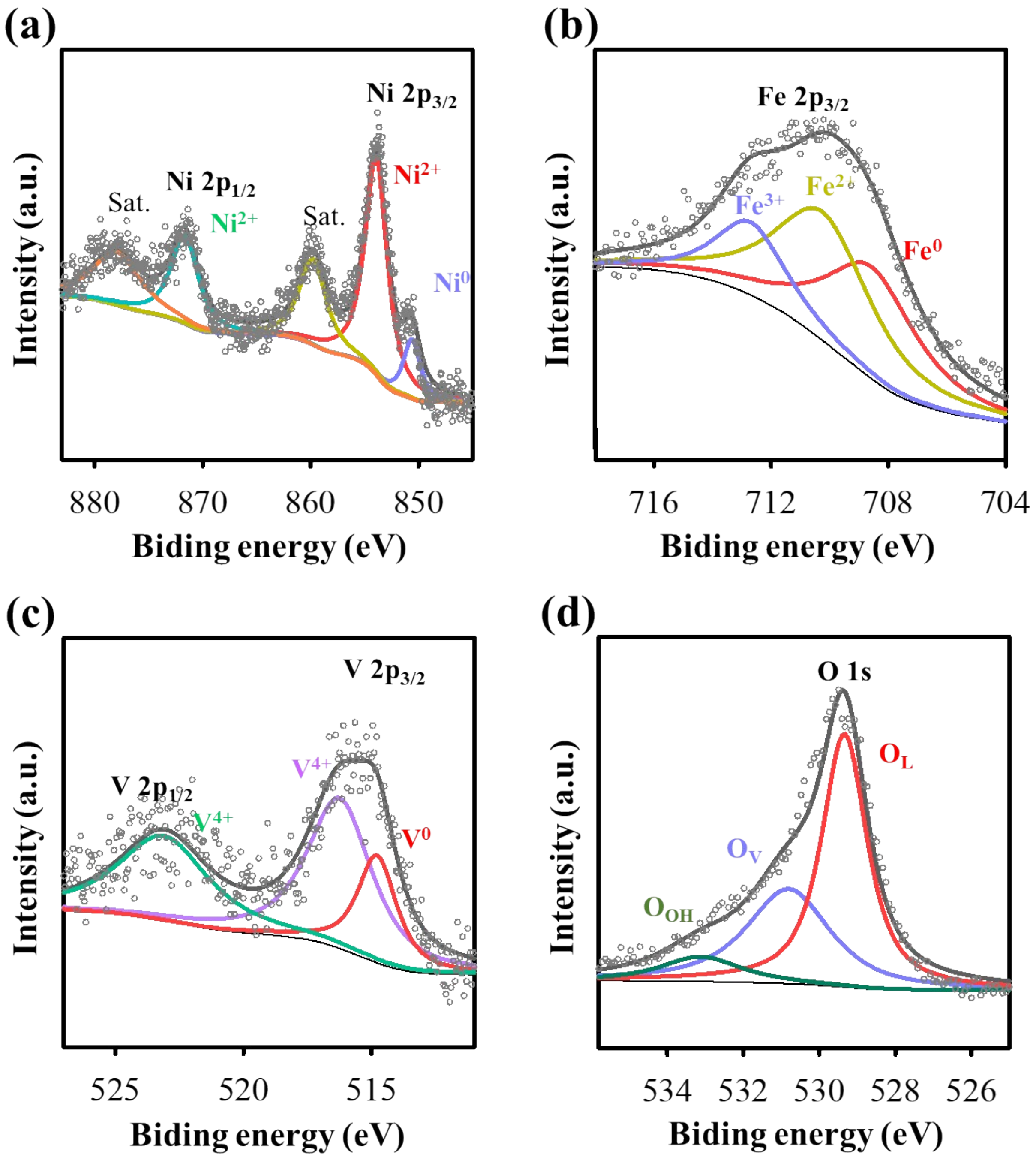

**Figure S9**. High-resolution XPS spectra of (a) Ni 2p, (b) Fe 2p, (c) V 2p, and (d) O 1s of the post-HER NFV-0.7 catalyst.

**Table S1.** Atomic percentage of metal elements of NFV-*n* thin films with various V ratios

| **Catalyst** | **Atomic(%)** | | | **Ni:Fe:V ratio** | |
|---|---|---|---|---|---|
| | **Ni** | **Fe** | **V** | **Target** | **Film** |
| **NiFe** | 59.3 | 40.7 | - | 1:1:0 | 1:0.68 |
| **NFV-0.2** | 52.9 | 40.5 | 6.6 | 1:1:0.2 | 1:0.76:0.11 |
| **NFV-0.5** | 47.1 | 42.7 | 10.2 | 1:1:0.5 | 1:0.95:0.23 |
| **NFV-0.7** | 51.0 | 33.4 | 15.6 | 1:1:0.7 | 1:0.67:0.31 |
| **NFV-1** | 39.9 | 37.5 | 22.6 | 1:1:1 | 1:0.94:0.56 |

**Table S2. The comparison of electrocatalytic OER performance for NFV-0.7 in 1 M KOH with other NiFe-based reported in the literature**

| No. | Catalyst | Method | Overpotential (mV) | | | | Ref |
|---|---|---|---|---|---|---|---|
| | | | @10 mA/cm$^2$ | @100 mA/cm$^2$ | @500 mA/cm$^2$ | @1000 mA/cm$^2$ | |
| 1 | NiFeV | Sputtering | 195 | 250 | 327 | 410 | This work |
| 2 | O-GQD-NiFe P.B.A. 1:20 | Sputtering | 259 | | | | 1 |
| 3 | Niv(OH)$_2$/FeOOH | metal ion adsorption method | 212 | 261 | | | 2 |
| 4 | Ni$_3$Fe oxide | Hydrothermal synthesis at 550 °C for 4 h | 291 | 356 | 447 | | 3 |
| 5 | Co(OH)$_2$@NiFe/NF | two-step electrodeposition | 191 | | | | 4 |
| 6 | NiFeOxHy-C/CNTs/CFP | one-step solvothermal method | 202 | | | | 5 |
| 7 | Fe-NiS$_2$/NCNT | hydrothermal method | | 247 | | | 6 |
| 8 | NiFe–NiFe$_2$O$_4$ nanofibers | solution blow spinning | 316 | | | | 7 |
| 9 | cRu-Ni$_3$N/NF | hydrothermal + nitrogenized | | 278 | | | 8 |
| 10 | NiFeW$_3$-LDHs | immersion treatment | 211 | 256 | | | 9 |
| 11 | CS-NiFeCr/NF | Electrodeposition | 220 | 280 | | | 10 |
| 12 | NiFeZnP | hydrothermal deposition | 203 | | | | 11 |

**Table S3. The comparison of electrocatalytic HER performance for NFV-0.7 in 1 M KOH with other NiFe-based reported in the literature**

| No. | Catalyst | Method | Overpotential (mV) | | | | Ref |
|---|---|---|---|---|---|---|---|
| | | | @-10 mA/cm$^2$ | @-100 mA/cm$^2$ | @-500 mA/cm$^2$ | @-1000 mA/cm$^2$ | |
| 1 | NiFeV | Sputtering | -98 | -317 | -447 | -512 | This work |
| 2 | NiFeP@TiO$_{2-x}$ | electrodeposition | | -273 | | | 12 |
| 3 | FeNi-HDNAs | hydrothermal for 2 h at 400 °C | -141 | | | | 13 |
| 4 | Fe–Ni$_2$P@PC/Cu$_x$S | hydrothermal at 60 °C for 20 h | -113 | | | | 14 |
| 5 | NiFe$_2$O$_4$/CoNi-S | Solvothermal + Eletrodeposition | -149 | | | | 15 |
| 6 | Ni(OH)$_2$@Ni$_2$Fe$_2$/NF-60 | electrodeposition | | -220 | | | 16 |
| 7 | NiFe$_{\text{EDTA}}$ | hydrothermal at 180 °C for 12 h | -163 | | | | 17 |
| 8 | NiFeP@NiP@NF | hydrothermal synthesis | -105 | | | | 18 |
| 9 | Mo-doped CoFe LDH/NF | electrochemical transformation | | -227 | -408 | -568 | 19 |
| 10 | Co$_9$S$_8$@NiFe-LDH-200 | electrosynthesis method | -145 | -288 | | | 20 |
| 11 | NiFe LDH/(NiFe)S$_x$/CMT | Hydrothermal at 120 °C for 1 h | -169 | | | | 21 |
| 12 | NiFe@C | Hydrothermal at 500 °C for 2 h | -195 | | | | 22 |

**Table S4. The comparison of the electrocatalytic performance of NFV-0.7 for Overall water splitting with other AEM electrolysis reported in the literature**

| Electrolyte | Catalyst |  | AEM membrane | Operation conditions |  |  | Ref. |
|---|---|---|---|---|---|---|---|
|  | Anode OER. | Cathode HER |  | Cell voltage (V) | Current density (mA/cm$^2$) | Temp. ($^o$C) |  |
| 1 M KOH | **NFV-0.7** | **NFV-0.7** | FAA3-PK-130 | **1.84** | **1000** | **60** | **This work** |
|  |  |  |  | **2.00** | **1000** | **25** |  |
| 1M KOH. | $IrO_2$ | Pt Black | PiperION | 1.9 | 1000 | 50 | 23 |
| 0.5M KOH | $IrO_2$ | Pt/C | FAA3-PK-75 | 1.8 | 1000 | 90 | 24 |
| 1M NaOH | $Ni_2Fe_1$ | $Ni_9Mo_1$/C | TMA | 1.8 | 906 | 60 | 25 |
| Water | $IrO_x$ | Pt/C | FAA-3 | 2.29 | 500 | 50 | 26 |
| 1M KOH | Ni/$CeO_2$-$La_2O_3$/C | $CuCoO_x$ | A201 | 1.9 | 470 | 55 | 27 |
| 1 M KOH. | $Co_3S_4$/NF | $Cu_{0.81}Co_{2.19}O_4$ NS/NF | X37-50 | 2 | 431 | 45 | 28 |
| DI water | Ni-Fe | Ni-Mo | Quaternary ammonia polysulfone | 1.8 | 400 | 70 | 29 |
| D.I water | $IrO_2$ | Pt Black | A-201 Tokuyama | 1.8 | 399 | 50 | 30 |
| 1M KOH. | $Ni_{12}P_5$/ $Ni_3(PO_4)_2$-HS | $Ni_{12}P_5$/ $Ni_3(PO_4)_2$-HS | Y.A.B., Foma | 1.8 | 357.6 | 50 | 31 |
| 1M KOH. | CoP | CoP | YAB | 1.85 | 335 | 50 | 32 |
| DI water | Ni | $Li_{0.21}Co_{2.79}O_4$ | Cranfield | 2.05 | 300 | 45 | 33 |
| D.I water | Ni | $CeO_2MnFe_{1.8}O_4$ | FAA-3-PK-130 | 1.8 | 300 | 25 | 34 |
| 0.5M KOH | $IrO_2$ | Pt/C | A-201, Tokuyama | 1.8 | 299 | 50 | 35 |
| 1M KOH | Ni | Pt-Ni | A-201 | 1.9 | 250 | 50 | 36 |
| 0.1M KOH. | Ni/$CeO_2$-$La_2O_3$/C | $CuCoO_x$ | Mg/Al LDH | 2.2 | 208 | 70 | 37 |
| 1M KOH. | Ni | $Cu_{0.7}Co_{2.3}O_4$ | qPVB/OH- | 2 | 100 | 55 | 38 |
| 10% K.O.H. | Ni | $NiCo_2O_4$ | qPPO | 1.85 | 135 | 50 | 39 |
| 0.1M KOH. | Ni | $Cu_{0.7}Co_{2.3}O_4$ | Cranfield | 1.9 | 100 | 55 | 40 |

**Faradaic efficiency (FE.)**

$$FE\ H_2(\%) = \frac{n_{H_2} \times F \times 2}{j \times t} \times 100\%$$

$$FE\ O_2(\%) = \frac{n_{O_2} \times F \times 4}{j \times t} \times 100\%$$

where *n* is the amount of generated gas (mol), *F* is the Faradaic constant (96 485.3 s A /mol), *j* is current density (A/cm$^2$), and *t* is time (s).

**Cell efficiency calculation**

The electrocatalytic efficiency of our single stack cell was calculated according to the below equation [41]:

$$Cell\ efficiency\ (\%) = \frac{H_2\ power}{Electrolyzer\ power} \times 100\%$$

The following equation calculated the $H_2$ power:

$$H_2\ power\left(\frac{W}{cm^2}\right) = hydrogen\ production\ rates\ (\frac{mol}{s.cm^2})\ \times\ lower\ heating\ value\ (L.H.V.)$$

Theoretically, the hydrogen production rate at 1000 mA/cm$^2$ is approximately $5.18\times10^{-6}$ mol/s.cm$^2$. A lower heating value (LHV) of 242,000 J/mol was used for $H_2$ power output.

Then, the $H_2$ power output is 1.25 W/cm$^2$

The following equation calculates the power of alkaline cell electrolysis:

- At 25 °C

$$Cell\ power\left(\frac{W}{cm^2}\right) = cell\ voltage\ (V) \times current\ density\ (\frac{A}{cm2})$$

$$Cell\ power\left(\frac{W}{cm^2}\right) = 2.00 \times 1 = 2.00$$

Finally,

$$Cell\ efficiency\ (\%) = \frac{1.25}{2.00} X\ 100\% = 62.5\%$$

- At 60 °C

$$Cell\ power\left(\frac{W}{cm^2}\right) = 1.84 \times 1 = 1.84$$

Finally,

$$Cell\ efficiency\ (\%) = \frac{1.25}{1.84} X\ 100\% = 67.9\%$$

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## References

1. Y.-C. Lin, S. Aulia, M.-H. Yeh, L.-Y. Hsiao, A. M. Tarigan and K.-C. Ho, *Journal of Colloid and Interface Science*, 2023.
2. F. Dong, H. Duan, Z. Lin, H. Yuan, M. Ju, X. Du, J. Gao, J. Yu and S. Yang, *Applied Catalysis B: Environmental*, 2023, 123242.
3. M. Yu, G. Moon, E. Bill and H. Tüysüz, *ACS Applied Energy Materials*, 2019, **2**, 1199-1209.
4. H. Wang, Y. Yan, W. Zhang, S. Sun and S. Yao, *Journal of Solid State Chemistry*, 2023, **323**, 124048.
5. Y. Qiao, Y. Pan, J. Zhang, B. Wang, T. Wu, W. Fan, Y. Cao, R. Mehmood, F. Zhang and F. Zhang, *Chinese Journal of Catalysis*, 2022, **43**, 2354-2362.
6. X. Liu, X. Zhao, S. Cao, M. Xu, Y. Wang, W. Xue and J. Li, *Applied Catalysis B: Environmental*, 2023, **331**, 122715.
7. R. A. Raimundo, V. D. Silva, E. S. Medeiros, D. A. Macedo, T. A. Simões, U. U. Gomes, M. A. Morales and R. M. Gomes, *Journal of Physics and Chemistry of Solids*, 2020, **139**, 109325.
8. J. Zhu, R. Lu, W. Shi, L. Gong, D. Chen, P. Wang, L. Chen, J. Wu, S. Mu and Y. Zhao, *Energy & Environmental Materials*, 2023, **6**, e12318.
9. H. Li, C. Zhang, W. Xiang, M. A. Amin, J. Na, S. Wang, J. Yu and Y. Yamauchi, *Chemical Engineering Journal*, 2023, **452**, 139104.
10. L. Fan, P. Zhang, B. Zhang, Q. Daniel, B. J. Timmer, F. Zhang and L. Sun, *ACS Energy Letters*, 2018, **3**, 2865-2874.
11. C. Kou, J. Han, H. Wang, M. Han and H. Liang, *Progress in Natural Science: Materials International*, 2023, **33**, 74-82.
12. K. Zhang, T. Wan, H. Wang, Y. Luo, Y. Shi, Z. Zhang, G. Liu and J. Li, *Journal of Colloid and Interface Science*, 2023, **645**, 66-75.
13. N. Yu, W. Cao, M. Huttula, Y. Kayser, P. Hoenicke, B. Beckhoff, F. Lai, R. Dong, H. Sun and B. Geng, *Applied Catalysis B: Environmental*, 2020, **261**, 118193.
14. D. T. Tran, H. T. Le, N. H. Kim and J. H. Lee, *Nano Energy*, 2021, **84**, 105861.
15. Y. Shi, X. Feng, H. Guan, J. Zhang and Z. Hu, *International Journal of Hydrogen Energy*, 2021, **46**, 8557-8566.
16. L. Zhang, T. Wang, H. Wu, H. Wang and F. Wang, *Journal of Alloys and Compounds*, 2022, **918**, 165564.
17. M. Li, Y. Li, J. Wang and Q. Zhong, *Journal of Electroanalytical Chemistry*, 2022, **922**, 116764.
18. F. Diao, W. Huang, G. Ctistis, H. Wackerbarth, Y. Yang, P. Si, J. Zhang, X. Xiao and C. Engelbrekt, *ACS Applied Materials & Interfaces*, 2021, **13**, 23702-23713.
19. G. Zhao, B. Wang, Q. Yan and X. Xia, *Journal of Alloys and Compounds*, 2022, **902**, 163738.
20. Y. Lu, C. Liu, Y. Xing, Q. Xu, A. M. S. Hossain, D. Jiang, D. Li and J. Zhu, *Journal of Colloid and Interface Science*, 2021, **604**, 680-690.
21. Y. Zou, B. Xiao, J.-W. Shi, H. Hao, D. Ma, Y. Lv, G. Sun, J. Li and Y. Cheng, *Electrochimica Acta*, 2020, **348**, 136339.

22. S.-W. Park, I. Kim, S.-I. Oh, J.-C. Kim and D.-W. Kim, *Journal of Catalysis*, 2018, **366**, 266-274.
23. G. A. Lindquist, S. Z. Oener, R. Krivina, A. R. Motz, A. Keane, C. Capuano, K. E. Ayers and S. W. Boettcher, *ACS Applied Materials & Interfaces*, 2021, **13**, 51917-51924.
24. A. Lim, H.-j. Kim, D. Henkensmeier, S. J. Yoo, J. Y. Kim, S. Y. Lee, Y.-E. Sung, J. H. Jang and H. S. Park, *Journal of Industrial and Engineering Chemistry*, 2019, **76**, 410-418.
25. D. Li, E. J. Park, W. Zhu, Q. Shi, Y. Zhou, H. Tian, Y. Lin, A. Serov, B. Zulevi and E. D. Baca, *Nature Energy*, 2020, **5**, 378-385.
26. D. Xu, M. B. Stevens, M. R. Cosby, S. Z. Oener, A. M. Smith, L. J. Enman, K. E. Ayers, C. B. Capuano, J. N. Renner and N. Danilovic, *ACS Catalysis*, 2018, **9**, 7-15.
27. C. C. Pavel, F. Cecconi, C. Emiliani, S. Santiccioli, A. Scaffidi, S. Catanorchi and M. Comotti, *Angewandte Chemie International Edition*, 2014, **53**, 1378-1381.
28. Y. S. Park, J. H. Lee, M. J. Jang, J. Jeong, S. M. Park, W.-S. Choi, Y. Kim, J. Yang and S. M. Choi, *International Journal of Hydrogen Energy*, 2020, **45**, 36-45.
29. L. Xiao, S. Zhang, J. Pan, C. Yang, M. He, L. Zhuang and J. Lu, *Energy & Environmental Science*, 2012, **5**, 7869-7871.
30. Y. Leng, G. Chen, A. J. Mendoza, T. B. Tighe, M. A. Hickner and C.-Y. Wang, *Journal of the American Chemical Society*, 2012, **134**, 9054-9057.
31. J. Chang, Q. Lv, G. Li, J. Ge, C. Liu and W. Xing, *Applied Catalysis B: Environmental*, 2017, **204**, 486-496.
32. J. Chang, L. Liang, C. Li, M. Wang, J. Ge, C. Liu and W. Xing, *Green Chemistry*, 2016, **18**, 2287-2295.
33. X. Wu and K. Scott, *International journal of hydrogen energy*, 2013, **38**, 3123-3129.
34. T. Pandiarajan, L. J. Berchmans and S. Ravichandran, *RSC Advances*, 2015, **5**, 34100-34108.
35. M. K. Cho, H.-Y. Park, H. J. Lee, H.-J. Kim, A. Lim, D. Henkensmeier, S. J. Yoo, J. Y. Kim, S. Y. Lee and H. S. Park, *Journal of Power Sources*, 2018, **382**, 22-29.
36. S. H. Ahn, S. J. Yoo, H.-J. Kim, D. Henkensmeier, S. W. Nam, S.-K. Kim and J. H. Jang, *Applied Catalysis B: Environmental*, 2016, **180**, 674-679.
37. L. Zeng and T. Zhao, *Nano Energy*, 2015, **11**, 110-118.
38. Y.-C. Cao, X. Wu and K. Scott, *International journal of hydrogen energy*, 2012, **37**, 9524-9528.
39. D. Chanda, J. Hnát, T. Bystron, M. Paidar and K. Bouzek, *Journal of Power Sources*, 2017, **347**, 247-258.
40. X. Wu and K. Scott, *Journal of Power Sources*, 2012, **214**, 124-129.
41. Y. S. Park, J. Jeong, Y. Noh, M. J. Jang, J. Lee, K. H. Lee, D. C. Lim, M. H. Seo, W. B. Kim, J. Yang and S. M. Choi, *Applied Catalysis B: Environmental*, 2021, **292**, 120170.