Supplementary Information

Enhancing CO_2 Reduction Efficiency through Electrolyte Immersion in Hierarchical Bismuth-Nickel Catalysts

Yongsu An[a], Yongju Lee[a], Yujing Ji[a], Young Dok Kim[a], Hyun Ook Seo[b], Duk-Young Jung[a]*

[a]Department of Chemistry, Sungkyunkwan University Suwon, 16419, Republic of Korea

[b]Department of Chemistry and Energy Engineering, Sangmyung University Seoul, 03016, Republic of Korea

***Corresponding Author:**

dyjung@skku.edu (D.Y. Jung), +82) 31-290-7074

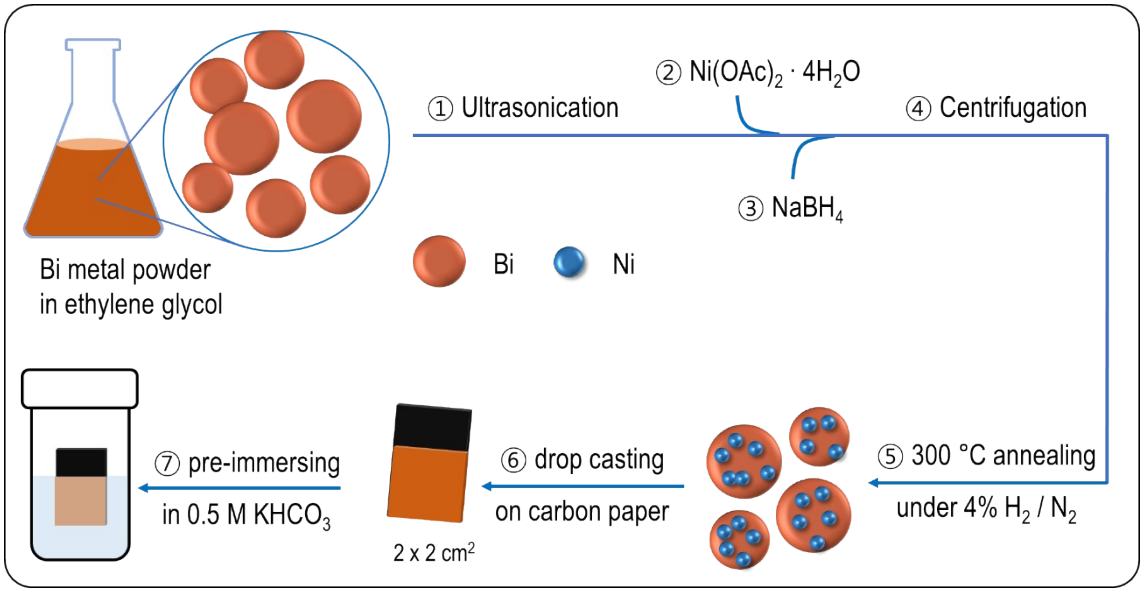

Figure S1. Scheme for preparation of the BiNi heterometallic working electrodes.

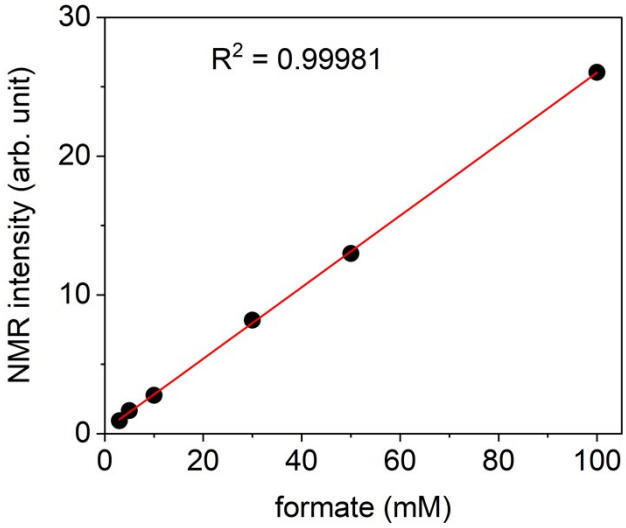

Figure S2. Calibration curves of $HCOO^-$ is obtained by plotting the relative area of $HCOO^-$ signal of standard samples containing 3, 5, 10, 30, 50 and 100 mM of $HCOO^-$.

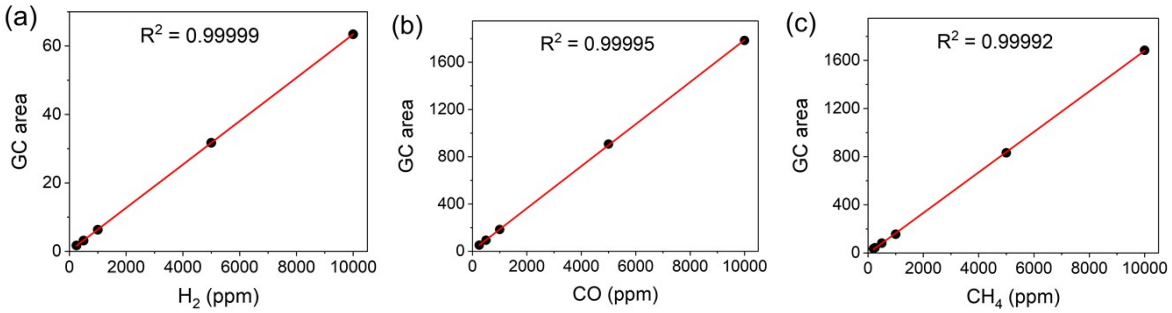

Figure S3. Calibration curves of (a) H_2, (b) CO and (c) CH_4 are obtained by plotting the area of standard gases containing 250, 500, 1000, 5000 and 10000 ppm of H_2, CO and CH_4.

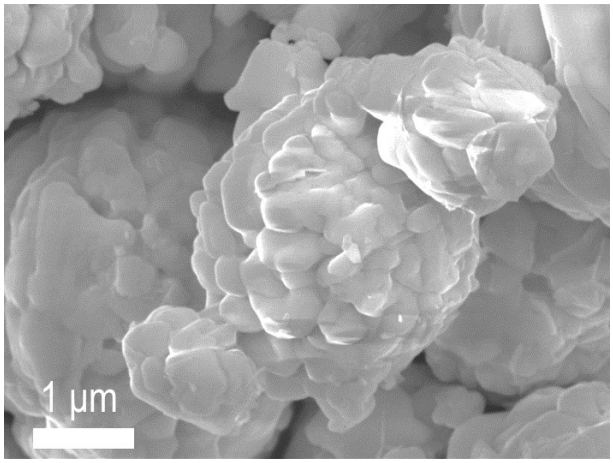

Figure S4. SEM image of as-received Bi metal.

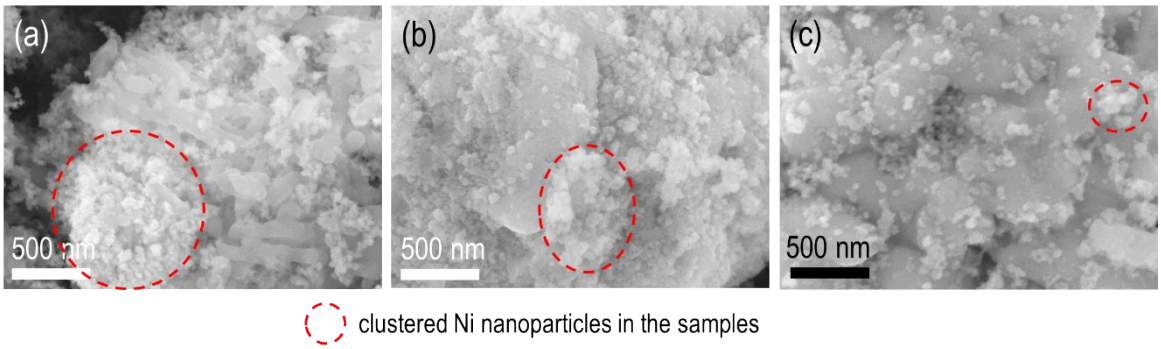

Figure S5. SEM image of pristine (a) $BiNi_{0.15}$, (b) $BiNi_{0.093}$ and (c) $BiNi_{0.038}$.

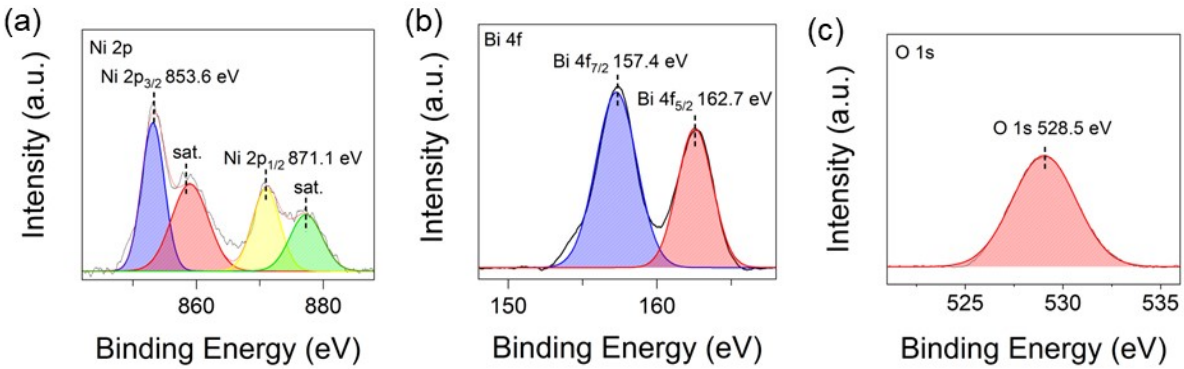

Figure S6. XPS analyses of the pristine $BiNi_{0.15}$, (a) Bi 4f, (b) Ni 2p and (c) O 1s spectra.

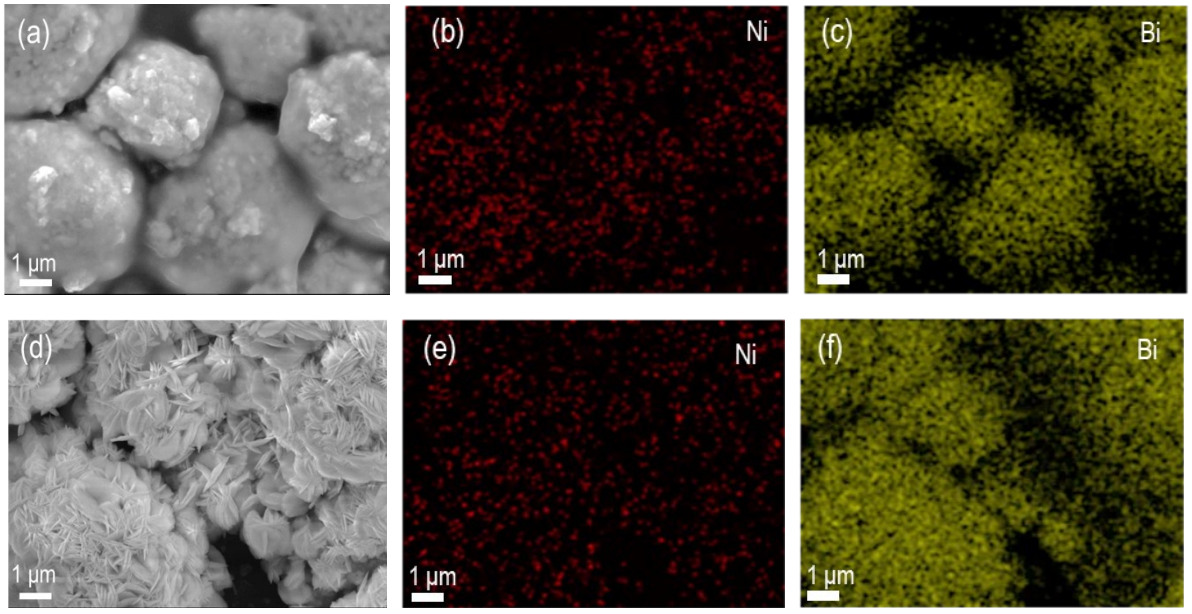

Figure S7. SEM and EDS images of $BiNi_{0.093}$ samples of pristine (a, b, c) and 2 days pre-immersed (d, e, f).

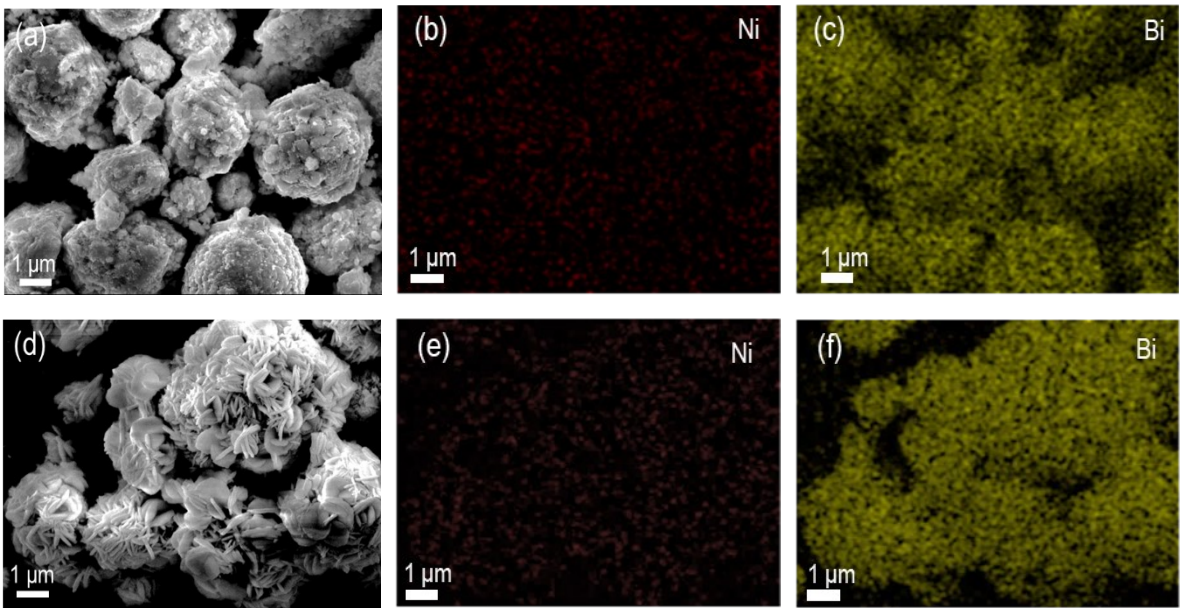

Figure S8. SEM and EDS images of $BiNi_{0.038}$ samples of pristine (a, b, c) and 2 days pre-immersed (d, e, f).

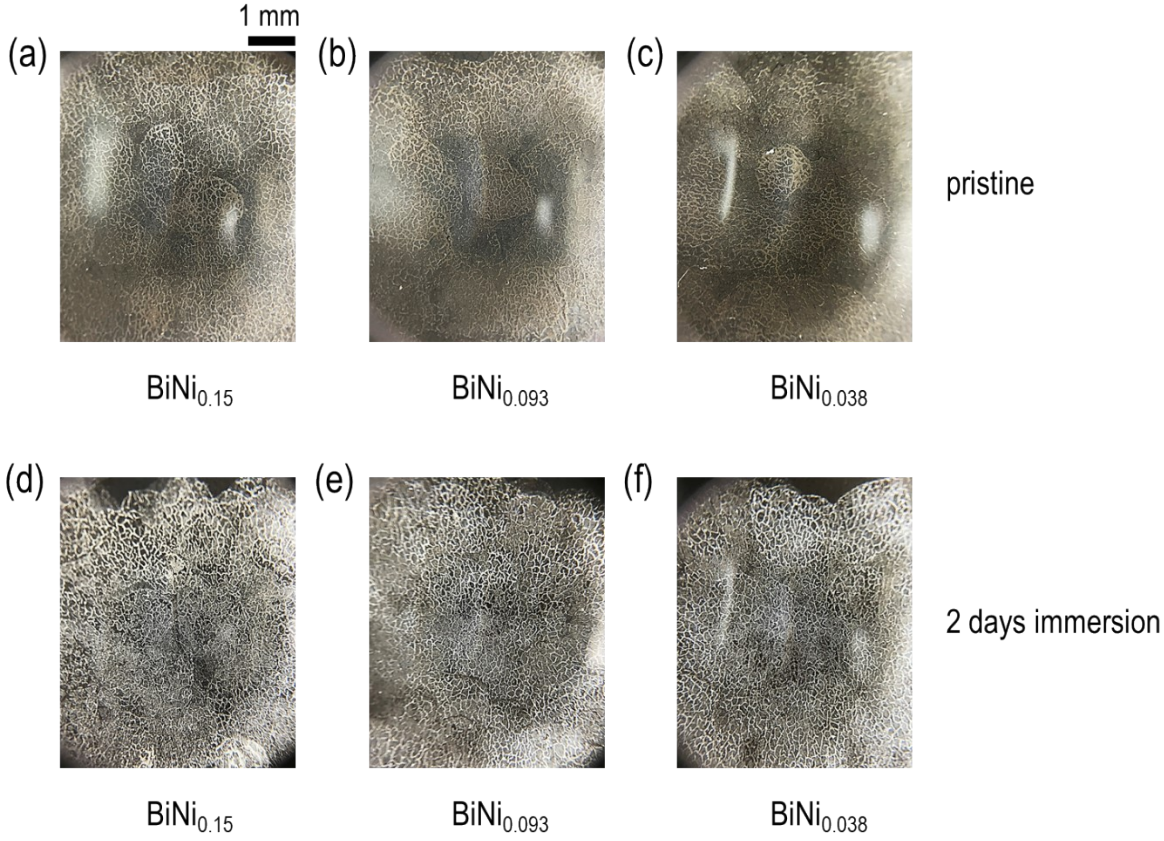

Figure S9. Optical microscope images of pristine $BiNi_{0.15}$ (a), $BiNi_{0.093}$ (b) and $BiNi_{0.038}$ (c), and 2 days pre-immersed $BiNi_{0.15}$ (d), $BiNi_{0.093}$ (e) and $BiNi_{0.038}$ (f), respectively.

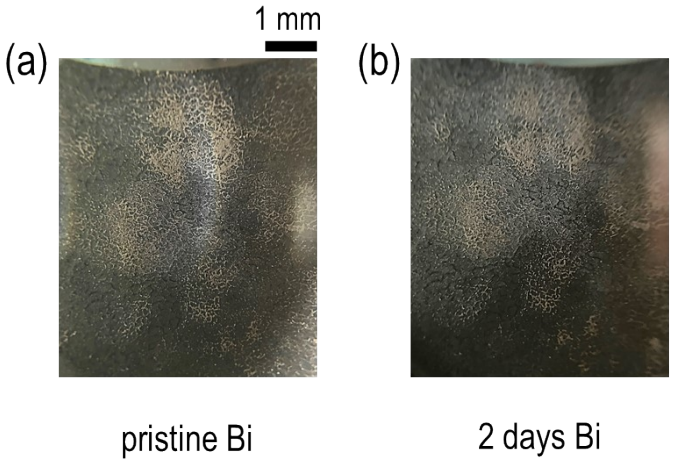

Figure S10. Optical microscope image of pristine Bi (a), and 2 days pre-immersed Bi (b).

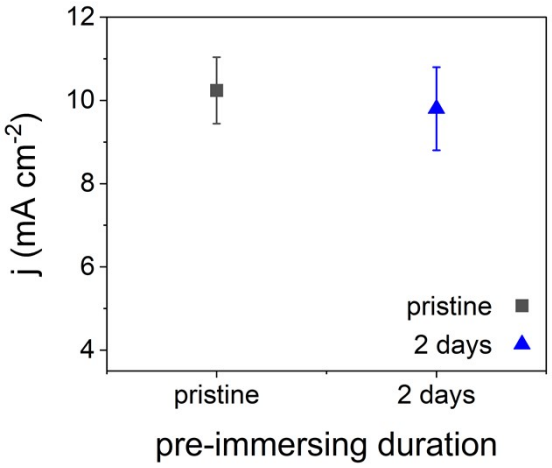

Figure S11. Current density of pristine and 2 days pre-immersed Bi metal.

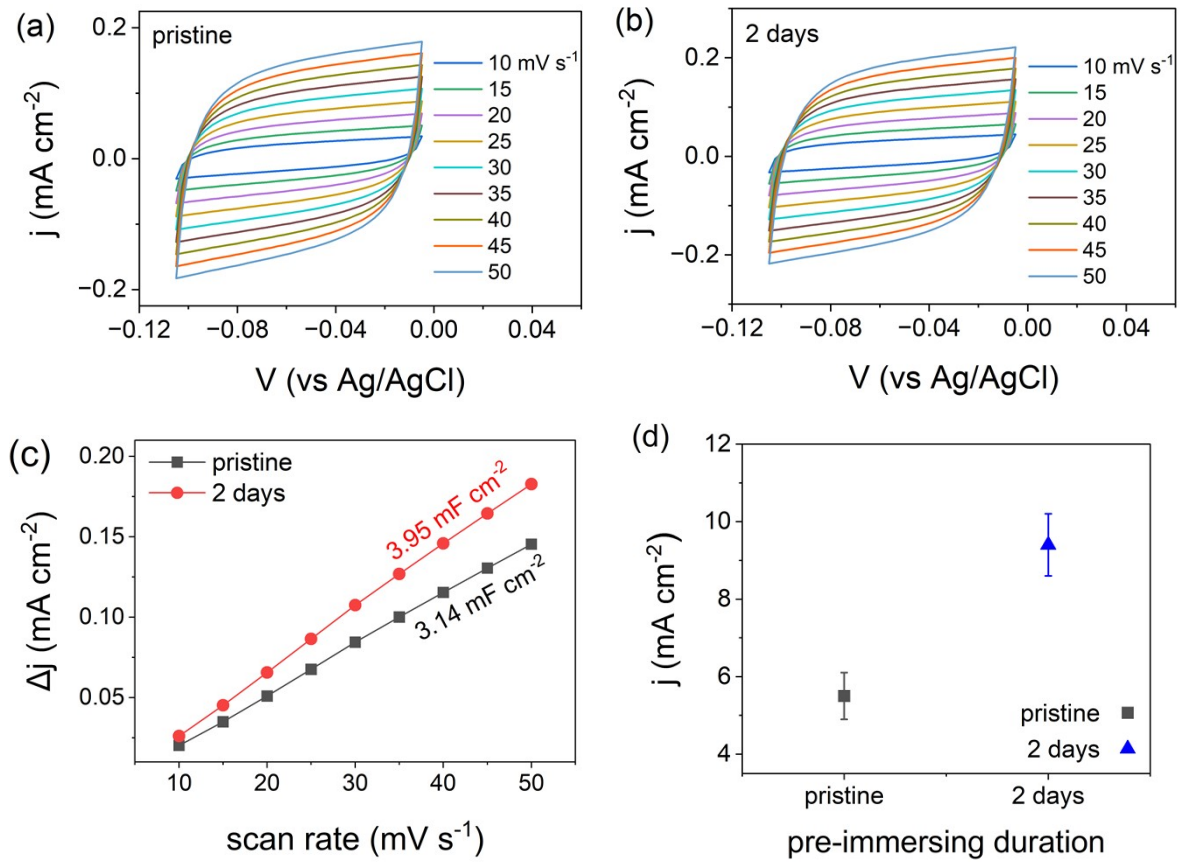

Figure S12. Cyclic voltammetry curves of (a) pristine and (b) 2 days pre-immersed $BiNi_{0.093}$ at different sweep rates. (c) electrochemical double-layer capacitance (C_{dl}) of samples and (d) current density of pristine and 2 days pre-immersed $BiNi_{0.093}$.

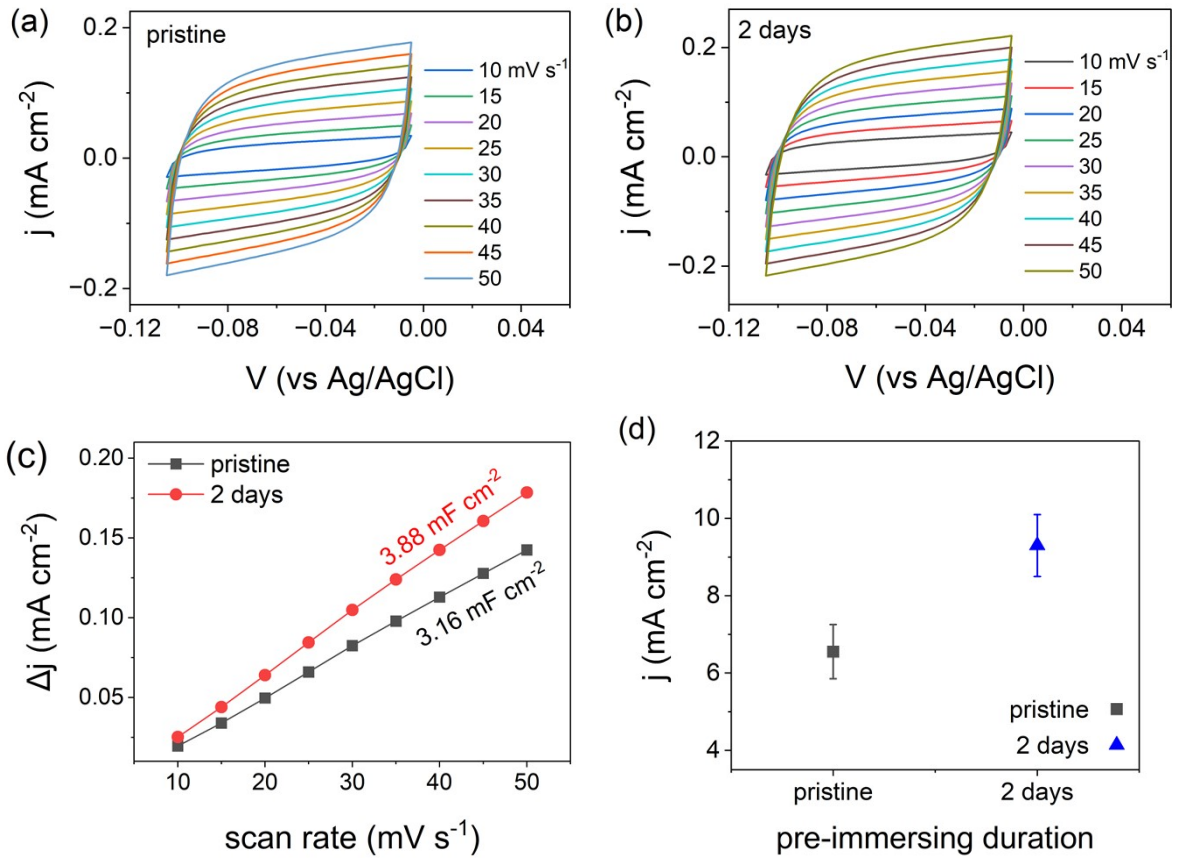

Figure S13. Cyclic voltammetry curves of (a) pristine and (b) 2 days pre-immersed $BiNi_{0.038}$ at different sweep rates. (c) electrochemical double-layer capacitance (C_{dl}) of samples and (d) current density of pristine and 2 days pre-immersed $BiNi_{0.038}$.

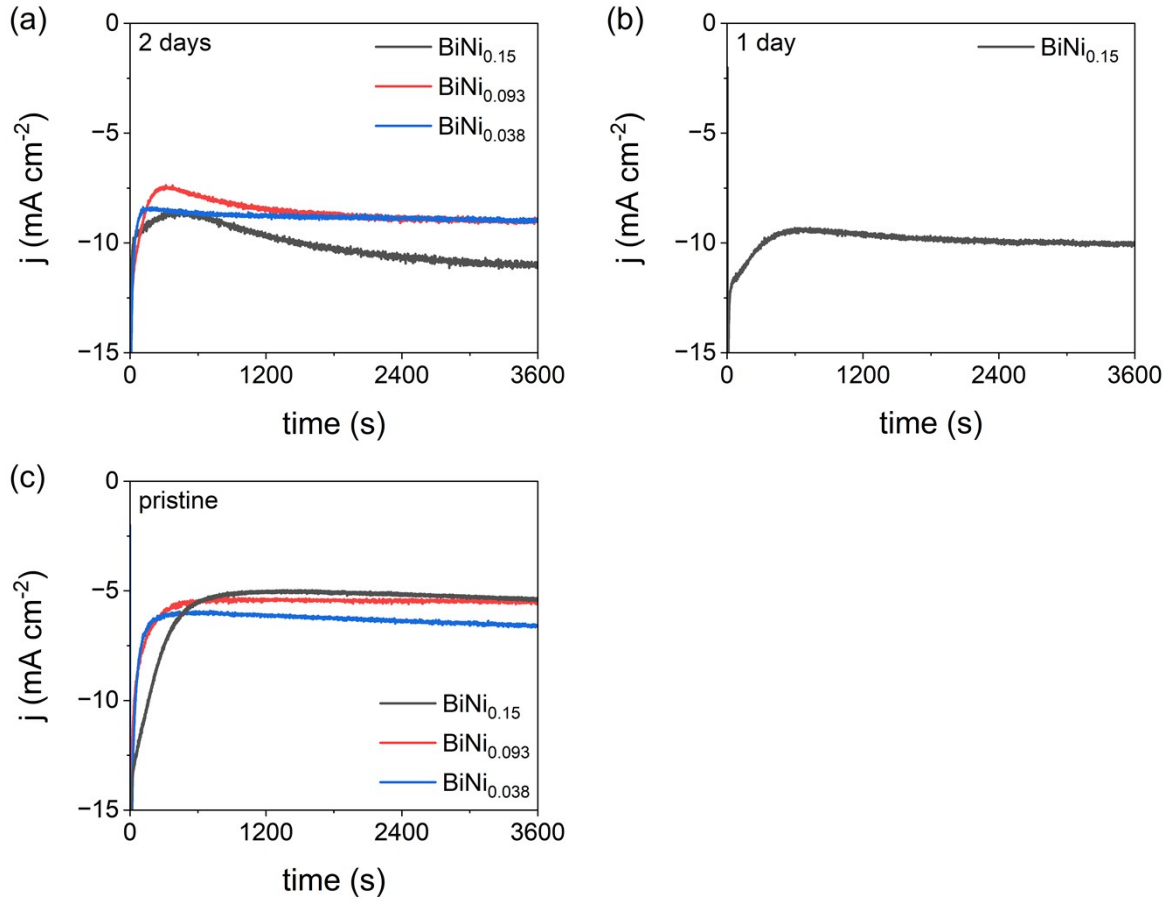

Figure S14. Chronoamperometry curves of (a) 2 days and (b) 1 day pre-immersed and (c) pristine catalysts at -1.5 V *vs*. Ag/AgCl (3M KCl) in CO_2-saturated 0.5 M $KHCO_3$ electrolyte, respectively.

Table S1. Molar ratio of Bi – Ni catalysts from ICP-OES.

Electrode Material	$BiNi_{0.15}$	$BiNi_{0.093}$	$BiNi_{0.038}$
Bi : Ni ratio (mmol) in the starting materials	1 : 0.33	1 : 0.17	1 : 0.056
As prepared powder of Bi-Ni catalysts	1 : 0.15	1 : 0.093	1 : 0.038
Pristine catalysts on carbon paper	1 : 0.16	1 : 0.091	1 : 0.037
1 day pre-immersing on carbon paper	1 : 0.12	-	-
2 days pre – immersing on carbon paper	1 : 0.11	1 : 0.075	1 : 0.028