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Enhanced Electrocatalytic Activity of low-cost NiO Microflowers on Graphene Paper for Oxygen Evolution Reaction

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ELECTRONIC SUPPLEMENTARY INFORMATION

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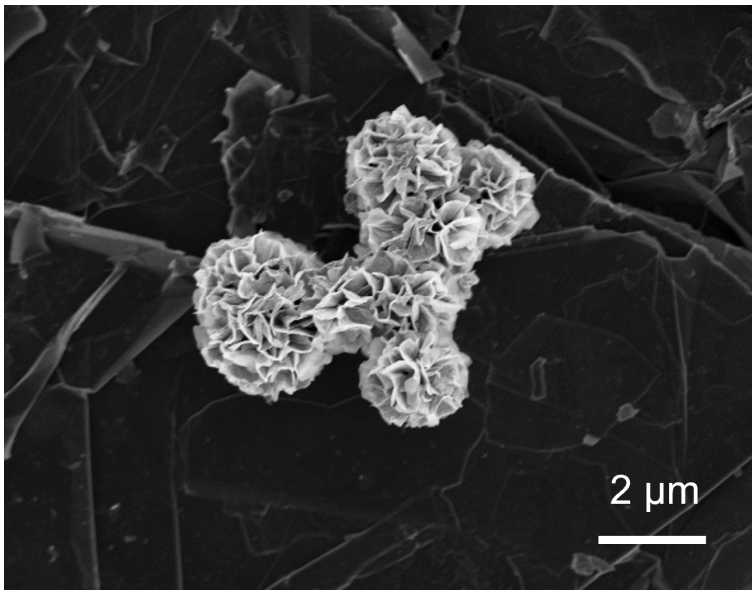

Figure S1: SEM images of NiO µFs on GP after electrochemical tests.

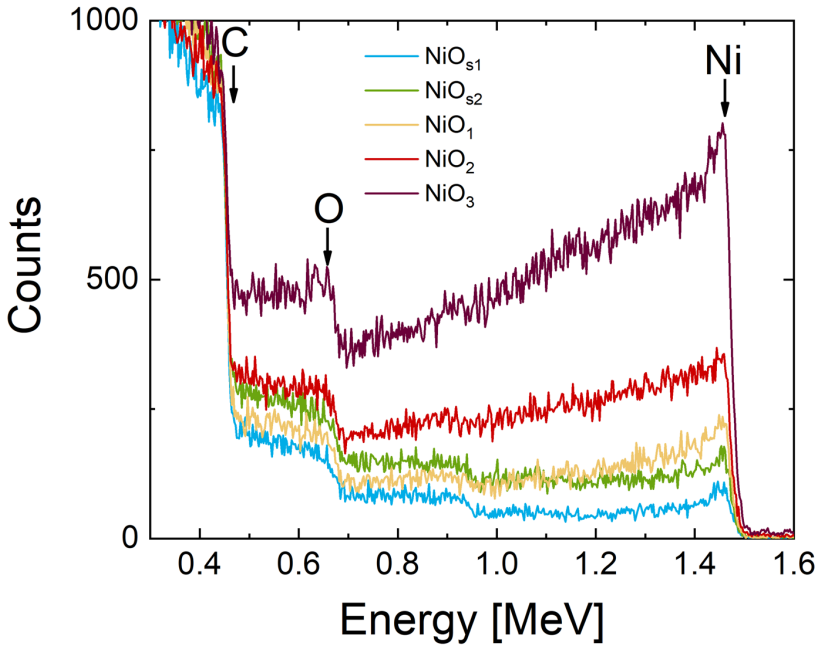

Figure S2: RBS spectra of NiO µFs on GP.

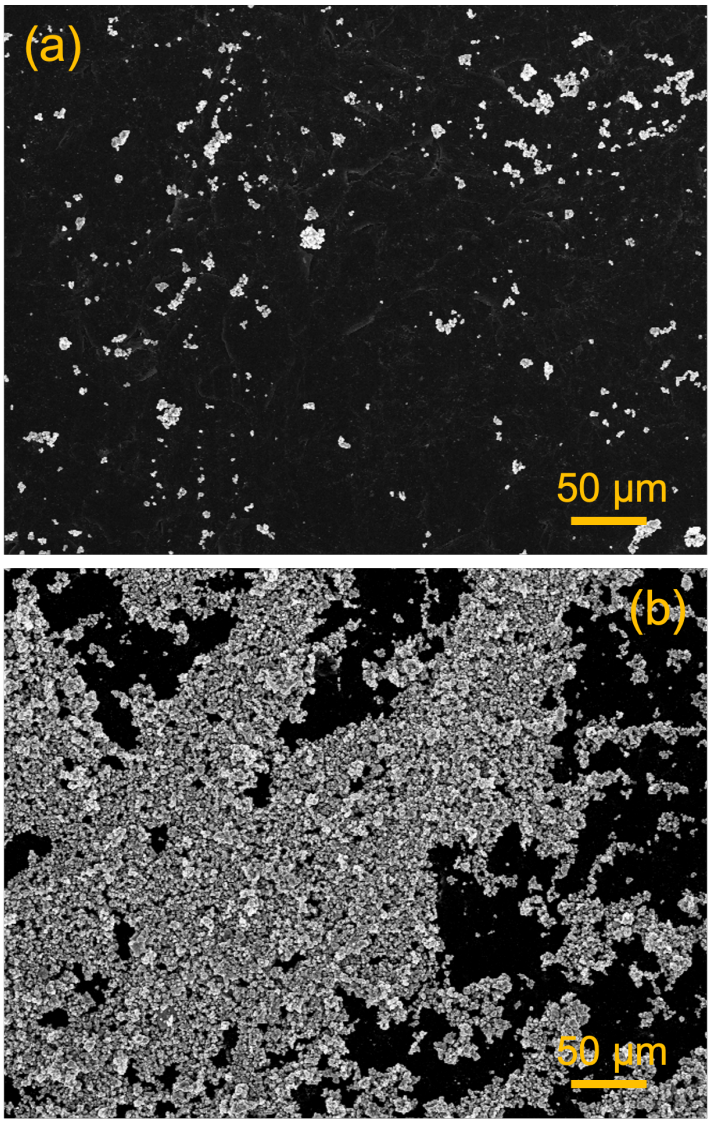

Figure S3: SEM images of NiO µFs on GP deposited via (a) spin coating or (b) drop casting.

Sample	R_u [Ω]	R_{ct} [Ω]	R_p [Ω]	C_{dl} [mF s^{n-1}]	n_1	C_p[mF s^{n-1}]	n_2
NiO_{s1}	4.67 ± 0.01	2.71 ± 0.03	18.6 ± 0.1	6.05 ± 0.08	0.8	2.38 ± 0.04	0.6
NiO_{s2}	4.44 ± 0.03	2.00 ± 0.06	12.9 ± 0.2	6.93. ±0.2	0.8	2.35 ± 0.2	0.6
NiO_{D1}	5.47 ± 0.02	0.68 ± 0.02	13.1 ± 0.1	6.89 ± 0.08	0.8	1.84 ± 0.05	0.8
NiO_{D2}	4.78 ± 0.01	0.61 ± 0.03	11.1 ± 0.1	7.3 ± 0.1	0.8	1.3 ± 0.5	0.7
NiO_{D3}	4.54 ± 0.01	0.43 ± 0.02	10.3 ± 0.1	9.87 ± 0.08	0.9	0.62. ±0.06	0.6

Table S1: EIS fitting parameters.

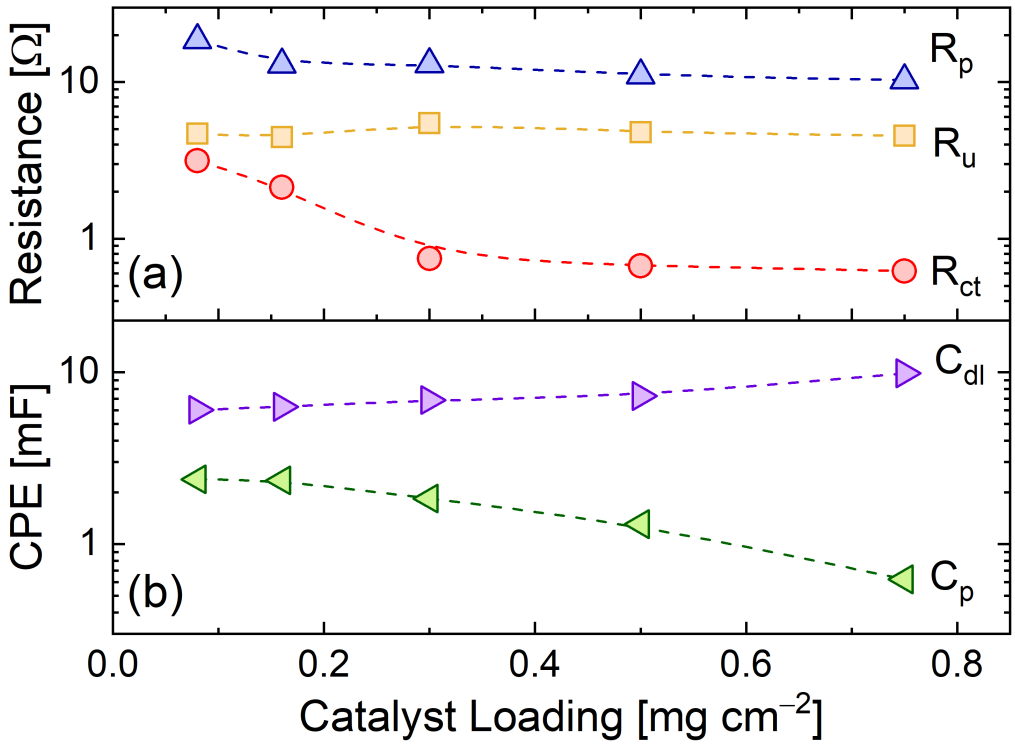

Figure S4: Behavior of equivalent circuit elements as a function of mass loading.

OER MECHANISM AT NICKEL-BASED ELECTRODES.

Nickel-based materials are considered some of the most promising transition metal catalysts for the Oxygen Evolution Reaction (OER) in alkaline media[1,2]. Subsequently to the immersion of NiO electrodes in an aqueous solution a layer of $Ni(OH)_2$ is spontaneously formed at open circuit potential[2]. During the oxidation/reduction cycling the Ni hydroxide layer grows after the conversion of Ni(II) to Ni(III) and the formation of NiOOH during the charge step and the re-formation of $Ni(OH)_2$ during the discharge step of the cyclic voltammetry[3]. The charge/discharge process of the NiO/ $Ni(OH)_2$ electrode can be described as follows[4]:

$$Ni(OH)_2 + OH^- \leftrightarrow NiOOH + H_2O + e^- \quad (S1)$$

$$NiO + OH^- \leftrightarrow NiOOH + e^- \quad (S2)$$

Upon the growth of the $Ni(OH)_2$layer, a significant increase in the OER activity is generally observed for a hydrous nickel oxide electrodes[5]. Besides the formation of a stable and optimal

$Ni(OH)_2$ layer and the formation of different charge/discharge phases[6] after potential cycling, an increase of roughness and of the number of electrochemically active sites on surface is observed[1].

In terms of a mechanistic analysis of the OER, the major difficulty is represented by the fact that the OER is a complex process involving the transfer of four electrons. Since electrons are transferred one by one, the process will be multistep[7]. Among different proposed mechanisms present in literature, Lyons *et al.*[2,7,8] suggested a mechanistic pathway which involves intermediate species in the Ni(III) valence state. For the case of anodic oxide covered Ni anodes such a pathway might be written as follows[9]:

$$[\mathrm{Ni(III)O}_m(\mathrm{OH})_n]^{p-} + \mathrm{OH}^- \rightarrow [\mathrm{Ni(III)O}_{m+1}(\mathrm{OH})_{n-1}]^{p-} \quad \text{(S3a)}$$

$$[\mathrm{Ni(III)O}_{m+1}(\mathrm{OH})_{n-1}]^{p-} \rightarrow [\mathrm{Ni(III)O}_m\mathrm{OOH}(\mathrm{OH})_{n-2}]^{(p-1)-} + \mathrm{e}^- \quad \text{RDS} \quad \text{(S3b)}$$

$$[\mathrm{Ni(III)O}_m\mathrm{OOH}(\mathrm{OH})_{n-2}]^{(p-1)-} + 2\mathrm{OH}^- \rightarrow [\mathrm{Ni(III)O}_m\mathrm{O}_2(\mathrm{OH})_{n-1}]^{p-} + \mathrm{H_2O} + \mathrm{e}^- \quad \text{(S3c)}$$

$$[\mathrm{Ni(III)O}_m\mathrm{O}_2(\mathrm{OH})_{n-1}]^{p-} + \mathrm{OH}^- \rightarrow [\mathrm{Ni(III)O}_m(\mathrm{OH})_n]^{p-} + \mathrm{O_2} + \mathrm{e}^- \quad \text{(S3d)}$$

According to this mechanism the rate determining step (RDS) for the OER is represented by the formation of a superoxy-(OOH) species by the addition of an OH^- ion on top of an adsorbed oxygen atom with a Tafel slope of around 40 $\mathrm{mV\ dec^{-1}}$.

MASS ACTIVITY DETERMINATION.

Mass activity is defined as the ratio between a fixed current density j and the catalyst loading. In our case we calculate the mass activity at a current density of 10 $\mathrm{mA\ cm^{-2}}$ by using the following expression:

$$\text{Mass activity} = \frac{j\ [\mathrm{A\ cm^{-2}}]}{\text{catalist loading}\ [\mathrm{mg\ cm^{-2}}]} \quad \text{(S4)}$$

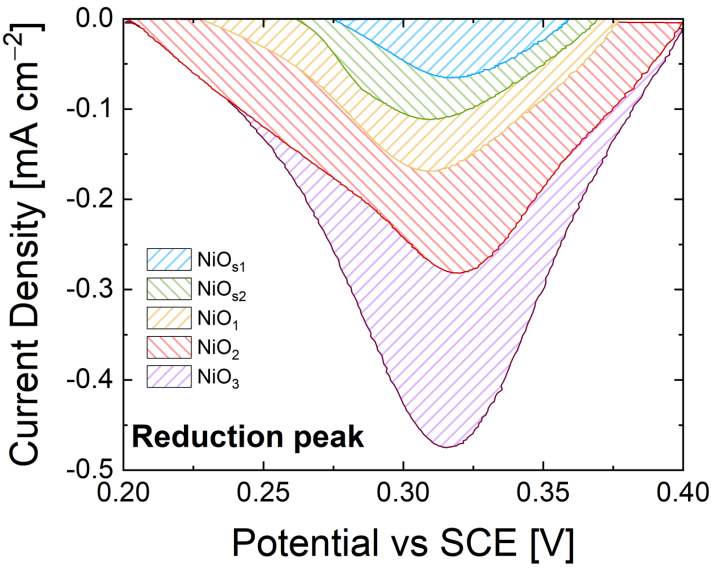

Figure S5: Reduction peaks of NiO electrodes after the first backward scan during CV.

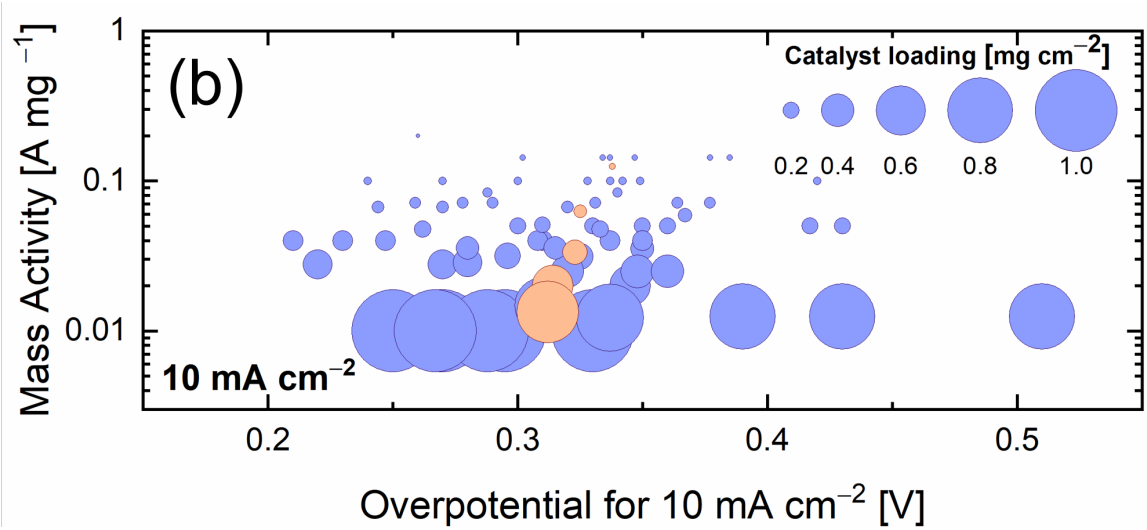

Figure S6: Mass activity at 10 mA cm^{-2} as a function of the overpotential and the catalyst loading [adapted from 10].

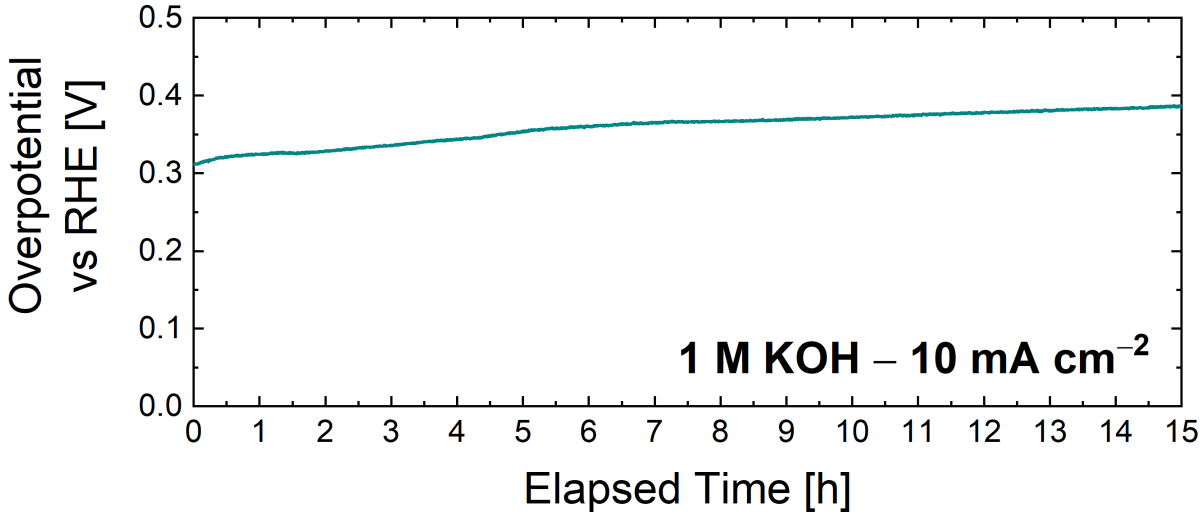

Figure S7: Chronopotentiometric test of NiO_{D2} electrode.

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