Electronic Supplementary Information

Recent advances in selective methanol oxidation electrocatalysts for the co-production of hydrogen and value-added formate

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Table S1. The catalytic properties of the existing catalysts for SMOR

Catalyst	Electrolyte	Scan rate /mV s^{-1}	Potential at a certain current density for SMOR/V vs. RHE	Faradaic efficiency of formate/%	Stability/h	Overpotential of HER/mV	Potential at a certain current density for SMOR&HER/V vs. RHE	Ref.
Part A: Single atom catalyst								
Cu_{SA}-Rh MAs/CF	1 M KOH + 4 M CH_3OH	5	1.40@50 mA cm^{-2} 1.44@100 mA cm^{-2} 1.46@150 mA cm^{-2} 1.47@200 mA cm^{-2}	~90	/	/	/	1
$Pt_1/Ti_{0.8}W_{0.2}N_xO_y$	0.5 M KOH + 0.5 M CH_3OH	50	0.82@560 mA mg^{-1}_{Pt}	90	10@0.8 V vs. RHE	/	/	2
Part B: Metal and metal alloy								
Ni/WC	1 M NaOH + 1 M CH_3OH	5	/	93.8	10@0.5 V vs. Ag/AgCl	/	/	3
Ni-NF-Af	1 M KOH + 0.5 M CH_3OH	5	1.345@100 mA cm^{-2}	~100	5@100 mA cm^{-2}	/	/	4
Ni-MOFs@350	1 M KOH + 1 M CH_3OH	5	1.37@100 mA cm^{-2}	98.4	Multistep CA (5 h/step)	/	/	5
Ni-MOFs-120/NF	1 M KOH + 0.5 M CH_3OH	5	1.37@10 mA cm^{-2} 1.44@100 mA cm^{-2}	/	20@1.4 V vs. RHE	/	/	6
NiCo@NF	1 M KOH +	5	1.30@50 mA cm^{-2}	/	50@50 mA	220@50 mA cm^{-2}	1.41@25 mA cm^{-2}	7

	1 M CH_3OH		1.42@100 mA cm^{-2}		cm^{-2}			
NiCo-NF-ET	1 M KOH + 0.5 M CH_3OH	5	1.228@10 mA cm^{-2} 1.272@50 mA cm^{-2} 1.291@100 mA cm^{-2}	~100	10@1.42 V vs. RHE	/	/	8
NiCu@Cu	1 M KOH + 2 M CH_3OH	5	1.32@10 mA cm^{-2}	>95	17@50 mA cm^{-2}	85@50 mA cm^{-2}	1.45@10 mA cm^{-2}	9
NiIr-MOF/NF	1 M KOH + 4 M CH_3OH	5	1.33@10 mA cm^{-2} 1.41@100 mA cm^{-2}	~100	20@10 mA cm^{-2}	17@10 mA cm^{-2}	1.39@10 mA cm^{-2}	10
FeRu-MOF	1 M KOH + 4 M CH_3OH	5	1.32@10 mA cm^{-2} 1.37@100 mA cm^{-2}	>90	24@40 mA cm^{-2}	42@10 mA cm^{-2}	1.40@10 mA cm^{-2}	11
NiCoMo	1 M KOH + 1 M CH_3OH	5	1.34@50 mA cm^{-2} 1.37@100 mA cm^{-2} 1.41@200 mA cm^{-2}	85.5	50	125@50 mA cm^{-2}	1.46@50 mA cm^{-2}	12
Part C: Oxide								
NiO/NF	1 M KOH + 1 M CH_3OH	10	1.53@100 mA cm^{-2}	/	20000 s@1.82 V vs. RHE	/	/	13
Co_3O_{4-x}/NF-P	1 M KOH + 1 M CH_3OH	/	1.318@10 mA cm^{-2}	>95	27@50 mA cm^{-2}	/	1.54@10 mA cm^{-2}	14
Co–N–C/CoO/CF	1 M KOH + 0.5 M CH_3OH	2	1.309@50 mA cm^{-2}	98.2	120@1.4 V vs. RHE	/	/	15
Nb_2O_5/NF	1 M KOH + 1 M CH_3OH	/	1.47@100 mA cm^{-2}	~100	Multistep CA (2 h/step)	/	/	16
CuO/CF	1 M KOH + 1 M CH_3OH	5	/	~100	24@1.82 V vs. RHE	/	/	17

CuO NS/CF	1 M KOH + 1 M CH_3OH	5	1.47@100 mA cm^{-2}	97	42@1.32 V vs. RHE	/	/	18
$B/CuCo_2O_4$	1 M KOH + 1 M CH_3OH	50	/	43	2@0.6 V vs. Ag/AgCl	/	/	19
$NiFe_2O_4$/NF	1 M KOH + 0.5 M CH_3OH	5	/	>95	6	/	/	20
$LaCo_{0.5}Fe_{0.5}O_3$	1 M KOH + 1 M CH_3OH	10	/	44	2@1.6 V vs. RHE	/	/	21
Part D: Hydroxide								
$Ni(OH)_2$/NF	1 M KOH + 0.5 M CH_3OH	5	1.36@100 mA cm^{-2}	~100	15@20 mA cm^{-2}	185@10 mA cm^{-2}	1.52@10 mA cm^{-2} 1.62@50 mA cm^{-2}	22
β-$Ni(OH)_2$/NF	1 M KOH + 1 M CH_3OH	5	1.398@10 mA cm^{-2}	99.98	9@1.6 V vs. RHE	/	1.684@10 mA cm^{-2}	23
LC–$Ni(OH)_2 \cdot xH_2O$	1 M KOH + 0.5 M CH_3OH	5	1.39@100 mA cm^{-2}	100	100000 s@1.42 V vs. RHE	/	/	24
Co^{2+}-doped $Ni(OH)_2$	1 M NaOH + 0.5 M CH_3OH	1	1.32@100 mA cm^{-2}	≥ 96.5	20@25 mA cm^{-2}	/	/	25
NiMn-LDHs	1 M KOH + 3 M CH_3OH	5	1.41@100 mA cm^{-2} 1.49@500 mA cm^{-2}	~100	20@100 mA cm^{-2}	/	/	26
NiFe-LDHs			1.45@100 mA cm^{-2} 1.62@500 mA cm^{-2}	/	/	/	/	
NiFe LDH@SnO_2/NF	1 M KOH + 0.5 M CH_3OH	5	1.396@10 mA cm^{-2}	/	12@100 mA cm^{-2}	/	/	27
NiFe-LDH/NiFe-	1 M KOH +	/	1.416@10 mA cm^{-2}	~100	28@20 mA	/	/	28

HAB/CF	3 M CH_3OH		1.538@100 mA cm^{-2}		cm^{-2}			
$Ni_{0.33}Co_{0.67}(OH)_2$/ NF	1 M KOH + 0.5 M CH_3OH	5	1.33@10 mA cm^{-2}	~100	20@1.35 V vs. RHE	/	1.5@10 mA cm^{-2}	29
NiCo-LDH-E-30/NF	1 M KOH + 1 M CH_3OH		1.31@10 mA cm^{-2} 1.36@100 mA cm^{-2}	>95	120@100 mA cm^{-2}	/	/	30
S–NiCo-LDH	1 M KOH + 1 M CH_3OH	/	1.26@10 mA cm^{-2} 1.39@100 mA cm^{-2}	~100	Multistep CA (2 h/step)	/	/	31
Co_xP@NiCo-LDH	1 M KOH + 0.5 M CH_3OH	5	1.24@10 mA cm^{-2}	~100	20@1.35 V vs. RHE	100@10 mA cm^{-2}	1.43@10 mA cm^{-2} 1.50@20 mA cm^{-2}	32
$NiFe_xP$@NiCo-LDH	1 M KOH + 0.5 M CH_3OH	5	/	100	10@0.96 V vs. RHE	100@10 mA cm^{-2}	1.42@10 mA cm^{-2}	33
$NiCo_xP$@ NiCo-LDH/CC	1 M KOH + 0.5 M CH_3OH	5	1.23@10 mA cm^{-2}	~100	10@1.35 V vs. RHE	132@10 mA cm^{-2}	1.43@10 mA cm^{-2}	34
NiCo-m	1 M KOH + 3 M CH_3OH	10	1.31@30 mA cm^{-2} 1.35@50 mA cm^{-2} 1.40@100 mA cm^{-2}	/	Multistep CA	200@50 mA cm^{-2}	1.50@20 mA cm^{-2}	35
$Cu_{0.33}$CoCo-LDH/CF	1 M KOH + 3 M CH_3OH	/	1.28@10 mA cm^{-2}	~100	24@20 mA cm^{-2}	/	/	36
Part E: Nonmetal alloy								
Ni_3C	1 M KOH + 0.5 M CH_3OH	/	/	100	50000 s@120 mA cm^{-2}	/	/	37
Cu_3N	1 M KOH + 1 M CH_3OH	/	1.35@10 mA cm^{-2}	>90	12	/	/	38
Ni-MoN/NF	1 M KOH +	5	1.48@100 mA cm^{-2}	99.8	/	49@10 mA cm^{-2}	0.56@10 mA cm^{-2}	39

	0.5 M CH_3OH					193@100 mA cm^{-2}		
$Ni_2Co_2Fe_1$-P	1 M KOH + 2 M CH_3OH	1	1.49@20 mA cm^{-2}	/	Multistep CA (1 h/step)	61@20 mA cm^{-2}	1.48@20 mA cm^{-2}	40
NiS	1 M KOH + 1 M CH_3OH	50	/	98	3@1.6 V vs. RHE	/	/	41
Ni_3S_2/CNTs	1 M KOH + 1 M CH_3OH	/	1.36@100 mA cm^{-2}	>95	20@100 mA cm^{-2}	/	/	42
Ni_3S_2-CNFs	1 M KOH + 1 M CH_3OH	5	1.40@100 mA cm^{-2}	99.82	3@1.62 V vs. RHE	/	/	43
CC@$NiCo_2S_4$	1 M KOH + 1 M CH_3OH	5	1.40@100 mA cm^{-2}	~100	3@1.7 V vs. RHE		1.32@10 mA cm^{-2}	44
FCNS@NF	1 M KOH + 1 M CH_3OH	2	1.42@100 mA cm^{-2}	98.67	10@1.4 V vs. RHE	/	/	45
h-NiSe/CNTs	1 M KOH + 1 M CH_3OH	5	1.57@50 mA cm^{-2} 1.66@100 mA cm^{-2} 1.75@200 mA cm^{-2} 1.91@400 mA cm^{-2}	97.97	20@1.62 V vs. RHE	/	/	46
CNFs@NiSe/CC	1 M KOH + 1 M CH_3OH	5	1.47@200 mA cm^{-2} 1.50@300 mA cm^{-2} 1.55@400 mA cm^{-2}	>98	20@1.62 V vs. RHE	/	/	47
$Ni_{0.9}Co_{0.1}Se$	1 M NaOH + 1 M CH_3OH	10	1.65@185 mA cm^{-2}	84	/	/	/	48
$Ni_{0.75}Fe_{0.25}Se_2$	1 M KOH + 0.5 M CH_3OH	50	/	99.7	10000 s@1.48 V vs. RHE	/	/	49

NiP_x-R	1 M KOH + 0.5 M CH_3OH	5	1.40@400 mA cm^{-2}	/	/	/	/	50
NiS_x-R			1.49@400 mA cm^{-2}			/	/	
$NiSe_x$-R			1.517@400 mA cm^{-2}			/	/	
Part F: Multi-component heterostructure catalyst								
Pt-Co_3O_4/CP	1 M NaOH + 2 M CH_3OH+ 3.5%NaCl	5	0.555@10 mA cm^{-2}	~93	/	50@10 mA cm^{-2}	0.55@10 mA cm^{-2}	51
Ru&Fe-WOx	1 M NaOH + 3 M CH_3OH	/	1.35@10 mA cm^{-2} 1.51@500 mA cm^{-2}	~100	37.5@500 mA cm^{-2}	32@10 mA cm^{-2}	1.5@100 mA cm^{-2} 1.62@500 mA cm^{-2}	52
CuS@CuO/CF	1 M KOH + 1 M CH_3OH	10	/	99%	6	/	/	53
CeO_2-RuO_2	0.5 M H_2SO_4 + 2.5 M CH_3OH	10	1.195@10 mA cm^{-2}	53.72	24@1.32 V vs. RHE	/	1.30@10 mA cm^{-2}	54
Fe_2O_3/NiO-NF	1 M KOH + 1 M CH_3OH	5	1.328@onset 1.654@500 mA cm^{-2}	>98	40@300 mA cm^{-2}	/	/	55
Bi_2O_3-SnO@CuO	1 M KOH + 1 M CH_3OH	5	1.53@100 mA cm^{-2}	~100	8@1.7 V vs. RHE	/	/	56
CNTs@CoO–$Ni(OH)_2$	1 M KOH + 1 M CH_3OH	5	1.36@100 mA cm^{-2}	>95	40@1.4 V vs. RHE	/	1.39@10 mA cm^{-2}	57
$Cu(OH)_2$@NiFe($OH)_x$	1 M KOH + 3 M CH_3OH	/	1.32@60 mA cm^{-2}	~100	22@10 mA cm^{-2}	/	/	58
Ni_3B/Ni	1 M KOH + 1 M CH_3OH	5	/	~100	24@100 mA cm^{-2}	/	/	59
Co-Ni-P/NF	1 M KOH + 0.5 M CH_3OH	5	1.33@100 mA cm^{-2}	100	20@100 mA cm^{-2}	145@100 mA cm^{-2}	1.45@100 mA cm^{-2}	60
Ni_2P-CoP/NF	1 M KOH +	/	1.16@10 mA cm^{-2}	99.8	20@20 mA	96@10 mA cm^{-2}	1.56@50 mA cm^{-2}	61

	0.5 M CH_3OH		1.27@50 mA cm^{-2} 1.30@100 mA cm^{-2}		cm^{-2}	160@100 mA cm^{-2}		
Cu_2Se/Co_3Se_4	1 M KOH + 1 M CH_3OH	5	1.39@10 mA cm^{-2}	100	20000 s@10 mA cm^{-2}	/	/	62

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