Supporting Information (SI)

Syngas Production from Electrochemical Reduction of CO_2: Current Status and Prospective Implementation

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A. List of electrocatalysts used for the CO_2 reduction to CO

Table S1. Detailed conditions and results achieved in experiments made with Ag-based electrodes for the reduction of CO_2 to CO (as the main C-based product).

Exp. Nr.	Cathodic Potential (V *vs.* NHE)	Electro-catalyst	Electrode size (cm^2)	Ag loading (wt %)	FE (%)	Current density ǂ (-mA·cm^{-2})	Catholyte	Anolyte	Test time (h)	Ref.
1	-1.5	Ag/C (GDE)	N/A	60	7	5	1 M KOH	1 M KOH	N/A	[1]
2	-1.56	Ag	1	-	30	50	0.5 M $KHCO_3$	0.5 M $KHCO_3$	2	[2]
3	-1.65	Ag/ g-C_3N_4	6.25	40	33	20	0.1 M KH_2PO_4 / K_2HPO_4	0.1 M KH_2PO_4 / K_2HPO_4	20	[3]
4	-3.5	Ag	N/A	-	33	80	0.2 M $KHCO_3$	KOH	7	[4]
5	-1.45	Ag/C	1	-	30	50	0.5 M $KHCO_3$	0.1 M KOH	8	
6	-2.96	Ag (SPE/CEM)	0.2	-	52.7	100	0.2 M K_2SO_4	0.2 M K_2SO_4	2	[5]
7	-1.46	Ag	N/A	-	60	50	0.5 M $KHCO_3$	KOH	7	[4]
8	-1.46	Ag	N/A	-	64.6	50	0.2 M K_2SO_4	0.2 M K_2SO_4	2	[5]
9	-1.5	Ag/Pc (GDE)	N/A	6.25	78	55	1 M KOH	1 M KOH	N/A	[1]
10	-1.8	Ag	N/A	-	80	70	0.5 or 0.8M K_2SO_4	2.5M KOH	1.5 h	[6]
11	-1.1	Ag	N/A	-	84	35	1 M $KHCO_3$	1 M $KHCO_3$	1	[7]
12	-1.02	Ag	1	-	86	300	0.5 M $KHCO_3$ (20 atm)	0.5M $KHCO_3$	N/A	[8]
13	-1.5	Ag/Pz (GDE)	N/A	2.51	88	65	1 M KOH	1 M KOH	N/A	[1]
14	-1.5	Ag/DAT (GDE)	N/A	8.62	89	73	1 M KOH	1 M KOH	N/A	[1]
15	-1.6	Ag/TiO_2	0.09	40	90	101	1M KOH	1M KOH	N/A	[9]
16	-1.02	Ag Np	N/A	-	92	18	0.5 M $KHCO_3$		N/A	[10,11]
17	-1.3	Ag (SPE/AEM)	0.2	-	92.3	20	0.2 M K_2SO_4	0.2 M K_2SO_4	2	[5]
18	-1.7	Ag/MWCNT (GDE)	-	-	95	350	1M KOH	1M KOH	N/A	[12]
19	-2	Ag	1.5	-	96	0.5	18 mol% EMIN-BF_4 in H_2O	100mM H_2SO_4	0-7	[13]
20	-0.7	Tri-Ag Nanoplates	0.785	-	96	1.25	0.1 M $KHCO_3$	0.1 M $KHCO_3$	168	[14]
21	-1.5	Ag	1.6	-	99	2.4	BMImCl with 20wt% H_2O	BMImCl with 20 wt% H_2O	10	[15]
22	-1.9	Ag NPs (GDE)	10	-	100	440	3M KOH	3M KOH	N/A	[16]

ǂ Total current density not considering the selectivity towards any product.

Table S2. Detailed conditions and results achieved on experiments made with Au-based electrodes for the reduction of CO_2 to CO (as the main C-based product).

Exp. Nr.	Cathodic Potential (V *vs.* NHE)	Electro-catalyst	Electrode size (cm^2)	Au loading (%)	FE (%)	Current density ǂ ($-mA\cdot cm^{-2}$)	Electrolyte	Test time (h)	Ref.
1	-1.91	Au	N/A	-	33	100	0.5 M $KHCO_3$	N/A	[2]
2	-1.15	Au	N/A	-	50	20	0.5 M $KHCO_3$	N/A	[17]
3	-2.22	Au/C	N/A	40	64	200	0.5 M $KHCO_3$	N/A	[2]
4	-0.96	Au/CNT	N/A	-	70	10	0.5 M $NaHCO_3$	4	[18]
4	-0.67	Au Np/ C cloth	0.6	-	78	1	0.5 M $KHCO_3$	8	[19]
5	-1.1	Au	N/A	-	80	7	0.1 M $KHCO_3$	0.5	[20, 21]
6	-1.08	Au Np/C	N/A	-	90	3	0.5 M $KHCO_3$	N/A	[22]
7	-0.82	Au Np/C-cloth	0.6	-	98	16	0.5 M $KHCO_3$	N/A	[19]

ǂ Total current density not considering the selectivity towards any product.

Table S3. The conditions adopted in experiments made with different electrodes from Ag and Au for the reduction of CO_2 to CO (as the main C-based product) and the obtained results.

Exp. Nr.	Cathodic Potential (V *vs.* NHE)	Electrocatalyst	Electrode size (cm^2)	FE (%)	Current density ‡ ($-mA \cdot cm^{-2}$)	Electrolyte	Test time (h)	Ref.
1	-0.59	WSe_2		24	18.95	$EMIMBF_4$	27	23
2	-1.4	Cu	0.002	38.1	20	$BmimPF_6$	N/A	24
3	-1.1	Zn Dendrite	N/A	50	14	0.5 M $NaHCO_3$	3	25
4	-1.4	Cu	N/A	50	20	Bmim-PF_6	N/A	24
5	-1.13	Pd	N/A	57.5	300	20 atm	N/A	8
6	-1	$[Ni(cyclam)]_2/C$	N/A	60	4.5	0.1 M KNO_3 pH 4.1	3.5	26, 27
7	-1.21	Rh	N/A	61	163	30 atm	N/A	28
8	-1.16	Ni-activated C fibres (ACF, GDE)	0.49	67	63	0.5 M $KHCO_{3,}$ 20 atm	N/A	29
9	-1.4	Cu hollow fibres		75	10	0.3 M $KHCO_3$	24	30
10	-0.8	Nitrogen-CNT	N/A	80	1.5	0.1 M $KHCO_3$	10	31
11	-1.7	Bi	0.3	81	4.1	MeCN containing 100 mM [BMIM]OTf	8	32
12	-1.75	Bi-CMEC/GCE	0.3	82	31	$[BMIM]PF_6$(MeCN solvent)	3	33
13	-3.5	Cu	3	84	70	MeOH	N/A	34
14	-2.2	In	N/A	85.3	4.9	Propylene Carbonate	N/A	35
15	-0.89	Pd NPs	1	90	8	0.1 M $KHCO_3$	N/A	36
16	-1.3	Cu/SnO_2		93	4.6	0.3 M $KHCO_3$		37
17	-1.16	FeTDHPP	N/A	94	0.31	DMF 0.1 M n-Bu_4NPF_6, H_2O	4	38
18	-0.65	Au IO (inverse opal)	N/A	95	0.4	0.1 M $KHCO_3$	3.5	39
19	-1.71	Bi-CMEC	0.3	95	5.8	Bmim-BF4 in MeCN	12	40
20	-1.12	Cu-In	N/A	95	2	0.1 M $KHCO_3$	7	41
21	-2	Cu/Ag	1.6	98	5.8	$EMIMBF_4$+ $BMIMNO_3$ with CoCl2	150	42
22	-1.25	CN/MWCNT		98	90	KCl	N/A	43
23	-0.764	MoS_2	N/A	98	65	4 mol% EMIM-BF_4 in H_2O	10	44
24	-1.95	Mn(bpy-Bu)$(CO)_3$Br	N/A	100	9.5	1.4 M CF_3CH_2OH/MeCN	0.5	45
25	-0.5	Ni-CODH	N/A	100	5	0.1 M Phosphate	N/A	46, 47

‡ Total current density not considering the selectivity towards any product.

C. Short-Review of H_2 Production electrocatalysts

Since Pt is the most active H_2 evolution catalysts, in the past few decades, several elements, such as Cu, Au, Pd, Rh, Fe and Mo,[48-50] Ni,[51-53] Ru,[54, 55] and Co,[56] have been investigated with the aim of finding a suitable replacement for Pt. Moreover, different techniques have been used to coat the electroactive materials: i) plasma or thermal spraying, ii) thermal decomposition, iii) electroplating or electrodeposition either in one- or in multi-steps,[57] and iv) *in-situ* activation.

Because of the promising results that have recently been achieved, HER catalysts, based on earth abundant elements, such as Co, Fe, and Ni, have at the centre of the attention in current research. [56, 58-63] For instance, Cobo et al.[56] developed a robust nano-particulate electro-catalytic material, the so called H_2-CoCat, which can be electrochemically prepared from cobalt salts in a phosphate buffer. This material consists of metallic Co coated with a cobalt-oxo/hydroxo-phosphate layer in contact with the electrolyte, and its unique feature is that it can mediate HER in a neutral aqueous buffer solution at modest overpotentials.[56] Other transition metal based catalysts for the HER have been benchmarked by McCrory *et al.*[64] by means of a standardized protocols (Fig. 9 in the main manuscript).

Some researches emphasized that coated-alloys showed a better performance and lower overpotentials in both acid and basic solutions rather than under neutral pH.[65] Thus, metal alloys have been studied on different substrates, *e.g.* CoMo alloys were prepared on titanium or steel substrates [63] and on glassy carbon electrodes.[64]

A considerable surface area of FeMo alloys, and their mix with rare earth metals, were reported to generate high rates of hydrogen evolution.[66] The experiments on electrodeposited FeMo alloys showed an overpotential drop of 0.15 - 0.3 V for HER as compared to mild steel, in a simulated commercial electrolyte for chlorate production.[67] Rosalbino *et al.*[68, 69] investigated HER on crystalline alloys, with composition: $Fe_{90}R_{10}$, and FeZnR (R: rare earth metals such as Ce, Sm, Y, La or Gd; Mm: mischmetal), in 1 M NaOH solution at 25 °C. The multiphase microstructure of some of these alloys were found to promote the hydrogen adsorption, in particular, Ce and Mm-containing alloys led to an increase of the HER kinetics on the electrode surface due to synergetic composition effects.[65]

Nickel-based catalysts and its alloys or composites are among the most investigated materials for HER electrode applications, mainly because of their high resistance towards alkaline solutions.[65] [70] The Ni structure and surface area have been enhanced by depositing it on active carbon fibres[29], making nickel-phosphorous-graphite (Ni-P-C_g) composites,[57] and alloying it with different metals (*i.e.* W;[71, 72] Fe;[73, 74]; Mo, Cr and Pd [75]) or metal oxides (*i.e.* MoO_2 and MoO_3).[76-78]

Polished polycrystalline Pt electrodes showed the highest HER activity in acidic media, operating at - 0.04 V of overpotential. Particularly, some alloys of Mo with Ni, Fe and Co, Mo/S and CoW also have demonstrated to be promising electro-catalysts for the HER. Indeed, electrodeposited NiMo and NiMoCo catalysts showed similar geometric activity in acid to such of Pt, achieving up to $-10\ mA\cdot cm^{-2}$ at -0.045 and – 0.05 V of overpotential, respectively. However, these materials demonstrated a lower specific activity than Pt, because they have 100- and 10-fold larger electrochemically active surface area (ECSA) than Pt. The stability of such electrodes was constant for 2 h of polarization experiments.

Instead, under a basic media, the polycrystalline Pt activity was reduced, operating at –0.10 V of overpotential at $-10\ mAcm^{-2}$, but no agreement exists for explaining the reason for this decreased activity.[64] However, a higher-surface area platinized electrode operates with a higher activity than a planar Pt surface, reaching – 0.04 V of overpotential at $-10\ mAcm^{-2}$ in 0.1 M NaOH. Several materials showed similar geometrical activity than Pt under basic media, *i.e.* NiMo, NiMoCo, CoMo, NiMo, NiFe and NiMoFe alloys, although they had 1-3 orders of magnitude higher surface area than Pt.[64] Other than their high efficiency for hydrogen evolution, additional interesting properties of those Mo-based metal alloys are their high melting point and good corrosion resistance. Indeed, the stability of such electrodes was quite constant for 2 h of polarization, and some of them were also tested for 24 h without any loss on activity.[64]

Au catalyst requires particular attention because it is a good candidate for the reduction of CO_2 to CO. Au is less expensive than Pt, is catalytically active for HER and is stable.[79-84] Xu [85] investigated the evolution of hydrogen in single crystal Au electrodes, and determined the influence of different impurities on the hydrogen evolution process. Organic molecules such as decacyclene have shown opposite effects on the evolution of hydrogen for Au (111) and (100) surfaces, *i.e.* it inhibits the reaction for Au (100) but enhances it for Au (111); instead, the addition of HNO_3 facilitates HER. Smiljanic *et al.* [86] used bimetallic surfaces of Au/Pd in an alkaline solution. In their study, Pd/Au (111) electrodes showed a significant catalytic activity towards a hydrogen evolution reaction in a 0.1 M NaOH solution compared to a pure Au (111) surface, where HER occured at a very high overpotential. Carbon paste electrodes (CPE), modified with nanomaterials as electro-catalysts, have recently attracted attention because of the HER. Thus, Siddhardha *et al*.[87] synthesized Au nanoparticles over graphene and carbon nanotube substrates, and prepared CPE for HER in an acid medium. The nanocomposites showed a $\sim$ 100 fold increased current density compared to an unmodified CPE, and achieved up to $\sim$ - 8.5 $mAcm^{-2}$ at -0.3 V *vs* RHE. Khanova *et al.*[88] described the kinetics of hydrogen evolution on electro-deposited Au electrodes as being dependent on both pH and ionic strength of the solution at high current densities and overpotentials.

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