From CO2 to Value-Added Products

Subjects: Electrochemistry

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The global warming and the dangerous climate change arising from the massive emission of CO2 from the burning of fossil fuels have motivated the search for alternative clean and sustainable energy sources. However, the industrial development and population necessities make the decoupling of economic growth from fossil fuels unimaginable and, consequently, the capture and conversion of CO2 to fuels seems to be, nowadays, one of the most promising and attractive solutions in a world with high energy demand. In this respect, the electrochemical CO2 conversion using renewable electricity provides a promising solution. However, faradaic efficiency of common electro-catalysts is low, and therefore, the design of highly selective, energy-efficient, and cost-effective electrocatalysts is critical. Carbon-based materials present some advantages such as relatively low cost and renewability, excellent electrical conductivity, and tunable textural and chemical surface, which show them as competitive materials for the electro-reduction of CO2.

carbon dioxide | electro-reduction | carbon-based materials | value-added products

1. Introduction

The energy supply currently depends mostly on fossil fuels, causing a continuous accumulation and, therefore, an excess of CO_2 in the atmosphere, bringning negative effects on the environment. The population and live standards growth make nor imaginable the decoupling of energy supply from fossil fuels. Faced with this situation, different altenatives have been proposed to mitagate the enviromental impact and dependence on nonrenewable energy sources. **The conversion of CO_2 into value-added products** by chemical reactions seems to be the most promising and attractive solution since, together with the reduction of the atmospheric CO_2 levels, CO_2 is efficiently recycled stablishing an ideal zero-emission carbon balance. CO_2 can be converted to added-value products by photochemical [1][2][3][4], thermochemical [5][6][7][8], radiochemical [9] [10], biochemical [11][12][13][14], and electrochemical strategies [15][16][17][18]. However, the most interesting alternative is the capture and use of CO_2 as raw material to produce various products (Table 1) through its electrochemical reduction since this is a flexible and controllable process with mild and safe operating conditions and low equipment cost, which also allows coupling environmentally friendly non-fossil energy from renewable sources. Taking into account these advantages, many efforts have been made worldwide in the development and improvement of the **technology available for CO_2 electro-conversion**.

Table 1. Equilibrium potential and Gibbs free energy for CO_2 reduction reactions.

Reduction Reactions	Gibbs Free Energy ΔG° (Kj mol^{-1})	Standard Potential E° (Volts vs. NHE)
$2CO_{2(g)} + 2H^{+} + 2e^{-} \rightarrow H_2C_2O_4$	+91.8	−0.475
$CO_{2(g)} + 2H^{+} + 2e^{-} \rightarrow HCOOH_{(aq)}$	+38.4	−0.199
$CO_{2(g)} + 2H^{+} + 2e^{-} \rightarrow CO_{(g)} + H_2O$	+19.9	−0.103
$CO_{2(g)} + 4H^{+} + 4e^{-} \rightarrow HCHO_{(aq)} + H_2O$	+27.5	−0.071
$CO_{2(g)} + 6H^{+} + 6e^{-} \rightarrow CH_3OH_{(aq)} + H_2O$	−17.3	+0.030
$CO_{2(g)} + 8H^{+} + 8e^{-} \rightarrow CH_{4(g)} + 2H_2O$	−130.8	+0.169

However, despite the fact that electro-reduction of CO_2 (CO_2RR) is thermodynamically viable, its transformation presents very slow reaction kinetics and usually requires significant energy expenditure [19] due to the high stability and inertness of the CO_2 molecule [20]. Therefore, an extensive research has been developed by the overall scientific community focused on the electrocatalyst design, since the efficiency and selectivity of the reduction reaction is strongly dependent on the electrode nature, properties, and configuration [21]. An ideal catalyst for CO_2 electroreduction requires: (i) Being able to mediate the transfer of electrons coupled to protons, (ii) having a low over potential for the activation of the CO_2 molecule, (iii) exhibiting a selectivity preferably towards a target product, and (iv) preserving structural integrity during prolonged operation.

Lately, carbon-based catalysts have attracted much attention due to their relatively low cost and renewability, good chemical stability, excellent electrical conductivity, tunable textural and chemical surface, and large surface area, containing micropores, mesopores, and macropores that favor adsorption, access, and diffusion of molecules to the internal active sites of the material [22]. Due to these particular characteristics, carbon-based materials have been extensively used as electrocatalysts for CO_2 reduction either as supports to disperse different metallic particles with several sizes (single-atoms, dual-atoms, nanoparticles) or as direct catalyst by functionalization with heteroatoms to prepare economical and sustainable metal-free electro-catalysts [23] . (Figure 1).

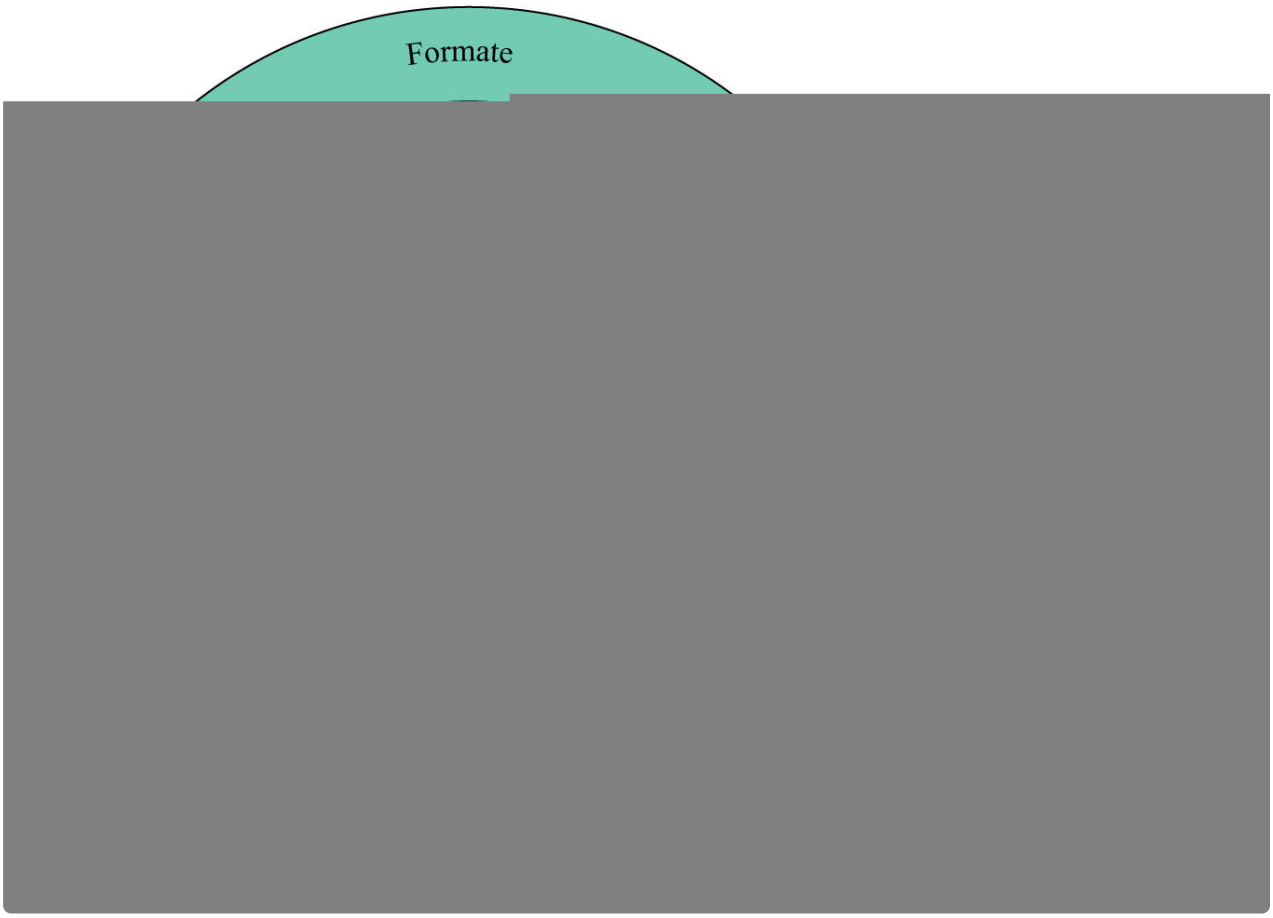

Figure 1. Value-added products using carbon- based catalysts.

2. Metal-Free Carbon Materials as Catalyst

Metal-free carbon-based catalysts emerge as an alternative to overcome the difficulties that arise when using metals as catalysts, such as their limited availability and poor durability that prevent their application on large scales. However, the activity of carbon materials itself is poor, so heteroatoms (N, B, S, P, F) are introduced into the carbon structure to promote electrocatalytic activity and selectivity [24]. Carbon doping with foreign heteroatoms affects the electronic structure of carbon materials since the different size and electronegativity of such foreign atoms compared to carbon atoms lead to a charge redistribution and, consequently, modify their electrochemical catalytic properties [25]. Additionally, the covalent chemical bonds between the carbon and the doped atoms avoid segregation problems occurring in metal-based catalysts leading to better operational stability [25]. Different heteroatoms have been used to dope carbon obtaining materials with good electrochemical performance in the CO_2 reduction, and among them, N and B have been the most studied.

2.1. N-Doped Carbon-Based Materials

The N atom has a similar size to the C atom but higher electronegativity [26], therefore the defects caused by nitrogen doping can break the electroneutrality of C atoms in the hexagonal carbon structure [27] leading to an

enhanced electronic/ionic conductivity without distortion in the local geometry that influences the electrocatalytic activity [28]. N-doped carbons have shown to be promising candidates as catalysts for the electro-reduction of CO_2 due to the low over-potentials obtained, the high activity, stability, and selectivity towards certain products ascribed to this surface properties modification. The nitrogen species are located in several places within the carbon skeleton, which results in different active sites. The electrocatalytic behavior of the N-doped carbons towards CO_2RR is deeply dependent on the type of nitrogenated surface group and its content [26].

2.1.1. N-Doping Methodology and N-Doped Catalyst Active Sites

Different carbon and nitrogen precursors have been used for the synthesis of N-doped carbon electrocatalysts (Table 2). Two main doping strategies have been developed*:* In situandpost-doping treatments. The first consists of simultaneously perform both the synthesis and doping of carbon-based materials at the same time; while in the second, the carbon material is first synthesized and then doped in a subsequent process [22][25]. After doping, four types of nitrogen species can be identified in the carbon skeleton by XPS: Pyridinic (398.5 eV), pyrrolic/pyridonic (399.9 eV), quaternary or graphitic N (401.0 eV), and oxidized pyridinic species (403.4 eV) [29][30]. The total amount of nitrogen fixed on the carbon structure and the nature of N functionalities clearly depends on the N precursor source, doping methodology, and carbon material.

Table 2. Carbon and nitrogen precursors to construction of electrocatalysts and active sites.

Sample	Main Product	Carbon Precursor	N Precursor	Type [a]	Synthesis Method	Nitrogen Species (% atomic) XPS					Active site	Ref
						N [b]	Pyri [c]	Pyrr [d]	G [e]	O [f]		
NR/CS-900	CO	CS (porous carbon nanosheets)	Polymerized Aniline with Ammonium Persistence to Polyaniline (Solid)	Post	Activation ($ZnCl_2$) and pyrolysis	5.30	1.45	1.05	2	0.8	Pyridinic	[31]
NCNTs	CO	CNTs	Acetonitrile- dicyandiamide	In situ	Liquid vapor deposition (CVD)	5.0	1.5	1.1	2.4	n.d.	Pyridinic	[32]
WNCNs-1000	CO	Coal, NaCl template method C-700	NH_3	Post	Pyrolysis	4.3	2.61	1.45	0.16	0.08	Pyridinic	[33]

NCNTs-ACN-850	CO	CNTs [a] (Acetonitrile)	Dicyandiamide [b]	In situ [c]	Liquid chemical vapor deposition [d]	4.9	1 [e]	0.5	3.4 [f]	n.d.	Pyridinic	[21]
CN/MWCNT	CO	MWCNT	NaN_3 reacts with $C_3N_2Cl_3$ to form g-C_3N_4	Post	Pyrolysis	0.12	n.d.	n.d.	n.d.	n.d.	n.d.	[34]
NCNT-3-700	CO	CNTs	Poly(diallyldimethylammonium chloride) (PDDA)	Post	Pyrolysis	1.75	0.5	0.625	0.5	0.125	Graphitic	[35]
CNPC-1100	CO	Coal	NH_3	Post	Ammonia etching/pyrolysis	4	1	1	1.5	0.5	n.d.	[36]
NG-800	CO	GF (Graphene foam) Ni-foam vapor deposition	gC_3N_4 (Solid)	Post	Pyrolysis	6.6	4.5	1.5	0.6	n.d.	Pyridinic	[37]
MNC-D	CO	ZIF-8	Dimethyformamide DMF	Post	Heat-treated	16.97	8	5	4	n.d.	Pyridinic	[38]
NPC-900	CO	Coal arantracite	Dicyandiamide (DICY)	In situ	Activation (KOH)/Pyrolysis	1.92	0.60	0.50	0.83	n.d.	n.d.	[27]
N-CWM	CO	Natural wood	Urea	Post	Pyrolysis	4.07	0.54	2.90	0.55	0.09	Pyridinic	[39]
N-graphene	Formate	Graphene oxide	Melamine (Solid)	In situ	Pyrolysis	5.5	3	0.9	1.6	n.d.	Pyridinic	[40]
PEI-NCNT/GC	Formate	Multiwalled CNT	Ammonia plasma/co-catalyst (PEI)	Post	Ammonia plasma enhanced chemical vapor deposition (PECVD)	11.3	n.d.	n.d.	n.d.	n.d.	n.d.	[41]

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HNCM/CNT	Formate	CNT	Dimethyformamide DMF	In situ	Pyrolysis	8.26	3.5	n.d.	4.8	n.d.	Pyridinic	[42]
N-C61-800	Formate	Fullerene PC61BM	Urea	In situ	Pyrolysis	2.57	0.39	0.54	1.64		Graphitic	[43]
CF-120	Syngas	CF (carbon foam)PU	NH_3	Post	Ammonia etching/pyrolysis	5.5	2.5	1.8	0.6	0.6	Pyridinic/Pyrrolic	[44]
3D N-CNTs/SS-750	Syngas	Melamine	Melamine	In situ	Pyrolysis	6.8	3.90	0.50	2.50	n.d.	n.d.	[45]
c-NC	Ethanol	Resol	Dicyandiamide	In situ	Pyrolysis/Template method-mesoporous materials	7	2.6	2.8	1.6	n.d.	Pyridinic/Pyrrolic	[46]
MNCs-5	Ethanol	Resol	Dicyandiamide	In situ	Pyrolysis/triblock-copolymer-templating method.	~6.2	2.1	2.8	1.3	n.d.	Pyridinic/Pyrrolic	[47]
GO-VB6-4	Ethanol-Acetone	Graphene oxide	B6 Vitamin	Post	heat treatment	2.3	2.3	n.d.	n.d.	n.d.	Pyridinic	[48]
NGM-1/CP	CH_4	Graphene	3-Pyridinecarbonitrile	In situ	Pyrolysis	6.52	1.45	3.35	1.72	n.d.	Pyridinic/Pyrrolic	[49]

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