The Role of Structured Carbon in Downsized Transition Metal-Based Electrocatalysts toward a Green Nitrogen Fixation

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Abstract: Electrocatalytic Nitrogen Reduction Reaction (NRR) to ammonia is one of the most recent trends of research in heterogeneous catalysis for sustainability. The stark challenges posed by the NRR arise from many factors, beyond the strongly unfavored thermodynamics. The design of efficient heterogeneous electrocatalysts must rely on a suitable interplay of different components, so that the majority of research is focusing on development of nanohybrids or nanocomposites that synergistically harness the NRR sequence. Nanostructured carbon is one of the most versatile and powerful conductive supports that can be combined with metal species in an opportune manner, so as to guide the correct proceeding of the reaction and boost the catalytic activity.

Keywords: nitrogen reduction reaction; carbon-based electrocatalysts; structured carbon

1. Introduction

The electrochemical conversion of the nitrogen molecule to the high-value ammonia product nowadays represents an interesting strategy to face the increasing world demand for a wide range of applications, starting from agricultural fertilizers to the challenging field of energy storage. To this day, the Haber-Bosch method represents one of the most important leaps in industrial chemistry and has allowed society to gain momentum during the industrial revolution [1]. An analysis from the Institute of Industrial Productivity reported in Chemical and Engineering News in 2019 stated in the title: “Industrial ammonia production emits more CO₂ than any other chemical-making reaction. Chemists want to change that” [2]. Actually, in evaluating the impact of this reaction on the environment, one needs to focus not only on the energy required to sustain high temperature and pressure. In fact, the hydrogen used in the process is historically derived from steam reforming (SMR) and the water gas shift reaction (WGSR). Nowadays, the ammonia synthesis process accounts for over 1% of the world’s energy needs, and this figure is not expected to shrink anytime soon [3]. Research is then focused on different strategies that rely on lower pressure and lower temperature processes [4,5], on hybrid designs with electrochemical production of hydrogen combined to the Haber-Bosch process [6], and finally, on the electrochemical Nitrogen Reduction Reaction (NRR). With the growing interest in NRR catalysts capable of high selectivity (i.e., able to suppress the Hydrogen Evolution Reaction (HER) at the cathode), carbon-based electrodes gained attention thanks to their low cost and versatility, both as an active catalyst and as a support. In particular, stabilization of the active site is of paramount importance in these kinds of materials, given the reliance on intrinsically unstable structures such as defects sites, unusual facets, or single-atom catalysts [7,8]. A vast number of studies have been carried out centered on this key topic,
ranging from the more classical approach of N- or B-monodoped porous carbon materials (common to the field of CO$_2$RR and ORR reactions) [9–13] to the more complex co-doping heteroatom strategy [14–17], and furthermore to tunable edge sites and topological intrinsic defects in the carbon matrix (as schematized in Figure 1). From this perspective, we will explore current use of carbon-based materials, and the design challenges it represents, while paving the way for future exploration on material engineering for the next generation of N$_2$ reduction catalysts.

Figure 1. Relevant techniques for carbon catalyst activation and their main combinations.

2. Electrocatalysts Design: The Key Aspects

Aqueous environment (that includes acidic, basic, or neutral solutions) represents the most widely adopted electrolyte that exploits the H$^+$ or OH$^-$ charge carriers. Stable materials in this reaction media comprise many types of different N$_2$ electrocatalysts, including transition metal-based materials (alloys, nitrides, sulfides, oxides, etc.), but also other classes, including heteroatom-doped metal-free carbon nano-textures and single-atom catalysts (SACs), where generally the doped carbon functions as support for the single-metal site. Sifting through the state-of-the-art, two main features emerged in the rational protocol plan for a promising N$_2$ electrocatalyst design: (i) adequate surface area and porous structure, and (ii) the formation of suitable defects to promote N$_2$ adsorption and conversion. It follows that heteroatom-doped (usually nitrogen or boron) carbon-based nanostructures (CNS) could represent a promising strategy to enhance NRR, given the wide range of existing CNS: the common carbon nanotubes (CNT), nano-horns (CNH), graphene and related structures (GO, rGO), but also more sophisticated materials such as carbon dots (CDs) are among the latest research frontiers in carbon-based nanomaterials due to fundamental features such as electrochemical high solubility in many solvents, large specific surface area and relevant edge sites for functionalization, low-cost ability for modification with attractive surface chemistry, and other modifiers/nanomaterials [18–23].

On the other hand, it is important to highlight that N-doped carbon catalysts could be subjected to degradation during the process, thus releasing ammonia into the electrolysis solution as an external source, not directly arising from NRR, affecting true activity evaluation. In consideration of all the other numerous difficulties in rigorously evaluating the activity of NRR catalysts [24], it is critical to perform required additional measurements [25], or have precise control of experimental parameters [26,27]. Nevertheless, N-doped carbon-based catalysts still represent one of the most investigated strategies: representative examples include a porous carbon material prepared by ZIF-8 treatment by Mukherjee et al. [28] and the N-doped carbon nanospikes (CNS) designed by Song et al. [29], as well as numerous
graphene-based structures. Concerning graphene as a representative case study, it has been demonstrated by several studies that a main general requirement to enhance catalytic performance is to endow an adequate charge carrier mobility, so as to promote charge transfer during NRR combined with a high structural stability [30,31]. Many different theoretical studies on NRR (and also on other electrochemical reduction processes) have indeed focused on graphene as the nanocarbon phase, in particular for the class of SAC electrocatalysts [32–34].

3. Electrocatalysts’ Design: The Role of Carbon

Analyzing the state-of-the-art concerning metal-free carbon-based electrocatalysts for NRR, the exploitation of OVs (Oxygen Vacancies) and NVs (Nitrogen Vacancies) [35], as well as CVs (Carbon Vacancies) (Figure 2), emerged as the main key concept to extensively investigate the role of carbon and its NRR catalytic properties. The potential activity of carbon is most exemplified in the case of the Defective reduced Graphene Oxide (DrGO)-based electrocatalyst with engineered defects, reported by Zhang et al. [36]. Through coupled experimental and computational analysis, the group was able to pin the high Faradaic Efficiencies (FEs) shown by the material (~22.0% at $-0.116$ V in acidic media, see Table 1) to the CVs created by the hydrothermal treatment, leading to unsaturated carbon sites (oxygen-containing functional groups, structural defects in the basal plane, and on edge sites). The computational part of the study showed, in particular, that *N$_2$ was most active on sites with a double CV (DrGO-DV), while on single CVs (DrGO-SV) and on terminal –COOH groups, the energetics were much less favorable toward N$_2$ reduction.

Figure 2. Different defects on DrGO: single Carbon Vacancy (a), double Carbon Vacancy (b), and carboxylic carbon (c). Energetics for main NRR intermediates on these defects are reported on the right side (d–f). Reprinted with permission from [36]. Copyright 2019 Elsevier Ltd.
Table 1. Carbon-based catalysts for NRR investigated in this review and their main catalytic parameters (ammonia formation rate and Faradaic Efficiency (FE)).

| Catalyst                        | Electrolyte | Potential/V vs. RHE | Rate/µgNH₃ H⁻¹ mg⁻¹cat⁻¹ | FE/% |
|---------------------------------|-------------|---------------------|--------------------------|------|
| N-DOPED CARBON                  | 0.1 M KOH   | −0.3                | 70.8 †                    | 10.2 |
| N-DOPED CARBON NANOSPINES       | 0.25 M LiClO₄ | −1.19               | 97.18 *                   | 11.56|
| S-, B-DOPED CARBON NANOFIBERS   | 0.5 M K₂SO₄ | −0.7                | 3.79 *                    | 22.4 |
| DEFFECTIVE RGO                  | 0.1 M HCl   | −0.116              | 7.1                       | 22   |
| S-DOPED GRAPHENE                | 0.1 M HCl   | −0.6                | 27.3                      | 11.5 |
| FTO                             | Ionic liquid| −0.8                | 1.3 †*                    | 30   |
| B-DOPED GRAPHENE                | 0.05 M H₂SO₄ | −0.5                | 49 †                      | 10.8 |
| F-DOPED CARBON                  | 0.05 M H₂SO₄ | −0.2                | 197.7                     | 54.8 |
| DEFFECTIVE G-C₃N₄               | 0.1 M HCl   | −0.2                | 8.09                      | 11.59|
| AU1-C₃N₄                        | 0.005 M H₂SO₄ | −0.1              | 1.96 †                    | 11   |
| RU SA/NC                        | 0.05 M H₂SO₄ | −0.2                | 120.9                     | 29.6 |
| MO SA/NPC                       | 0.1 M KOH   | −0.3                | 34.0                      | 14.6 |
| ISAS-FE/NC                      | 0.1 M PBS   | −0.4                | 62.9                      | 18.6 |
| FE SA/NC                        | 0.1 M KOH   | 0.0                 | 7.48                      | 56.55|

† Calculated from reported values in the paper. * µgNH₃ h⁻¹ cm⁻², for lack of data to calculate the mass normalized rate.

However, most publications make use of heteroatoms through non-metal and metal doping, to modulate the adsorption and desorption of NRR reaction intermediates and products by inducing charge and spin densities on C atoms and by enhancing the electron transfer. The carbon nanostructure’s flexibility defines its main role as a support for most catalyst designs. Some representative examples are discussed here in more detail to better explain this concept.

3.1. Case of Graphene (X-Doped) to Limit HER

A wide range of experiments have been performed in both aqueous and non-aqueous electrolytes, such as ionic liquids, on transition metal-based but also metal-free X-doped carbon materials (X = non-metal heteroatom). FE approximately above 10% (see Table 1 for data comparison) were reported in aqueous environment [37], while higher FE could be achieved in non-aqueous electrolytes [38] as a result of the much lower availability of protons and therefore the diminished competition with the HER process. There is no doubt that operating in aqueous environment represents the best manageable condition in view of a real application for the electrocatalyst, i.e., in ion-exchange PEM electrolyzers, as well as the most appealing choice from an environmental impact point of view [47].

Among various non-metal heteroatoms, the incorporation of N into graphene represents a common strategy to tailor the electronic properties of this carbon texture. Nitrogen-doped graphene (N-graphene) has been demonstrated to find applications in energy storage and conversion [48,49], but also in the field of nano-electronic device design [50,51]. N-graphene can be synthesized by using both a bottom-up method starting from N-containing precursors or through a post-treatment of graphene and graphite oxide (GO), introducing the N atoms as a final step. Despite being frequently investigated as a metal-free electrocatalyst in several processes such as ORR, HER, and CO₂RR [52–55], in the case of NRR in aqueous electrolytes, it appears that inclusion of a transition metal active site, i.e., in the form of single atom, is imperative for obtaining promising activities. The combined properties of high charge-mobility (graphene component acting as an electronic reservoir) to the synergic metal-N active site for N₂ bond breaking play a fundamental role for an efficient electrochemical N₂ fixation [56].

Most recently, B-doped graphene in the form of nanosheets has been reported to be highly selective toward N₂ reduction to ammonia, with the Faradaic Efficiencies exceeding 10% [39]. It has been proven that boron doping in the graphene texture results in a redistribution of electron density; therefore, it provides excellent active sites for N₂ adsorption and the consequently enhancement of ammonia reduction. Moreover, the positively charged
boron active sites can strongly inhibit the binding of protons (under acidic conditions) to disfavor the competing HER, thus providing high FE for ammonia formation. N2 reduction experiments showed that B-doped graphene was able to efficiently catalyze the formation of ammonia in acidic environment, with the maximum rate and FE reaching $1.6 \times 10^{-10}$ mol s$^{-1}$ cm$^{-2}$ and 10.8%, respectively, at $-0.5$ V vs. RHE (also see Table 1 for data comparison).

Another very recent example involved the use of the F-doped 3D porous carbon network synthesized by Liu et al. via a procedure consisting of crystallization of UiO-66 (a metal organic framework based on Zr nodes) in the presence of PTFE, pyrolysis, and final HF etching, leading to the metal-free F-doped carbon texture [40]. The resulting catalytic material showed outstanding NRR selectivity of 54.8% at $-0.2$ V in 0.05 M H$_2$SO$_4$, by simultaneously suppressing H$^+$ reduction and promoting N$_2$ activation near the F atom (Figure 3). In particular, the active site was assessed with DFT calculations and located on the 5th carbon atoms on defective graphene slabs.

![Figure 3](image-url)

**Figure 3.** Current density for NH$_3$ (a), FE (b), and yield rate for NH$_3$ of F-doped carbon and pristine carbon at different applied potentials (c). Comparison of F 1s XPS spectra for F-doped carbon and pristine carbon (d), TEM (e), and HAADF-STEM images (f), and corresponding EDS elemental mapping results for F-doped carbon. Adapted with permission from [40]. Copyright 2020 Wiley-CHC Verlag and Co. KGaA Weinheim.

### 3.2. Graphitic Carbon Nitride (g-C$_3$N$_4$)

Graphitic carbon nitride (g-C$_3$N$_4$) has been attracting increasing attention over recent years, coming to prominence for its many useful properties [57,58]. Importantly, its preparation is carried out by means of relatively simple strategies and starting from cheap precursors (most notably melamine and urea). It has shown great versatility as a metal-free photocatalyst [21,59–61] and in other non-photocatalytic processes, including electrocatalysis [62,63]. A first paper on g-C$_3$N$_4$ with NVs was published by Lv et al. [41], in which the defective C$_3$N$_4$ showed uncharacteristic activity toward NRR (8.09 µg h$^{-1}$ mg$_{cat}^{-1}$, FE 11.6% at $-0.2$ V, see Table 1), ten times higher than the pristine material (0.74 µg h$^{-1}$ mg$_{cat}^{-1}$ at the same potential). DFT calculations showed that after introducing a NV at the N$_2$C site, N$_2$ could adsorb on the g-C$_3$N$_4$ in the form of di-nuclear end-on coordinated mode. The electrons on adjacent carbon atoms are transferred to the adsorbed N$_2$, namely an electron back-donation process, resembling what generally takes place in transition metals with d-orbital electrons being donated to the π N-N antibonding orbitals.

Although these results seem promising, it is still necessary to significantly boost the NH$_3$ formation rate. To this end, many transition-metal SACs supported on g-C$_3$N$_4$ have been studied, mainly in theoretical publications. Chen et al. [64] worked on a series of...
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single-metal atoms anchored onto the NVs in graphitic carbon nitride (Ti, Co, Mo, W, and Pt on g-C3N4). Among these various TM metals, it was found that NRR proceeded smoothly on the single tungsten (W) atom anchored on a g-C3N4 monolayer via the associative enzymatic pathway, and a small negative potential of −0.35 V can onset the N2 fixation, while suppressing the competing HER. Along this path, Wang et al. [42] synthesized an Au1 catalyst supported on g-C3N4 that showed an ammonia formation rate of 1305 µg h−1 mgAu−1 (Table 1), much higher (22.5×) than bulk Au nanoparticles supported on carbon nitride. DFT calculation results revealed that both Au1/C3N4 and Au NPs/C3N4 proceed with an alternating hydrogenation mechanism, but the lower required energy on Au single atoms explains the enhanced NH4+ formation and FE on Au1/C3N4.

3.3. C2N Monolayer

Another interesting example group based on carbon nanostructures for NRR is represented by nitrogenated holey graphene–C2N monolayer support. Wang et al. investigated the series of Zn, Mo, Ru, Rh, Pd, and Ag single transition-metal atoms supported on C2N for NRR electrocatalysis [65]. The C2N monolayer is constituted by 6-fold cavities, the corner of which is the most stable site for the attachment of a single transition-metal atom. Among all the catalysts, the Mo–C2N monolayer appeared to be the most promising, as a result of the better stabilization of the *N2H intermediate (i.e., a low overpotential for this key intermediate) and also because of the stronger adsorption of *N2H with respect to that of *H, thus resulting once again in the useful suppression of hydrogen evolution. N2 adsorbs on the Mo center in an end-on configuration, accompanied by an elongation of the N2 bond and a transfer of spin moment from the catalyst to the adsorbed N2 molecule. These results indicate that the Mo–C2N monolayer could significantly activate the N2 molecule.

4. The Concept of Downsized TM-Electrocatalysts: From Single to Quadruple—Atoms Dispersed on Structured Carbon Types

Following recent trends in nanoparticles synthesis, many efforts have been focusing on anchoring single TM atoms on different supports because of the overlap of their HOMOs with N2 LUMO. This overlap is instrumental to the weakening of the N-N triple bond and is the first step to a competitive NRR mechanism. SACs, in a way, bridge the gap between metal complexes, i.e., homogeneous catalysis, with the bulk heterogeneous catalysts. The single-atom nature of these material allows for much larger mass activities, addressing the issues of atom economy so critical for the transfer to the industry. The SACs concept was introduced not without problems of its own: to avoid the formation of nanoparticles, different synthetic routes were studied but, generally, it is still difficult to obtain high metal loadings without nanoparticles’ formation, with notable exceptions [66]. In this landscape, carbon-based material arose as a natural support structure, given the low price, ease of functionalization, and ability to stabilize TM atoms thanks to heteroatom doping (e.g., TM-N4 structures) [67,68].

Many of these solutions, however, are not as compelling as a first glance would suggest: to ensure the atomic dispersion, SACs loading is often lower than 1% [69–72] because the single atoms, as their loading increases, usually have a higher tendency to stick together and form clusters or even nanoparticles. This low density of catalytic sites is sometimes obscured using TM mass normalized activities. Even if these metrics are useful to highlight the boosted activity of SACs with respect to bulk or even nanoscale materials, most often it is difficult to have meaningful comparisons with non-metal catalysts. As an example, the figures of merit cited previously and reported by Lv et al. (8.09 µg h−1 mgcat−1 for defective carbon nitride) [41] and Wang et al. (1305 µg h−1 mgAu−1 for Au single-atom supported on carbon nitride) [42] are in fact very similar, given the low Au amount of 0.15% on the SAC (see Table 1 for a more meaningful comparison).

To address the loading limits, an approach involving double-atom catalysts (DACs) was first proposed. These materials can be homometallic or heterometallic in nature (TM2 or TM1-TM2) and principally differ on how the two TM are fixed on the support: Some catalysts show direct bonding between two metallic atoms, working as a single active site
for the reaction of interest. Others have the two different atoms “singularly” stabilized on the underlying structure, relying on a more synergistic effect between the two active sites [73,74]. Moreover, recent papers suggest the possibility of triple- or even quadruple-atom catalysts [75,76]. These solutions have been investigated as a way to further augment the density of the TM sites on the support, and are, as of now, mainly in the theoretical stage. The big challenge is, then, to prepare a high-loading catalyst in precise atomic form, pinpointing the activity to the peculiar structure of the catalytic site.

5. The Advantage of Single to Multiple Atoms

Carbon-supported SACs currently represent the most widely studied material of the NRR catalyst family in experimental papers. This is possibly due to assessed synthetic routes already in place [7] based on a decade of research stemming from the first seminal work [77]. Zeng et al. synthetized a material based on ruthenium single atoms supported on N-doped carbon [43]. To ensure the retention of the single-atom nature, the Ru salt was adsorbed on the porous structure of ZIF-8 (Figure 4). After pyrolysis, the obtained material had a Ru loading of 0.18% and displayed a record activity of 120.9 µg h⁻¹ mg⁻¹ at −0.2 V, with 29% selectivity toward NRR in 0.05 M H₂SO₄ (Table 1).

![Figure 4.](image)

By using N₂-TPD (temperature-programmed desorption) analysis and theoretical calculations, the authors concluded that Ru SAs/N-C facilitated the adsorption of *N₂, and the ΔG value for N₂ dissociation on Ru₁-N₃ and Ru₁-N₄ moieties is lower than that on Ru (101), which results in enhanced NRR activity. Regarding earth-abundant metals, the most explored solutions are Fe- and Mo-based materials, inspired by natural
nitrigenase enzymes. In particular, Han et al. explored the activity of atomically dispersed molybdenum on NC obtained by pyrolysis of glucose and hydroxylamine in the presence of ammonium molybdate [44]. This synthesis resulted in a very high metal loading of 9.5% without the formation of metal clusters/nanoparticles or amorphous carbon. The catalyst activity was evaluated to be 34.0 µg h⁻¹ mg⁻¹cat⁻¹, with 14.6% selectivity at −0.3 V in 0.1 M KOH. Lü et al. anchored Fe single atoms on N₄ moieties on a N-doped carbon framework [45]. The relatively high loading (4.2%) was possible thanks to its synthesis, in which a modified ZIF-8 structure (with Zn and Fe nodes) was pyrolyzed. After acid leaching, the resulting porous structure was tested for NRR with a rate of 62.9 µg h⁻¹ mg⁻¹cat⁻¹ and a selectivity of 18.6% at −0.4 V in 1 M PBS solution. Finally, Wang et al. synthetized a Fe-based SAC supported on N-doped graphene sheets with a very low overpotential for NRR [46]. Shifting the start of nitrogen fixation to higher potentials, this material exhibited a FE of 56% at 0 V thanks to little competition of HER. The NH₃ rate of formation, however, turned out to be modest (7.48 µg h⁻¹ mg⁻¹cat⁻¹) due to the low currents at this potential (see Table 1 for data comparison). Many more materials have been studied in theoretical works based on different transition metals and many supports [78–80]. Even more interestingly, a lot of computational papers explored the differences in binding energies between SACs and DACs [81–83]. Chen et al. [81] compared SACs/C₂N to homonuclear DACs/C₂N, finding that the energetics involved in NRR seems more favorable on DACs in all the cases taken into consideration. In particular, Mn₂/C₂N showed preferred adsorption of N₂ compared with proton and H₂O and, in so doing, suppressing HER. Arachchige et al. [83] again compared SACs and DACs, this time supported on graphene (GY), and Ru₂@GY stood out as the best catalyst for N₂ reduction via the enzymatic pathway. Moreover, the study suggested that the DAC TM catalysts might offer much better performance in catalyzing multiple-step reactions, such as NRR, penalizing the simple HER process. Many additional computational studies have focused on the exploration of DACs’ stability and applicability as NRR catalysts [84–89], looking at both homonuclear and heteronuclear examples. However, in recent years, even DACs have been overshadowed, as scientists have started to consider the theoretical possibilities with higher numbers of neighboring active atom catalysts. Ma et al. [90], for example, compared energetics over TMₓ-GY (x = 1–3 and TM = Mn, Fe, Co, and Ni) homometallic materials and found that these TACs were not able to absorb and activate N₂*. Finally, Li et al. [76] considered Mo species supported on graphene from Mo₃@GDY to Mo₄@GDY (Figure 5), noting that for some energetic parameters, Mo₃@GDY showed better performances than the single-atom species, with a predicted onset potential of only −0.32 V.

Figure 5. Simulated structures for GDY and Mo₃@GDY from a planar and vertical view. Reprinted with permission from [76]. Copyright 2021 American Chemical Society.
6. Guidelines to Future Approaches

As pointed out mainly in Sections 4 and 5, until now, the majority of new studies on NRR electrocatalysts with atomic features have been based on theoretical studies rather than experimental approaches, which therefore leaves a void in the state-of-the-art regarding the two issues of new carbon-based electrocatalysts: their synthesis and characterization.

According to the fundamental information collected by the computational approach, here, we attempt to set useful guidelines for future developments to fill the gap between theory and practice. Among the variety of transition metals and carbon support structures adopted, the following common targets have predominantly emerged.

First, the role of carbon structures has not been restricted only to a simple conductive support, but according to the improved structural specificities (i.e., presence of single or multiple doping atoms), has a direct role in the electrocatalysis process. In the future, it will be imperative to find the precursors whose resulting “carbons” will have the best textural and chemical characteristics—such as porosity, defects, and dopants, as well as exploiting the nanoscale structuring—in order to maximize NRR activity.

Second, the synergy between the transition metal component and the carbon texture should be based on the rational distribution of the electrocatalytic centers obtainable from both an atomic-scale design but also from its adequate concentration on the catalysts’ surface. The combined structural properties of both affect the NRR reaction mechanism and consequently NRR efficiency.

Third, to assist an NRR catalyst toward high selectivity, the availability of the proton can be manipulated to limit the occurrence of the HER. Catalyst structures/features (i.e., defects, edges, and steps) and/or catalyst–electrolyte combinations should provide the right pathways to promote high selectivity and better efficiency.

Finally, taking into account the insights of computational investigations, including DFT free energy calculations for different surface structures and several attempts to understand the NRR reaction mechanism, a fundamental future step will be the translation to applicative studies of atomic-scale materials. The few papers on double-atom catalyst design show great promise in these types of materials, but it is important to introduce new synthetic methods to obtain such kind of structures. Computational studies have also suggested the stability of these materials and yet, given the intricacies of the nitrogen reduction reaction, it is critical to assess their continued activity against poisoning, breakage, and deactivation.

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