# **1** Supporting information

## 1.1 Separation of the chemical potentials of electrons and protons in a fuel cell

As the most likely degradation reaction intermediate, we investigate the formation of ammonia at the nitrogen doping site with  $e^-$  and  $H^+$  present at the electrode-electrolyte interface:

$$\text{N-G} + ne^- + nH^+ \rightarrow \text{G} + \text{NH}_3$$

N-G denotes the nitrogen doped graphene flake and *n* the number of transfered  $e^-$  and  $H^+$ . It is very challenging to model realistic electrochemical interfaces and appropriate computational methods are still debated.<sup>1–3</sup> However, in general, the separation of the chemical potentials of electrons and protons in a fuel cell can be assumed as a dissociation and ionization of 1/2 H at the anode (hydrogen oxidation). The resulting proton moves through the electrolyte from the anode to the cathode. The energy associated with proton is equivalent to its work function,  $\phi(H^+)$ , which can be correlated to the negative of the energy of the HOMO by Koopman's theorem.<sup>2</sup> An adequate approximation of the proton energy was calculated with restricted open shell Hartree-Fock theory (E((H<sup>+</sup>) = 312.64 kcal mol<sup>-1</sup>). Accordingly, the electron is moved through the electrochemical interface to the Fermi level of the electrode. The chemical potential for protons and electrons combined is  $\mu(H^+ + e^-)$  and is independent of the electrochemical environment.<sup>2</sup>.]

### 1.2 Computational details

The calculations were performed using hexagonal 6 x 5 graphene flakes. In agreement with literature data, the energetically favorable electronic structure of the 6 x 5 graphene flake used in this study was calculated as triplet.<sup>4,5</sup> Three different nitrogen containing graphene flakes were constructed, containing graphitic (N-g), pyrollic (N-pyr) and pyridinic (N-p) species, shown in Fig. 1. The edge zig-zag and arm-chair carbon and nitrogen atoms were terminated with hydrogen atoms.



Fig. 1 6x5 graphene flakes containing a) pyridinic N, b) pyrrolic N and c) graphitic N species. The flakes represent the initial state of the ivestigated material in the cathode.

#### 1.3 Electronic structure and charge distribution

According to chemical reactivity theory, the interaction energy between the graphene sheet and hydrogen atoms is governed by both the coulombic interactions between atomic charges and the frontier orbitals. Here we show, that the extra electron provided by the nitrogen dopant in the graphene flake has no direct influence on the reactivity of the zigzag edge, but influences the reactivity of neighboring carbon atoms due to a positive partial charge shift.

Figure 2 illustrates the electron density of pristine graphene, pyridinic N-graphene, protonated pyridinic N-graphene (2a) and pyridinic N-graphene with two adsorbed H atoms (3d) for the two highest occupied molecule orbitals. The highest occupied orbitals are either two single occupied molecule orbitals ( $\alpha SOMO1$  and  $\alpha SOMO2$ ) for the molecules in triplet state or *HOMO* and *SOMO* for the molecules in doublet state. According to literature, the electrons in pristine graphene are predominantly located at the zigzag edges, see Figure 2 a), e) and i), which is related to the chemical reactivity at the zigzag edges.<sup>6</sup> The introduction of an impurity like a nitrogen dopant and the lower edge, Figure 2 b) and f), shows a localization of the  $\alpha SOMO2$  electron density at the opposite edge, most likely due to the higher electronegativity of nitrogen. Protonation of the nitrogen atom does not significantly influence the *SOMO* electron density, Figure 2 c), g) and k). Figure 2 d), h) and l) show that the adsorption of two hydrogen atoms at the nitrogen site does reinforce the electron density in reaction sites. Through the strong delocalization of the electrons an orbital driven interaction between the reaction partners, i.e. graphene and hydrogen atoms, is not expected. The electron density distribution was modeled with B3LYP functional, which has shown to yield sufficient accuracy.<sup>7</sup>

The charge distribution in a molecule provides a suitable qualitative non-quantum chemical measure for the determination of reactive

sites. The analysis of Mulliken charges in pristine graphene, pyridinic N-graphene, protonated pyridinic N-graphene (2a) and pyridinic N-graphene with two adsorbed H atoms (3d) is shown in Figure 3 and the Mulliken charges of each analyzed atom summarized in Table 1. The comparison of the charges in pristine graphene and pyridinic N-graphene shows that the nitrogen atom induces a negative charge, but does not significantly influence the charges on neighboring carbon atoms. This indicates that the nitrogen atoms is the most reactive site. The comparison between pyridinic N-graphene and protonated pyridinic N-graphene (2a) shows a significant positive charge shift on the neighboring carbon atoms (2 and 4) due to the opening of the double bond between carbon an nitrogen. A significant negative charge shift to the nitrogen atom was observed in both protonated structures (2a and 3d, Figure 3 c) and d)), leaving it as the most reactive site for hydrogen adsorption.



Fig. 2 a) 6x5 pristine graphene flake, b) pyridinic N-graphene c), protonated pyridinic N-graphene and d) pyridinic N-graphene with two adsorbed H atoms. T denotes the molecule in triplet state. e) - I) Electron distribution in the highest occupied molecule orbitals (HOMO) and single occupied molecule orbitals (SOMO). The calculations were performed in H<sub>2</sub>O at B3LYP/6-31G(d)/PBF level of theory.

	Table 1	Mulliken charges on	carbon and nitrogen atoms,	as numbered in Figure 3.
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Fig. 3 a) 6x5 pristine graphene flake, b) pyridinic N-graphene c), protonated pyridinic N-graphene and d) pyridinic N-graphene with two adsorbed H atoms. T denotes the molecule in triplet state. The calculations were performed in H<sub>2</sub>O at B3LYP/6-31G(d)/PBF level of theory.

#### 1.4 Model systems for the calculation of activation energies of hydrogen adsorption



**Fig. 4** Pyridinic N graphene in a) optimized ground state and b) optimized transition state. Values represent the bond length between nitrogen and hydrogen atoms.

## 1.5 Accuracy of employed DFT models

To evaluate the accuracy of the commonly used B3LYP functional for the presented reactions, selected reactions were recalculated using PBE0/6-31G(d) and M06-2X/6-31G(d) functionals and compared to the  $\Delta$ G values obtained by B3LYP/6-31G(d). The comparison of the three functionals shows that M06-2X delivers smaller  $\Delta$ G and PBE0 larger  $\Delta$ G values than B3LYP, but do not change the thermodynamics and tendencies of the reactions. We conclude that the accuracy of the B3LYP functional is adequate and deviations from M06-2X and PBE0 are insignificant.<sup>7</sup>

Table 2 Overall Gibbs free energy of reaction pathways a and c of the removal of pyridinic N at 20 ° C in 1.0 atm H<sub>2</sub>O partial pressure. Calculated with B3LYP, PBE0 and M06-2X functionals.

	Overall Gibbs free energy $\Sigma(\Delta G)$ [kcal mol <sup>-1</sup> ] / Step										
	Pathway a	B3LYP	M06-2X	PBE0	Pathway c	B3LYP	M06-2X	PBE0			
Reaction step	1a  ightarrow 2a	-65	-72	-67	$1c \rightarrow 2c$	-65	-72	-67			
·	2a  ightarrow 3a	-103	-114	-107	2c  ightarrow 3c	-77	-89	-81			
	3a  ightarrow 4a	-145	-161	-149	3c  ightarrow 4c	-139	-148	-135			
	$4a \rightarrow 5a$	-149	-164	-151	4c  ightarrow 5c	-161	-165	-153			
	$5a \rightarrow 6a$	-207	-220	-206							
	$6a \rightarrow 7a$	-272	-287	-270							

## References

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