

Article

DFT-Guided Next-Generation Na-Ion Batteries Powered by Halogen-Tuned C₁₂ Nanorings

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Abstract

Recent research on the design and synthesis of new and upgraded materials for secondary batteries is growing to fulfill future energy demands around the globe. Herein, by using DFT calculations, the thermodynamic and electrochemical properties of Na/Na⁺@C₁₂ complexes and then halogens (X[−] = Br[−], Cl[−], and F[−]) as counter anions are studied for the enhancement of Na-ion battery cell voltage and overall performance. Isolated C₁₂ nanorings showed a lower cell voltage (−1.32 V), which was significantly increased after adsorption with halide anions as counter anions. Adsorption of halides increased the Gibbs free energy, which in turn resulted in higher cell voltage. Cell voltage increased with the increasing electronegativity of the halide anion. The Gibbs free energy of Br[−]@C₁₂ was −52.36 kcal·mol^{−1}, corresponding to a desirable cell voltage of 2.27 V, making it suitable for use as an anode in sodium-ion batteries. The estimated cell voltage of these considered complexes ensures the effective use of these complexes in sodium-ion secondary batteries.

Keywords: cell voltage; Gibbs free energy; secondary battery; DFT



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1. Introduction

Establishing sustainable renewable energy resources is one of the key goals for the twenty-first century to minimize CO₂ emissions [1,2]. Modern civilization must deal with the dilemma of briskly shifting towards renewable energy sources and electric automobiles, all the while grappling with the ever-growing impacts of greenhouse gas emissions. Renewable energy is used frequently, typically in the form of wind and solar power [3–10]. It demands daily electrical energy storage, for which secondary batteries seem to be a promising development in technology. One of the best storage options for renewable energy technologies is Na-ion secondary batteries because of their high energy density, broadened operational lifetime, and excellent reversible capacity [11–14]. Sodium-ion batteries face several challenges because of the rapid development of electric vehicles and smart power grids, including scarce supplies, high costs, insufficient safety, and a bottleneck in the improvement of energy density, power density, and cycle performance [15–18]. With growing demand for Na-ion batteries, issues related to the cost and availability of Na supplies are becoming more serious.

The development of sodium-ion batteries (SIBs) can be credited to various factors such as sodium's abundance, cost-effectiveness, and ease of access [19–26]. Researchers even claim that deposits of lithium will probably be depleted in the near future [27–29]. Sodium resources are globally available due to their lower cost as compared to lithium. Solid-state batteries (SIBs) are gaining considerable attention in the arena of electrical energy storage [30–32]. Because of the clear advantages of low cost and the abundance of charging devices available worldwide, as one of the most promising next-generation energy storage technologies, sodium-ion batteries (SIBs) share the same internal components and operating principles as lithium-ion batteries (LIBs) [33]. Carbon is an element that is found extensively in the atmosphere, the crust, and living organisms. It can interact with other elements in chemistry to form a wide variety of compounds. Over the past few decades, research on pure carbon molecules has gained a lot of interest [34–42]. There are a multitude of types of carbon clusters, including rings composed of single or polycyclic compounds, graphite or bowl-shaped clusters, hard carbon, closed-cage fullerenes, graphene nanotubes, etc. [43–45]. Graphite has been used as anode materials for lithium–anion batteries for decades, but they are found to be not suitable for SIB because of their thermodynamic stability. Recently, hard carbon materials have been identified as the most promising anodes for commercial sodium-ion batteries (SIBs) due to their cost-effectiveness. Dahn et al. were the first ones to report the use of hard carbon derived from glucose as an anode in SIBs. Although it showed good reversible capacity, its storage capacity remained lower than that of lithium-ion batteries (LIBs) [46]. Hu and co-workers developed a layer-by-layer solid electrolyte interphase (SEI) on hard carbon with a flexible, organic-rich outer layer and an inorganic-rich inner layer, leading to improved cycling performance and rate capability [47]. However, the limited performance of hard carbon and the still-unclear storage mechanisms have hindered the practical adoption of SIBs over LIBs [48]. Maier and co-workers introduced synthetic hollow nanosphere hard carbon anodes, which exhibited excellent rate capabilities [49]. Wan et al. recently synthesized multi-shelled hollow carbon nanospheres (MS-HCNs) as high-performance anodes for SIBs. They observed that specific capacity increased with the number of shells, with four-shell HCNs demonstrating a reversible capacity of 360 mAh g^{-1} at 30 mA g^{-1} . However, the sloping charge–discharge profiles remained unchanged with the increase in shell number [50]. In addition to carbon-based anodes, various Sn-, Sb-, and SnSb-based anode materials have been explored. Palaniselvam et al. synthesized tin-based composites and reported excellent cycling stability over 100 cycles [51]. A two-dimensional Sb@TiO_{2-x} anode demonstrated high specific capacity, good rate performance, and retained up to 95% of its capacity over multiple cycles [52].

These findings highlight that improving the electrochemical performance of anode materials often requires complex strategies—such as interface engineering, the integration of multi-dimensional nanostructures, the use of ultra-small nanoparticles, and heteroatom adsorption [53]. To address these challenges, graphene has emerged as an effective support material due to its high surface area, flexibility, and excellent conductivity [54]. For instance, Luo et al. designed a flexible, hierarchical conductive network in which Sn quantum dots (QDs) were encapsulated in 2D reduced graphene oxide (RGO) scrolls, further embedded in 1D N, S co-adsorbed carbon nanofibers (NS-CNFs). The RGO layer improved conductivity and electrolyte interaction, while the NS-CNFs prevented Sn QD aggregation. This 3D Sn/NS-CNFs@RGO composite exhibited outstanding cycling stability (373 mAh g^{-1} after 5000 cycles at 1 A g^{-1}) and excellent rate performance (189 mAh g^{-1} at 10 A g^{-1}) [55]. Although Sn and Sb alloy-based anodes perform well initially, they suffer from significant volume expansion during the repeated sodiation/desodiation cycles, leading to capacity decay and limiting their long-term application in SIBs [56]. Researchers have attempted to

overcome this issue by designing nanostructures with large hollow interiors to accommodate volume changes and improve sodium-ion diffusion kinetics.

Small carbon nanorings have attracted increasing interest due to their regenerative activity and structural stability [57–60]. In particular, carbon nanocluster rings—composed of multiple carbon atoms in ring-like geometries—have gained attention for their unique electronic and structural properties, following Hoffmann’s theoretical proposal in 1966 [61–65]. The first successful synthesis of carbon nanorings was achieved by Kawase in 2003 [66]. These nanorings, characterized by π -conjugation and high ring strain, posed significant challenges for synthesis and structural control [67]. Subsequent advancements involved using various coupling reactions with active metal catalysts, eventually enabling the controlled synthesis of carbon nanorings [68–70]. Ullah et al. researched both the electrical and thermodynamic aspects of the F-adsorbed carbyne C_{10} ring to create the $C_{10}F$ complex and its potential as an anode material in alkali-ion batteries using DFT and DLPNO-CCSD(T) calculations. Li/Li⁺ and Na/Na⁺ produce electrochemical cell voltages of 3.12 V and 2.80 V, respectively [71]. Tayyaba Murtaza et al. theoretically examined the potency of a pristine and halogen-adsorbed Graphdiyne analogue (GDY-28) as an anode material for sodium-ion batteries (NIBs). These designs result in greater cell voltages, which vary from 0.17 V for pure GDY-28 to 0.20 V and 0.52 V for $X^-@GDY-28$ (where $X^- = F^-$, Cl^- , and Br^-) [72]. In another work, by using density functional theory (DFT), Parimala et al. computationally evaluated the attachment of Na and Na⁺ ions on $Ga_{12}N_{12}$, $Ga_{12}P_{12}$, and $Ga_{12}As_{12}$ nanocages as materials used as anodes for sodium-ion rechargeable batteries (SIBs). Furthermore, in contrast with the empty nanocages of SIBs, enveloping the complexes with halogens (F^- , Cl^- , and Br^-) led to increased cell voltage (V_{cell}). Fluorine-encapsulated Na/ $Ga_{12}N_{12}$ has a higher V_{cell} than chlorine and bromine, based on the overall facts [73]. The scientific community has also focused on the role of the solvent (electrolyte), which plays a critical role in electrochemical studies. In computational research, solvation effects are investigated using advanced methods such as density functional theory (DFT) combined with implicit and explicit solvent models. These models have proven effective in accurately predicting electrochemical series [74]. These methods are used to explore the redox nature, Gibbs free energy of solvation, and charge transfer mechanism [75], which are helpful in understanding the estimated cell voltage of batteries in practice. Herein, by using DFT calculations, the thermodynamic and electrochemical properties of Na/Na⁺@ C_{12} complexes and then halogens ($X^- = Br^-$, Cl^- , F^-) as counter anions in the gas phase are studied for the enhancement of Na-ion battery cell voltage and overall performance.

2. Computational Methodology

DFT calculations were performed by using the Gaussian 09 package [76] and the results were further visualized by using GaussView 5.0 software [77]. DFT-based approaches are more precise and frequently used for atomic property analysis and structural optimization. Among the dispersion-corrected DFT methods, the range-separated ω B97XD functional is commonly employed for electronic and thermodynamic property analysis [78–82]. ω B97XD, along with the 6-31 + G (d, p) people basis set, was implemented for all property analyses of the considered structures. Optimization is performed to determine the correct structure of each isolated and complex structure. Optimization was followed by frequency calculations, which confirmed that all structures designed are true minima structures on the potential energy surface with positive frequencies. Zero-point corrected energy values obtained from the frequency calculation were used for interaction energy calculations.

Interaction energy is calculated from the zero-point corrected energies by using Equation (1), as presented below:

$$E_{\text{int}} = E_{\text{complex}} - (E_{\text{surface}} + E_{\text{analyte}}) \quad (1)$$

All calculations were performed in gas phase, and the absolute voltage values are therefore qualitative estimates. Cell voltage is actually the parameter used to estimate the potential of surface usage in secondary batteries. Cell voltage was calculated by implementing the Nernst Equation (2), given as:

$$V_{\text{cell}} = -\Delta G_{\text{cell}}/Fz \quad (2)$$

where z represents the atomic charge on the sodium atom/ion, F is for Faraday constant, and $-\Delta G_{\text{cell}}$ illustrates the change in the Gibbs free energies of the complexes.

Molecular orbital behavior was analyzed by performing Frontier molecular orbital analysis. In this analysis, we obtained information about the nature of the highest occupied (HOMOs) and lowest unoccupied molecular orbitals (LUMOs). This energy gap gives insight into the reactivity and electronic stability of a complex. The complex is either more reactive and electronically less stable or less reactive and electronically more stable. The difference between these frontier orbitals is known as the HOMO and LUMO gap ($E_{\text{H-L}}$), which is calculated by using Equation (3) below:

$$E_{\text{H-L}} = E_{\text{LUMO}} - E_{\text{HOMO}} \quad (3)$$

Natural bond orbital charge analysis was also performed to determine the shifting of charge from the sodium atom/ion towards the adsorbent surface or vice versa. The total density of state spectra was generated to explore the density of electronic states, the position of the frontier molecular orbitals before and after sodium adsorption, and the nature of electronic contribution during complexation.

3. Results and Discussions

3.1. Interaction of Na/Na⁺ with the C₁₂ Nanoring

First of all, the pure C₁₂ nanoring without symmetry constraints was optimized, and a stable geometry is shown in Figure 1. The nanoring consists of alternating double and triple bonds. The bond distance between adjacent triple and double bonds is 1.24 and 1.36 Å, respectively, which is comparable to 1.33–1.34 Å for C₁₂ obtained using the GA/SA technique, as highlighted in the study performed by D.P. Kosimov [83]. Four potential adsorption sites are available in the C₁₂ nanoring: the carbon–carbon bonds, the ring center, the top of the ring, and directly above a carbon atom. These sites are proposed based on a previous study by Ullah et al. on halide adsorption in a C₁₀ nanoring for alkali metal batteries [71]. Among all of these four possible adsorption sites, Na/Na⁺ are adsorbed and optimized to obtain the most stable position. In the optimized structure of Na@C₁₂, the Na atom occupies the top central position on the ring with an average distance of 1.46 Å. For Na⁺, the most suitable and stable position is the placement of Na⁺ on one side of the carbon nanoring, with a bond distance of 2.46 Å. Interaction energies calculated for Na@C₁₂ and Na⁺@C₁₂ are $-50.08 \text{ kcal mol}^{-1}$ and $-18.72 \text{ kcal mol}^{-1}$, respectively. These results are similar to the early reported data on the interaction between sodium and three-dimensional porous carbon and have higher adsorption energy [84]. The calculated values for Na@C₁₂ and Na⁺@C₁₂ prove that atomic sodium's interaction with C₁₂ is stronger than that with the sodium cation. Previous work by Kosar et al. also showed the stronger interaction of an alkali metal (lithium) atom compared to a Lithium metal cation with

pure C_{60} nanomaterials [85]. The HOMO and LUMO values of pure C_{12} are -8.14 and -2.25 eV, respectively, along with an energy gap of 5.88 eV. The HOMO and LUMO values changed to -6.73 and -1.51 , respectively, after adsorption with pure Na, and the respective energy gap was 5.21 eV. In the case of Na^+ , the HOMO and LUMO values were -11.12 and -5.35 eV, respectively, along with the H-L energy gap of 5.76 eV. The location of HOMO and LUMO densities on the pure C_{12} and its complexes with sodium/sodium cation are equally distributed on the C_{12} ring, which shows delocalization of electronic density within the nanoring. The HOMO and LUMO densities are present on C_{12} in the case of sodium/sodium cation adsorption on the C_{12} nanoring, which shows the shifting of electronic density from sodium towards the C_{12} nanoring. The more pronounced effect is seen in the LUMO density distribution on the sodium atom-adsorbed C_{12} complex, where densities are shifted towards the C-C bonds in the C_{12} nanoring. These results confirmed stronger electronic density interactions in $Na@C_{12}$ than in $Na^+@C_{12}$ complexes.

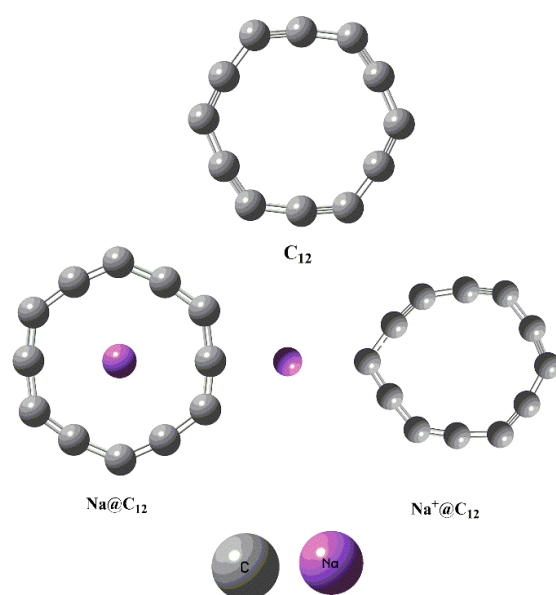


Figure 1. Optimized structures of the C_{12} nanoring and sodium atom (Na)- and sodium cation (Na^+)-adsorbed C_{12} complexes.

3.2. Electrochemical Properties of $Na/Na^+@$ Complexes C_{12}

By assuming the C_{12} nanoring as an anode for a sodium-ion battery, the following reactions occur between the anode and cathode:

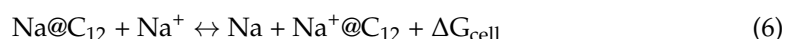
Anode:



Cathode:



Overall, the cell reaction is as follows:



The overall Gibbs free energy change of the cell (ΔG_{cell}) for the complete reaction occurring in a cell can be calculated using the following Equation (7):

$$\Delta G_{\text{cell}} = G(Na) + G(Na^+@C_{12}) - G(Na^+) - G(Na@C_{12}) \quad (7)$$

Here, G represents the Gibbs free energy of given complexes. The Gibbs free energy and cell voltage for Na/Na^+ -adsorbed C_{12} complexes are $30.57 \text{ kcal mol}^{-1}$ and -1.32 V , respectively. Another strategy was adopted to obtain the cell voltage in a favorable range. In this strategic way, the C_{12} is adsorbed with the first three halide ions (F^- , Cl^- , and Br^-). The negative value of cell voltage depicts the destruction of the C_{12} surface, which is not acceptable in practical applications, as reported in the literature [86].

3.3. Adsorption of the C_{12} Nanoring with Halogens (Br^- , Cl^- , and F^-)

The C_{12} nanoring adsorbed with halogens (Br^- , Cl^- , and F^-) by placing each halogen on four possible orientations. It was observed that for the adsorbed halogens on the C_{12} nanoring, the most stable position is at one side of the carbon. After optimization, the bond distance between C and Br^- is $1.93 \text{ \AA}$ in the $\text{Br}^-@ \text{C}_{12}$ complex. The bond distance between C and Cl^- is $1.78 \text{ \AA}$, and in C_{12} and F^- , the bond distance is $1.37 \text{ \AA}$. Optimized geometries are presented in Figure 2. Adsorption of Br^- with the C_{12} nanoring shows stronger interaction as it is reflected through the interaction energy value of $-50.32 \text{ kcal mol}^{-1}$. In the case of Cl^- , the interaction energy is $-47.95 \text{ kcal mol}^{-1}$, and the strongest interaction is observed in the case of F^- with C_{12} ($-84.79 \text{ kcal mol}^{-1}$). Researchers have observed strong interaction between halogens and carbon-based materials and their uses in secondary batteries, as we observed in the current study [87].

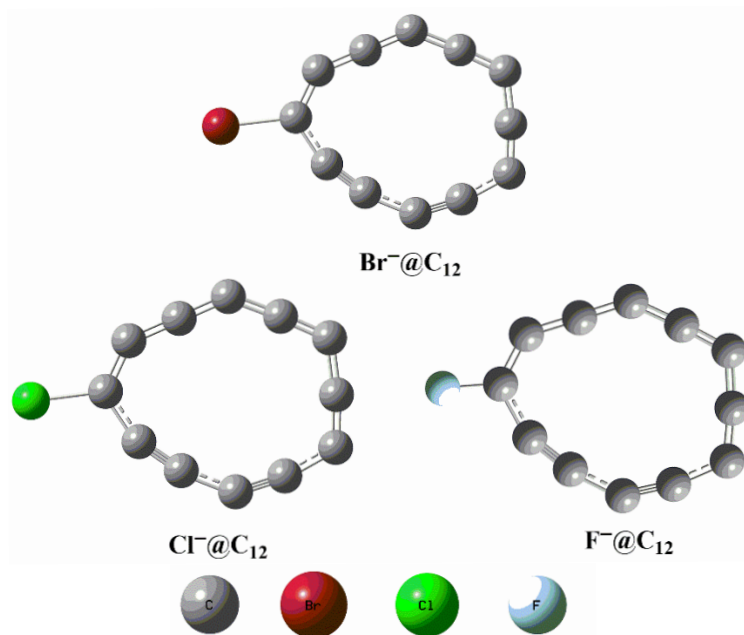


Figure 2. Optimized structures of halogen-adsorbed C_{12} complexes.

After adsorption with bromine, the values of HOMO and LUMO change to -3.69 and 1.82 eV , respectively, with a gap of 5.52 eV . Upon adsorption of chlorine, the values of HOMO and LUMO change to -3.66 and 1.86 eV , respectively, with a gap of 5.53 eV . After adsorption with fluorine, the HOMO and LUMO energy values change to -3.54 and 2.03 eV , respectively, and have a gap of 5.58 eV , showing strong interaction between halide ions and the carbon nanoring. In halide-adsorbed complexes, the HOMO and LUMO densities are equally distributed on the C_{12} nanoring. The large amount of HOMO is present on the halide ion, which shows that it is an electron-rich region and has the ability to provide density to the nanoring. This is confirmed from a smaller LUMO density localization on the halide, as well as in each of the halide-adsorbed C_{12} complexes.

3.4. Adsorption of Na/Na⁺ on Halides@C₁₂ Complexes

The presence of halide ions is supposed to enhance the interaction between Na⁺ and the C₁₂ nanoring as compared to Na. The reason for the greater interaction energy of Na⁺/X[−]@C₁₂ is the electrostatic force of attraction between Na⁺ and the X[−]@C₁₂ nanoring.

After placing sodium in the middle of the ring adsorbed with Br[−], the bond distance between C and Br[−] is 1.92 Å, and the average distance of Na in the center of the ring is 1.20 Å (see Figure 3). In case of Na⁺, the bond distance between C and Br[−] is 1.89 Å and the average distance of Na⁺ from the center of the ring is 1.45 Å. The optimized complex of Na⁺/Cl@C₁₂ showed that the bond distance between C and Cl[−] is 1.75 Å and the average distance of Na⁺ from the center of the ring is 1.46 Å. In the case of fluorine, the bond distance between C and F[−] is 1.38 Å, and the average distance of Na from the center of the ring is 1.21 Å. After placing Na⁺ in the center of the ring, the bond distance between C and F[−] is 1.35 Å, which is less than the former ones. The average distance of Na⁺ from the ring in the center is 1.49 Å. In the case of the sodium cation, interaction with the halogen-adsorbed carbon nanoring is stronger, due to which the bond length is decreased as compared to interaction with the sodium atom. As reported in the literature, halide anions shifted their electronic density towards the GDY-28 surface after adsorption of the selected halide anions on the GDY-28 nanoflake. The nanoflake therefore works as a strong Lewis base, increasing the interaction between Na⁺ and the halides@GDY-28 nanoflake. Specifically, the electrostatic interactions between the cationic Na⁺ and the more strongly nucleophilic F[−] halide anion of the halides[−]@GDY-28 nanoflake is responsible for the significant interaction energy of the Na⁺/halide anion@GDY-28 nanoflake. Among all halides, the strongest interaction is observed for the Na⁺/F[−]@GDY-28 nanoflake because of the higher electronegative nature of F[−] compared to the other two halide anions (Cl[−] and Br[−]) [72]. Moreover, in the case of Na/Na⁺ adsorbed on the halogen-adsorbed Ga₁₂N₁₂ surface, the sodium cation showed high values of interaction energy relative to the sodium atom [73].

Interaction energies for both Na/Na⁺ with halides@C₁₂ nanorings were also calculated and given in Table 1. For Na⁺ at Br[−]@C₁₂, the interaction energy value is −103.82 kcal mol^{−1}, which shows its stronger interaction with the carbon nanoring as compared to atomic Na with the Br[−]@C₁₂ complex. For Na⁺ at the Cl[−]-adsorbed C₁₂, the interaction energy value is −103.04 kcal mol^{−1}, which shows its stronger interaction with the carbon nanoring as compared to Na. Lastly, Na and Na⁺ are adsorbed on the F[−]@C₁₂ complex where their interaction energies are −14.56 and −103.64 kcal mol^{−1} for Na/F[−]@C₁₂ and Na⁺/F[−]@C₁₂ complexes, respectively. As reported in the literature, Murtaza et al. adsorbed pure GDY_28 with halides to design a sodium-ion secondary battery, and the respective interaction energies are −14.10 and −53.62 for Na and Na⁺ adsorbed on Br[−]@C₁₂, −16.32 and −56.40 kcal mol^{−1} for Na and Na⁺ adsorbed on Cl[−]@C₁₂, and −28.46 and −90.75 kcal mol^{−1} for Na and Na⁺ adsorbed on F[−]@C₁₂, respectively [72].

Table 1. Bond distance Å, interaction energy E_{int} (kcal mol^{−1}), Gibbs free energy of the cell ΔG_{cell} (kcal mol^{−1}), and cell voltage V_{cell} (V) of pure C₁₂, Na@C₁₂, Na⁺@C₁₂, Br[−]@C₁₂, Br[−]/Na@C₁₂, Br[−]/Na⁺@C₁₂, Cl[−]@C₁₂, Cl[−]/Na@C₁₂, Cl[−]/Na⁺@C₁₂, F[−]@C₁₂, F[−]/Na@C₁₂, and F[−]/Na⁺@C₁₂ complexes.

Complexes	Bond Distance (Å)	E _{int} (kcal mol ^{−1})	ΔG _{cell} (kcal mol ^{−1})	V _{cell} (V)
Pure C ₁₂	1.30	----	----	----
Na@C ₁₂	C-Na = 1.46	−50.08	30.57	−1.32
Na ⁺ @C ₁₂	C-Na ⁺ = 2.46	−18.72		
Br [−] @C ₁₂	C-Br [−] = 1.93	−50.32		

Table 1. Cont.

Complexes	Bond Distance (Å)	E _{int} (kcal mol ^{−1})	ΔG _{cell} (kcal mol ^{−1})	V _{cell} (V)
Br [−] /Na@C ₁₂	C-Br [−] = 1.92 C-Na = 1.20	−51.47	−52.36	2.27
Br [−] /Na ⁺ @C ₁₂	C-Br [−] = 1.89 Na ⁺ -C = 1.43	−103.82		
Cl [−] @C ₁₂	C-Cl [−] = 1.78	−47.95	-----	-----
Cl [−] /Na@C ₁₂	C-Cl [−] = 1.78 Na-C = 1.20	−50.32	−52.56	2.28
Cl [−] /Na ⁺ @C ₁₂	C-Cl [−] = 1.74 Na ⁺ -C = 1.49	−103.04		
F [−] @C ₁₂	C-F [−] = 1.37	−84.79		
F [−] /Na@C ₁₂	C-F [−] = 1.38 Na-C = 1.21	−14.56	−58.31	2.52
F [−] /Na ⁺ @C ₁₂	C-F [−] = 1.35 Na ⁺ -C = 1.46	−103.64		

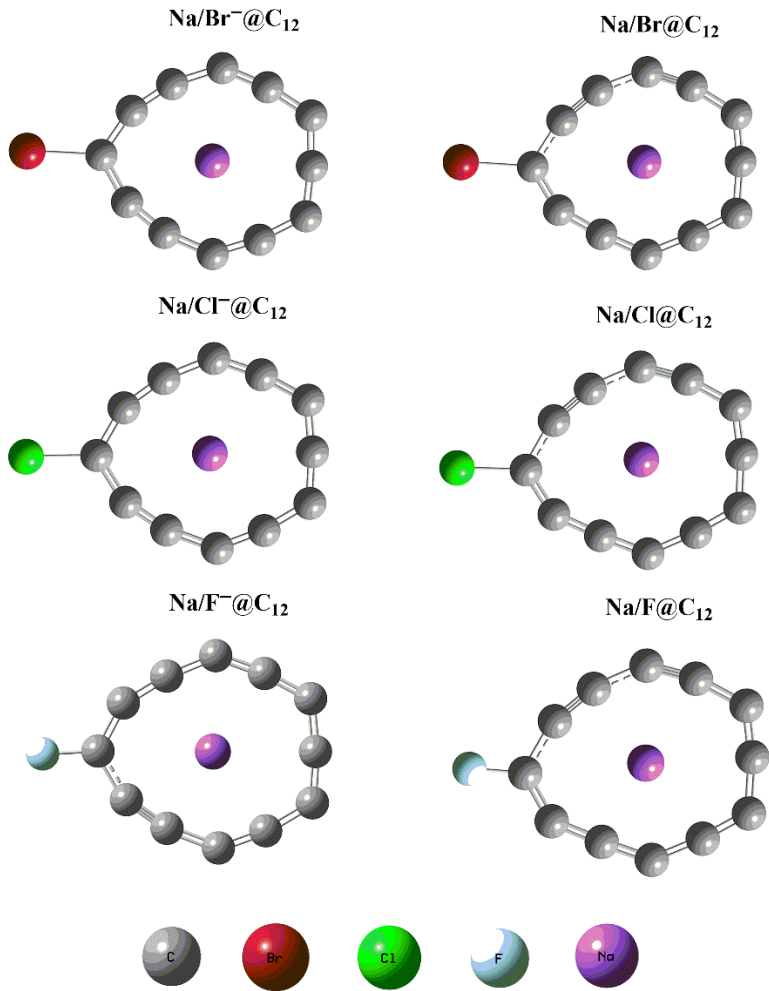


Figure 3. Optimized structures of Na/Na⁺ adsorbed on halide (Br[−], Cl[−], and F[−])-adsorbed C₁₂ complexes.

By placing the Na atom in the center of the adsorbed carbon nanoring with bromine, with an obvious change in HOMO and LUMO values and in their energy, a gap is noticed. The values of HOMO, LUMO, and energy gap are −2.73, 2.14, and 4.87 eV. But the interaction between the Na cation and the halogen-adsorbed nanoring is stronger, as compared to the Na atom. As shown for Na/Br[−]@C₁₂, the HOMO and LUMO and their gap values are

−7.46, −2.22, and 5.41 eV, respectively, and stabilize the complex. By placing the Na atom in the center of a carbon nanoring adsorbed with chlorine, the HOMO and LUMO energies and energy gap values are −2.67, 2.15, and 4.82 eV. But for the Na cation with $\text{Cl}^-@C_{12}$ complexes, −7.67, −2.21, and 5.46 eV are the HOMO and LUMO energies and their energy gap values, respectively. By placing the Na atom in the center of the adsorbed carbon nanoring with F^- , the energy values of the frontier molecular orbitals (FMOs = HOMO and LUMO) and energy gap are −2.53, 2.16, and 4.69 eV. But for Na cation@ $\text{F}^-@C_{12}$, the values are −7.68, −2.12, and 5.56 eV for HOMO and LUMO energies and their energy gaps, respectively. It is clear that the sodium cation interacts more strongly with halides adsorbed on carbon nanorings and stabilizes the complexes. The reason is the shifting of electronic charge from halide anions towards the surface of the C_{12} nanoring in each of the halides $^-@C_{12}$ complexes as discussed *vide infra*. When the Na cation is adsorbed on the halides $^-@C_{12}$ complexes, the electrostatic interactions occur between Na^+ and the anionic surface of halides $^-@C_{12}$. But when the sodium atom is adsorbed, there is electronic repulsion between sodium and the C_{12} surface in each of the halides $^-@C_{12}$ complexes. Due to these interactions, Na cation adsorption is electronically stronger compared to the sodium atom, as reported in previous reports on halide-adsorbed carbon-based nanomaterials for sodium-ion batteries [88–90]. The localization of HOMO and LUMO is presented in Figure 4, which clearly shows the localization of HOMO on the halide and C_{12} nanoring in sodium cation-adsorbed halides $^-@C_{12}$ complexes. A small amount of LUMO is also seen on the halide and C_{12} nanoring, which illustrates the shifting of charge from the halide to the ring and then from the ring towards the sodium cation. On the other side, HOMO is found on C-C bonds in the C_{12} nanoring in atomic sodium-adsorbed halides $^-@C_{12}$ complexes. A sufficient amount of LUMO is also seen on the top of the sodium atom, which illustrates the shifting of charge from the halide to the ring and also from the sodium atom towards the C_{12} nanoring, which results in electronic repulsion, as discussed *vide supra*.

In secondary batteries, the major goal is to increase cell voltage. The required cell voltage is obtained if there is strong interaction between the sodium cation and the halide-adsorbed nanomaterials because stronger interaction results in higher interaction energies and Gibbs free energies, which results in achieving the required cell voltage. In the current work, an increase in interaction energy favors the increase in the Gibbs free energy of the cell (ΔG_{cell}) for the designed complexes. Gibbs free energy increased due to the strong interaction between Na/ Na^+ and halide (Br^- , Cl^- , and F^-) $@C_{12}$ complexes. This increase in Gibbs free energy produces a larger cell potential and increases the cell voltage of the C_{12} nanoring. The chemical reaction of the C_{12} nanoring with the sodium atom/cation is endothermic in nature, but the reaction becomes exothermic after introducing halide ions into the C_{12} nanoring. The Gibbs free energies of bromide-adsorbed C_{12} , chloride-adsorbed C_{12} , and fluoride-adsorbed C_{12} complexes for complexation with sodium atom/cations are −52.36, −52.56, and −58.31 kcal mol $^{-1}$, respectively. A higher Gibbs free energy corresponds to an increase in the cell voltage of these complexes. The calculated cell voltages for Br^- , Cl^- , and F^- -adsorbed C_{12} nanorings in the gas phase are 2.27 V, 2.28 V, and 2.52 V, respectively, for potential use in sodium-ion batteries. These values are significantly higher than the cell voltage of the unadsorbed C_{12} nanoring, which is −1.32 V. The Gibbs free energy of the pure C_{12} nanoring is calculated as 30.57 kcal mol $^{-1}$.

The positive Gibbs free energy makes the C_{12} nanoring unfavorable for the generation of the required cell voltage, which is also clear from its calculated cell voltage (−1.32 V). Among all complexes, the desired cell voltage is obtained for the $\text{Br}^-@C_{12}$ complex. In a previous report by Murtaza et al., the required cell voltage of the halide-adsorbed porous carbon nanosheet is the desired cell voltage [72], which justifies our result. The reason

for the better cell voltage of the bromide-adsorbed C_{12} nanoring is the strong interaction between the sodium atom and cation with the $Br^-@C_{12}$ nanoring, as discussed *vide supra*.

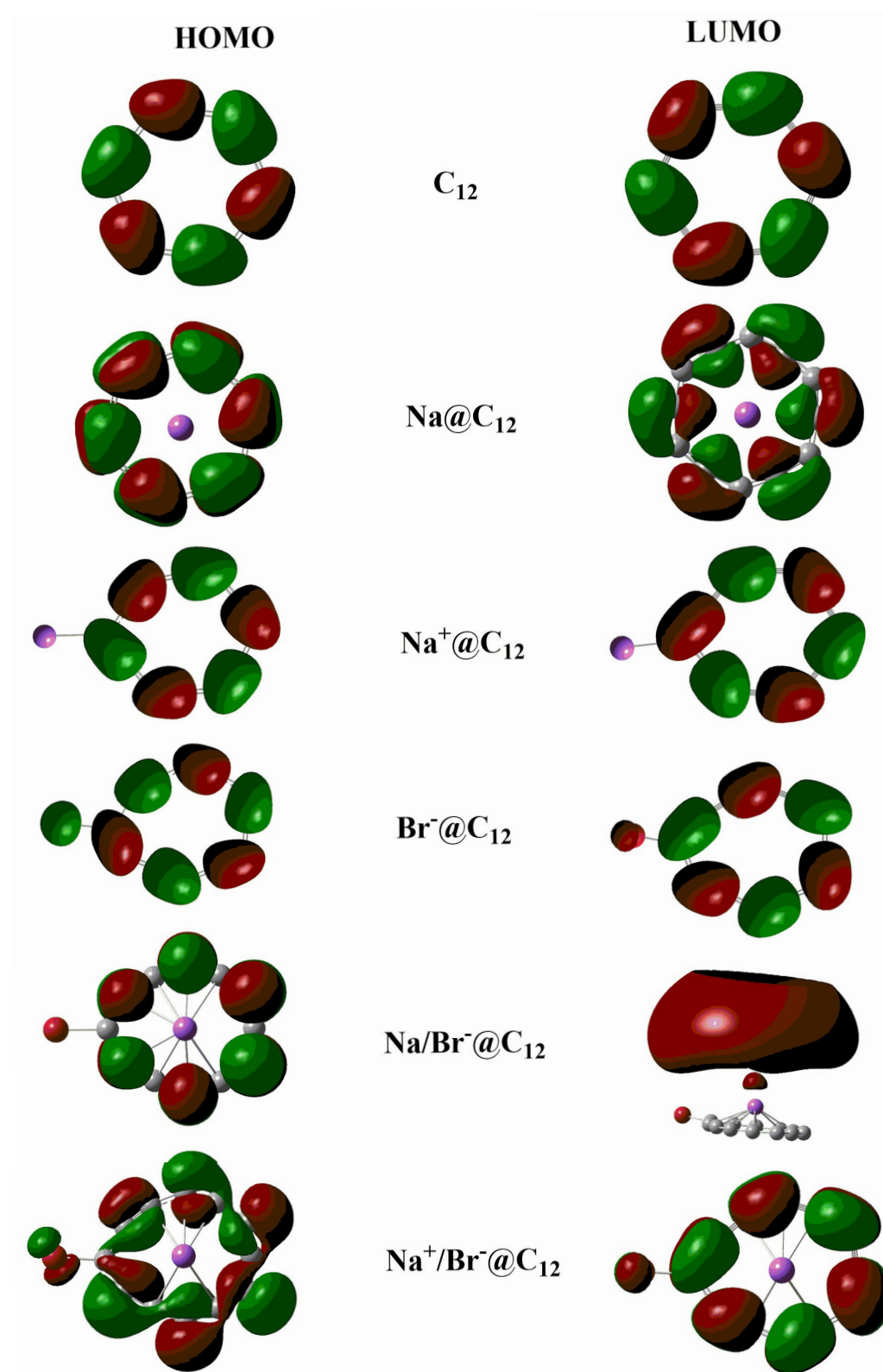


Figure 4. Frontier molecular orbitals such as HOMO and LUMO of pure C_{12} , $Na@C_{12}$, $Na^+@C_{12}$, $Na/Br^-@C_{12}$, and $Na^+/Br^-@C_{12}$.

3.5. NBO Charge Analysis

Natural bond orbital (NBO) charge analysis was performed using the same method (ω B97XD/6-31 + G (d, p)). From the NBO results reported in Table 2, the overall charge on the C_{12} nanoring is 0.00 |e| and the surface is neutral. After Na adsorption with C_{12} , the charge on sodium is 0.96 |e|, and the surface charge changes to -0.96 |e|, showing that charge is transferred from Na to the carbon surface. When the C_{12} ring is adsorbed with Na^+ , the charge on the cation is 0.97 |e|, and the surface charge is at a positive value of 0.02 |e|, showing the fact that charge has been transferred from the carbon surface towards the cation. Upon adsorption of halogens (Br^- , Cl^- , and F^-) on the carbon surface, an obvious change in carbon surface charge is observed due to the transfer of charge from halide ions towards the surface, as halogens are electronegative in nature and are anions, so they have a tendency to donate electrons to the surface. Values of charges obtained through NBO analysis show that after adsorption of Br^- on the C_{12} nanoring, charge on the halide ion is -0.01 |e|, and charge on the surface changes from 0.00 |e| to -0.98 |e|. This indicates that charge is transferred from the halide ion towards the carbon surface. Upon adsorption of Na with the Br^- -adsorbed carbon nanoring, charge on Na is 0.95 |e|, on Br^- , it is 0.01 |e|, and the surface charge is -1.96 |e|. This shows greater charge transfer from the halide towards the carbon surface. When Na^+ is adsorbed, charge on the halide changes to 0.10 |e|, on Na^+ , it is 0.96 |e|, and charge on the carbon surface is -1.06 |e|. When Cl^- is adsorbed on the carbon nanoring, charge on Cl^- is -0.07 |e|, and the surface charge is -0.92 |e|. This indicates that the charge is transferred from Cl^- towards the carbon surface. Upon adsorption of Na with this complex, charge on Cl^- changes from -0.07 |e| to -0.05 |e|, and the surface charge becomes -1.89 |e|. Likewise, in the case of $Cl^-/Na^+@C_{12}$, the surface charge changes to -0.98 |e|, and charge on Cl^- is 0.02 |e|, indicating that charge is transferred towards the sodium cation. In the case of fluorine adsorption with the pure carbon nanoring, the charge on F^- is -0.37 |e| and on the carbon surface, it is -0.62 |e|, showing that from F^- , the charge is transferred towards the nanoring's surface. Upon adsorbing Na, charge on Na is 0.95 |e|, charge on F^- changes from -0.37 |e| to -0.39 |e|, and charge on the carbon surface is -1.56 |e|. In the case of Na^+ , charge on F^- is -0.33 |e|, on Na^+ , it is 0.96 |e|, and charge on the surface is -0.62 |e|. It is clear from the above analysis that charge is transferred from Na and halogens towards the carbon surface.

Table 2. HOMO–LUMO energies, energy gap (E_{H-L} gap), NBO charges on the pure C_{12} surface (NBO_s), NBO charges on the pure sodium metal/cation (NBO_m), and NBO charges on each halide ion (NBO_x) in pure C_{12} , $Na@C_{12}$, $Na^+@C_{12}$, $Br^-@C_{12}$, $Br^-/Na@C_{12}$, $Br^-/Na^+@C_{12}$, $Cl^-@C_{12}$, $Cl^-/Na@C_{12}$, $Cl^-/Na^+@C_{12}$, $F^-@C_{12}$, $F^-/Na@C_{12}$, and $F^-/Na^+@C_{12}$ complexes.

Complexes	E_H eV	E_L eV	E_{H-L}	NBO_s e	NBO_m e	NBO_x e
Pure C_{12}	−8.14	−2.25	5.88	0.00	----	----
$Na@C_{12}$	−6.73	−1.51	5.21	−0.96	0.96	----
$Na^+@C_{12}$	−11.12	−5.35	5.76	0.02	0.97	----
$Br^-@C_{12}$	−3.69	1.82	5.52	−0.98	----	−0.01
$Br^-/Na@C_{12}$	−2.73	2.14	4.87	−1.96	0.95	0.01
$Br^-/Na^+@C_{12}$	−7.64	−2.22	5.41	−1.06	0.96	0.10
$Cl^-@C_{12}$	−3.66	1.86	5.53	−0.92	----	−0.07
$Cl^-/Na@C_{12}$	−2.67	2.15	4.82	−1.89	0.95	−0.05
$Cl^-/Na^+@C_{12}$	−7.67	−2.21	5.46	−0.98	0.96	0.02
$F^-@C_{12}$	−3.54	2.03	5.58	−0.62	----	−0.37
$F^-/Na@C_{12}$	−2.53	2.16	4.69	−1.56	0.95	−0.39
$F^-/Na^+@C_{12}$	−7.68	−2.12	5.56	−0.62	0.96	−0.33

3.6. Partial Density of State (PDOS) and Total Density of State (TDOS) Analysis

TDOS analysis is used to study density of states, which provides information about the values of energy states in occupied and unoccupied orbitals in pure form (C_{12} nanoring) and adsorbed complexes. TDOS gives information about the complexes, and PDOS gives additional information about the involvement of individual species (C_{12} nanoring, sodium atom/cation, and halide ions ($X^- = Br^-$, Cl^- , F^-) in each of the complexes. Graphical representations of TDOS and PDOS spectra are given in Figure 5. From Figure 5, energy gaps in the case of pure C_{12} and after adsorption with Na/ Na^+ are quite visible, as discussed in the FMO analysis. Adsorption with Na shows a significant difference in the shifting of energy states, hence proving stronger interaction with the pure C_{12} nanoring as compared to Na^+ . The PDOS peak of Na shows more involvement in HOMO than the sodium cation. The overlapping of the peaks is shown in both, but more overlapping is seen in sodium, which justifies the FMO results. The graphs show that TDOS peaks are quite intense for the $Na@C_{12}$ complex and depict their high electrostatic interactions.

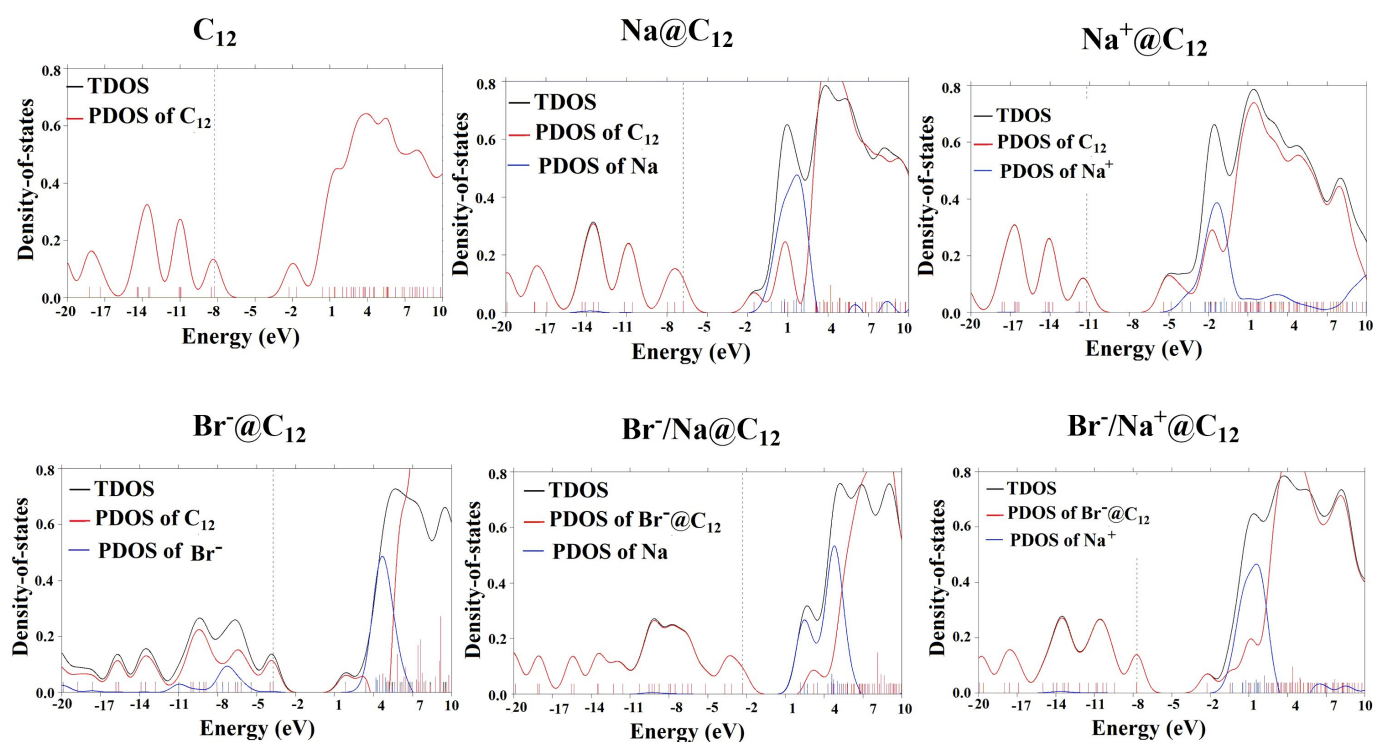


Figure 5. Partial density of states (PDOS) and total density of states (TDOS) of the pure Na/ Na^+ -adsorbed C_{12} nanoring and the Na/ Na^+ -adsorbed $Br^-@C_{12}$ complex.

We noticed that halides have prominent involvement in the HOMOs of all of the halide-adsorbed C_{12} complexes. The reason may be the formation of new orbitals due to shifting of electronic density from halides to the C_{12} nanoring. By adsorbing Na and Na^+ on halide-adsorbed C_{12} complexes, there is a significant change in energy states for the sodium cation as it interacts more strongly with the halide-adsorbed C_{12} complexes as compared to the sodium atom. In the above case, the Na^+ -adsorbed halogen-adsorbed carbon nanoring shows more intense peaks due to strong electrostatic interaction with the halide-adsorbed C_{12} nanoring. The overlapping of the peaks also depicts the stronger interactions between the sodium cation and the halide-adsorbed C_{12} complexes. The spectra of DOS analysis support the FMO results.

4. Conclusions

The electrochemical properties of a C₁₂ nanoring are explored by using the DFT method to assess its potential application as an anode material in Na-ion batteries. For this purpose, the thermodynamic stability of Na@C₁₂ and Na⁺@C₁₂ was analyzed, whereby sodium forms more stable complexes than the sodium cation. The E_{int} of sodium atom is −50.08 and that of the sodium cation is −18.72 kcal mol^{−1} with C₁₂. The small change in Gibbs free energy and cell voltage of −1.32 V is not acceptable for the practical use of the sodium-adsorbed C₁₂ nanoring. Using another strategy, counter halide anion (F[−], Cl[−], and Br[−]) adsorption on the C₁₂ nanoring is investigated in this study to examine the cell voltage. Adsorption of Na/Na⁺ on the halogen-adsorbed (X[−] = Br[−], Cl[−], F[−]) C₁₂ significantly enhances the change in Gibbs free energy value, which ultimately increases their cell voltage. The strong interaction of Na⁺ is seen with halide-adsorbed C₁₂ complexes in comparison with the Na atom. These interactions result in increasing interaction energies, Gibbs free energies, and, ultimately, increasing cell voltage. The cell voltage increases as the electronegativity of halide ions increases. In the gas phase, Br[−]@C₁₂ exhibits a Gibbs free energy of −52.36 kcal·mol^{−1}, corresponding to a cell voltage of 2.27 V. Overall, these calculations were performed in the gas phase without the implementation of an electrolyte, and we conclude that these are qualitative estimations.

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