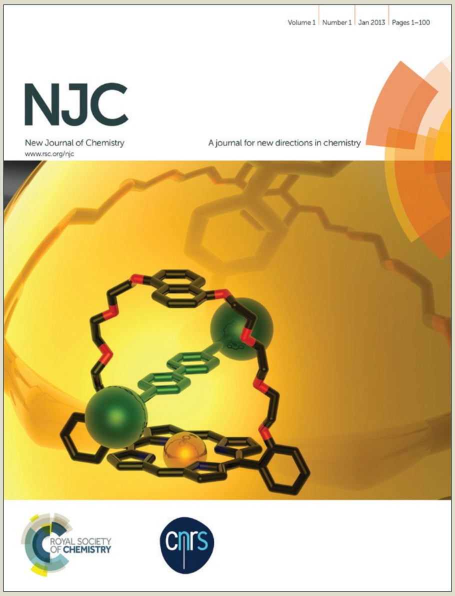
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In-situ formation of bromobenzene diazonium ions and their spontaneous reaction with carbon-coated $LiFePO_4$ in organic media

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Abstract

In this article, the spontaneous reaction, in organic media, of bromobenzene diazonium ions with carbon coated-$LiFePO_4$ particles is reported. The formation of bromobenzene diazonium ions from the corresponding amine and tert-butyl nitrite was also investigated. The modified powders and the reaction mixture were analyzed to get more insight on the grafting mechanism. The modified powders were characterized by thermogravimetric analyses to assess the loading of grafted molecules and inductively coupled plasma atomic emission spectrometry to estimate the number of mole of desinserted Li^+ ions after reaction. Gas chromatography coupled with mass spectrometry measurements provided the yield of diazotization that was determined for various experimental conditions. It was demonstrated that the nature of the substrate strongly affected the yield of diazotization. Although $LiFePO_4$/C is spontaneously reducing *in-situ* generated bromobenzene diazonium ions to form the grafted layer, a significant fraction of diazonium ions is involved in side reactions. The oxidation of $LiFePO_4$/C by tert-butyl nitrite is decreasing the diazotization yield when using $LiFePO_4$/C as substrate. The utilization of 4-bromobenzene diazonium tetrafluoroborate salt resulted in a slightly higher loading of grafted groups but also a higher oxidation of $LiFePO_4$/C. The presence of by-products in solution after grafting reaction suggested also that all species generated by reduction of 4-bromobenzene diazonium ions are not forming a grafted layer. It has been shown that the grafting mechanism is very similar for *in-situ* generated diazonium ions and diazonium salt with grafting efficiencies of about 10 and 14%, respectively.

1. Introduction

Rechargeable batteries based on lithium ions are currently considered as the dominant technology in the field of energy storage because of their high energy density [1]. Lithium-ion batteries using $LiFePO_4$ as cathode are attracting major interest because this iron-based compound is environmentally benign, inexpensive, and structurally stable during charge/discharge processes [2-5]. However, $LiFePO_4$ suffers from poor rate capability because of its low ionic conductivity at the electrolyte/active material interface [6,7] and has been found to be unstable in humid environment [8] or in air [9-13]. An attractive approach to mitigate these issues is based on surface modification of $LiFePO_4$ to change surface properties, to increase its stability and provide more efficient materials. $LiFePO_4$ has been modified by inorganic [14-16] and organic [17-19] coatings. For the latter, the diazonium chemistry has been used to graft a variety of different functional groups [20-22].

Madec *et al.* functionalized $LiFePO_4$ powder with redox molecules in order to assist the insertion of Li^+ ions [23]. They also reported the grafting of nitrophenyl group at the surface of $LiFePO_4/C$ [24]. Delaporte *et al.* functionalized the carbon coating of $LiFePO_4$ with aminophenyl, bromobenzene and trifluoromethylsulfonimidebenzene groups and found a slight improvement of the electrochemical performance, for an optimum loading of molecules, at high cycling rate [25,26]. The enhanced electrochemical performance was attributed to a better distribution of the electrode components limiting the formation of agglomerates and the better wettability with the electrolyte [26]. Very recently, coating $LiFePO_4$ with a polyphenylene layer has been shown to increase the electrical conductivity, insure high rate capability and excellent stability to the resulting cathode materials [27].

In this study, the spontaneous grafting reaction of bromobenzene groups, from the corresponding *in-situ* generated diazonium ions, on $LiFePO_4/C$ surface was investigated. A detailed characterization of the modified powders coupled with analysis of the reaction mixture after grafting allowed determining the diazotization and grafting yields. Thermogravimetric analyses (TGA) were realized to assess the loading of grafted molecules onto the $LiFePO_4$/C surface. Inductively coupled plasma atomic emission spectrometry (ICP-AES) measurements were performed to quantify the amount of deinserted Li^+ (e.g. oxidation level) from the $LiFePO_4$/C powders after grafting. The analysis of the reaction mixture after the grafting reaction by gas chromatography coupled with mass spectrometry (GC/MS) revealed the formation of various by-products in solution and that the diazotization of the amine precursor was incomplete. The effect of the reaction conditions (eg. tert-butyl nitrite and amine concentration) and the substrate onto which the grafting occurred were also investigated.

2. Experimental section

2.1. Modification procedure

For the surface functionalization, the $LiFePO_4$/C powder denoted nanometric $LiFePO_4$/C and composed of nanometric spherical particles with an average size < 1 µm and a carbon content of 2 to 3 wt. % was provided by Hydro-Québec (Varennes, Canada). To compare the effect of the substrate on the yield of diazotization, the same reactions were also carried out with acetylene black carbon (Alfa Aesar) and an uncoated $LiFePO_4$ (Hydro-Québec). All grafting reactions were carried out in organic media. Typically 1.5 g of $LiFePO_4$ or $LiFePO_4$/C or a mass (0.34 g) of acetylene black carbon (AB) corresponding to the same surface area (~12-18 $m^2.g^{-1}$), is dispersed in 50 ml of acetonitrile (HPLC grade), followed by the addition of 1.25, 5 or 20 mmol of *p*-bromoaniline (Aldrich). The mixture was stirred until complete dissolution of the amine and sonicated for 10 min. Thereafter, one equivalent (e.g. same number of moles as the amine) of tert-butyl nitrite (Aldrich) was added to the mixture to generate *in-situ* the bromobenzene diazonium ions. The influence of the concentration of tert-butyl nitrite was also evaluated by employing 2 equivalents with respect to *p*-bromoaniline. The modification was also realized using 1.25 and 5 mmol of 4-bromobenzene diazonium tetrafluoroborate salt (Aldrich). To investigate the effect of tert-butyl nitrite on $LiFePO_4/C$, reactions were also carried out without *p*-bromoaniline by adding only 1.25, 5 and 20 mmol of tert-butyl nitrite in 50 mL of acetonitrile containing 1.5 g of $LiFePO_4/C$. The reaction was carried out during 16 h at room temperature under ambient air. Thereafter, the mixture was vacuum filtered using a Büchner assembly and a Nylon filter with a pore size of 0.47 µm. The modified powder was washed with an excess of acetonitrile (HPLC grade), followed by DMF and acetone (ACS grade). Finally, the modified powder was dried under vacuum at 70 °C for at least 12 h prior to characterization.

2.2. Characterization

In order to estimate the loading of grafted molecules, thermogravimetric analyses (TGA) were carried out under a constant air flow of 90 $mL.min^{-1}$ from 30 to 750 °C, using a TA Instruments TGA (Q500)/Discovery MS. The amount of lithium in the samples was assessed by inductively coupled plasma atomic emission spectrometry (ICP-AES) on Thermo Jarrell Ash Trace Scan. Typically, 40 mg of modified powder was added to 30 mL of 18 M nitric acid and the solution was brought to the boil until the transparency. After dilution with a 5% HNO_3 solution, the solutions were ready for analysis. The lithium content was evaluated from a calibration curve made with various Li solutions prepared from a lithium atomic spectroscopy standard solution (Fluka, [Li] = 1000 ppm, prepared with $LiNO_3$ and 0.5 M HNO_3).

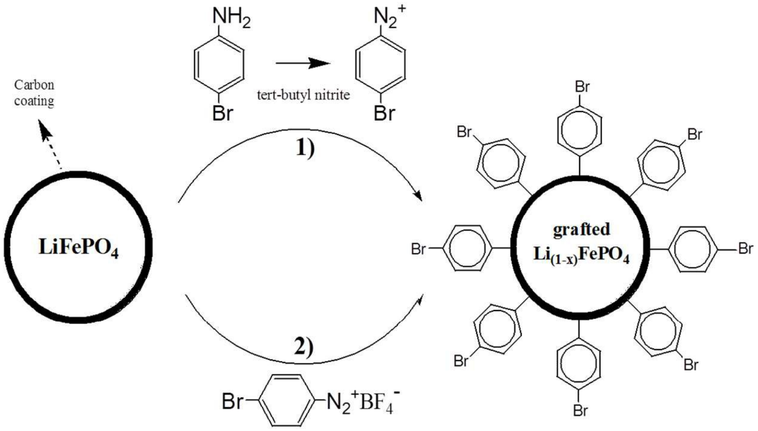
2.3. Analysis of reaction mixture

The amount of *p*-bromoaniline remaining in solution after reaction was determined by gas chromatography coupled to a mass spectrometer (GC/MS) and using a calibration curve established by using solutions with different concentrations of *p*-bromoaniline and a constant concentration of nonane as internal standard. Nonane was chosen because of its stability and inertness with reactants in solution. The concentration of *p*-bromoaniline was estimated by integration of its associated peak of the gas chromatogram. After filtration, acetonitrile of the reaction vessel and from the powder washings were combined. To the resulting 250 mL solution completed with acetonitrile, 250 µL of nonane (1.4 mmol) was added. Other by-products were also detected during the GC/MS analysis. However, in this case a calibration curve was not made for each of these species and only their concentration relative to that of nonane was determined. These solutions were analyzed with an Agilent Technologies, 7890A system and an Agilent HP-5MS 30 m (5% Phenyl Methyl Siloxane) column. The temperature in the inlet was 220 °C to immediately vaporize the sample (0.6 µL) and a split ratio 10:1 was applied. A helium flow of 20 $mL.min^{-1}$ and a heating rate of 10 °C were employed, between 50 and 280 °C to obtain a good separation of different species. Electronic impact source was used to ionize volatile molecules and the mass spectrometer was employed to identify the different fragments ranging from 40 to 800 m/z.

3. Results and discussion

3.1. General description of the experimental procedure

The mechanism of spontaneous grafting of bromophenyl groups on $LiFePO_4$/C by using *in-situ* generated diazonium ions was investigated. Firstly, the formation of the diazonium ions from the *p*-bromoaniline was monitored (Scheme 1, step 1). Secondly, more insight in the grafting reaction was obtained by analysis of the soluble solution reaction products, the evaluation of the lithium content of the grafted $LiFePO_4$ and the corresponding loading of grafted groups. The efficiency of the grafting reaction by using the 4-bromobenzene diazonium tetrafluoroborate salt was also investigated (Scheme 1, step 2).



Scheme 1. Schematic representation of grafting reaction by reduction of 1) *in-situ* generated bromobenzene diazonium ions and 2) 4-bromobenzene diazonium tetrafluoroborate salt. A schematic representation of the organic layer on carbon coated $LiFePO_4$ and the delithiated phase is shown.

3.2. Characterization of modified powders

The loading of grafted molecules present at the surface of the modified $LiFePO_4$ was evaluated by thermogravimetric analysis (TGA) according to a procedure described in the literature [11,25,28] and in Supplementary Information (Figure ESI1). Table 1 shows that the loading of grafted molecules increases when both the concentration of amine precursor (entry 1-3) and the diazonium salt (entry 9-10) used for the modification is increased. In all cases, the loading of grafted molecules is very low (< 2 wt. %) and found to be higher with the diazonium salt than with *in-situ* generated diazonium ions.

Table 1. TGA and ICP data for different samples depending on the modification conditions. The grafting efficiency is given by the moles of grafted molecules/moles of deinserted lithium ions ratio.

MODIFICATION CONDITIONS				**TGA**		**ICP**		
Entry	Diazonium salt (mmol)	Amine (mmol)	TBN (mmol)	Grafted molecule (wt. %)	Corresponding grafted bromobenzene groups (mol*10^{-5})	x in $Li_{(1-x)}FePO_4$	Li^+ desinserted (mol*10^{-4})	Grafting efficiency (%)
1	-	1.25	1.25	0.43	4.1	0.047	4.47	9.2 (*11.6*)*
2	-	5	5	0.87	8.3	0.067	6.37	13 (*18.2*)*
3	-	20	20	0.98	9.4	0.121	11.5	8.2 (*14.3*)*
4	-	0	1.25	-	-	0.012	1.14	-
5	-	0	5	-	-	0.032	3.04	-
6	-	0	20	-	-	0.108	10.3	-
7	-	1.25	2.5	0.74	7.1	0.081	7.70	9.2
8	-	5	10	1.07	10	0.112	10.6	9.4
9	1.25	-	-	1.35	12.9	0.086	8.18	15.8
10	5	-	-	1.84	17.6	0.149	14.17	12.4

* *Values in parentheses refer to the grafting efficiency when the oxidation of tert-butyl nitrite is not taking into account.*

Subsequently, the lithium content of the bromophenyl-modified $LiFePO_4$/C powders was determined by ICP-AES. Table 1 reports the amount of deinserted lithium ions from $LiFePO_4$/C samples following modification with different concentration of amine and tert-butyl nitrite and diazonium salt. Firstly, increasing the equimolar concentrations of amine and tert-butyl nitrite in solution leads to an increase of the amount of Li^+ deinserted from $LiFePO_4$. Secondly, a similar trend is observed when a diazonium salt is used. Thirdly, an increase is also noticed when the concentration of tert-butyl nitrite is increased while keeping the amine concentration constant (compare entry 1 with 7 and entry 2 with 8). Table 1 also shows that the amount of deinserted lithium ions is significantly higher following reaction with the diazonium salt. The increase of the concentration of deinserted lithium ions with an increase of the diazonium salt and amine precursor concentration is in agreement with a mechanism presented in Scheme 1 and which is involving $LiFePO_4$/C as electron source for the reduction of diazonium ions [24].

3.3. Grafting efficiency

Comparing the number of moles of grafted groups with that of deinserted lithium ions allow to evaluate the grafting efficiency which is found to be about 10 and 14% for the grafting with *in-situ* generated diazonium ions and the diazonium salt, respectively. In order to understand the difference of reactivity between *in-situ* generated diazonium ions and the diazonium salt, $LiFePO_4/C$ was left to react with tert-butyl nitrite alone (without the amine) and the amount of deinserted lithium ions (and oxidation of $LiFePO_4/C$) was determined by ICP-AES. Table 1 shows that a significant amount of lithium ions are deinserted and their concentration increases linearly with that of tert-butyl nitrite (Figure ESI2 in Supplementary Information). It can be observed that for the highest concentration of tert-butyl nitrite employed (entry 6, Table 1), the quantity of deinserted lithium ions corresponds to almost 90% of that observed for the reaction of $LiFePO_4/C$ with *in-situ* generated diazonium ions (entry 3, Table 1). Subtracting the amount of lithium ions deinserted by reaction of $LiFePO_4/C$ with tert-butyl nitrite alone from that found during reaction with *in-situ* generated diazonium ions allow to compute a corrected grafting efficiency of about 15% (Table 1, values in parentheses). This value is similar to that obtained for reaction with the diazonium salt (see Scheme ESI1 in Supplementary Information). One should note that this calculation assumes that the reaction of tert-butyl nitrite with $LiFePO_4/C$ is not affected by the presence of the amine. This is most likely incorrect since a fraction of tert-butyl nitrite reacts with the *p*-bromoaniline in solution, thus the quantity of nitrite available to oxidize $LiFePO_4/C$ is much lower.

The 15% grafting efficiency reported here is similar to that obtained for the attachment of benzenetrifluoromethylsulfonimide groups at the $LiFePO_4/C$ surface [26] but significantly lower than the value of about 25% reported earlier for grafting of nitrophenyl groups [24]. In the latter case, the grafting reaction was carried out by using the corresponding diazonium salt. However, the difference of grafting yield cannot be solely attributed to the fact that diazonium salt and *in-situ* generated diazonium ions are used. A higher grafting yield is anticipated with the nitrophenyl diazonium, which is characterized by a more positive reduction potential [21]. This has been previously demonstrated for the electrochemical grafting of 4-nitrobenzene, 4-carboxybenzene and N,N-diethylaniline groups on gold electrode that was characterized by faradaic efficiency of 53, 36 and only 14%, respectively [29]. These results suggest that a significant fraction of the reduced diazonium ions is forming by-products.

3.4. In-situ formation of diazonium ions

In order to get more insight into the grafting process involving *in-situ* generated diazonium ions, GC/MS measurements of the reaction solution were performed to identify the various by-products formed during the grafting reaction. Firstly, the yield for the formation of diazonium ions was monitored. The GC/MS results included in Table 2 clearly indicate that the diazotization reaction is incomplete when equimolar concentrations of *p*-bromoaniline and tert-butyl nitrite (TBN) are used. The yield of diazotization increases with an increase of the concentration and ranged from 40 to 55% in our experimental conditions. The slow kinetics for the diazotization of the *p*-bromoaniline (second-order rate constant of 4.41×10^{-3} $L.mol^{-1}.s^{-1}$ at 22 °C) [30] is at the origin of these low yields, as several hours are needed to completely diazotize the amine in acetonitrile (see Figure ESI3 that presents a plot of the variation of *p*-bromoaniline concentration upon reaction with tert-butyl nitrite, Supplementary Information).

Table 2. Yield of diazotization (%) estimated by GC/MS experiments as a function of the concentration of amine and tert-butyl nitrite (TBN) used for the modification. The remaining amine in solution (unreacted amine) is quantified by GC/MS and the diazonium ions amount by difference.

Entry	Amine [TBN] (mmol)	Unreacted amine (mmol)	Diazonium ions (mmol)	Yield of diazotization (%)
1	1.25 [1.25]	0.754	0.5	40
2	5 [5]	2.59	2.41	48
3	20 [20]	9	11.0	55
4	1.25 [2.5]	0	1.25	100
5	5 [10]	0.2	4.8	96

Previous reports have shown that the diazotization reaction depends on the nature of the amine and is fast in the case of 3-aminopyridine, when performed in acidic media [31], and incomplete with 4-nitroaniline [32]. Nonetheless, a significant increase of the diazotization yield is observed upon doubling the tert-butyl nitrite concentration and maintaining that of the amine constant at 1.25 mmol. However, even if complete diazotization is achieved for these concentrations, the loading of grafted molecules and deinserted lithium ions remained smaller than that found by grafting with the diazonium salt (compare entries 7-8 with 9-10, Table 1). This is most likely due to the fact that the *in-situ* generated diazonium ions formed in acetonitrile were less stable than the diazonium salt and decomposed rapidly to form various colored by-products (see Figures ESI4 and ESI5 in Supplementary Information). This is confirmed by GC/MS that was used to analyze by-products formed by reaction of *in-situ* generated diazonium ions with a substrate and that showed the presence of a significant amount of bromobenzene (Table 3). Table 3 also shows that other by-products were formed in solution during the grafting reaction. These competitive reactions led to a decrease of available aryl radicals for the grafting process. In addition, insoluble products were also present in the filtrate after reaction (not analyzed by GC/MS) and are most likely resulting from the degradation or reaction of *in-situ* generated diazonium ions in solution. Hence, the amounts of diazonium ions reported in Table 2 refer to the highest quantity of diazonium ions available in solution and are overestimated. However, it was not possible to analyze every species in solution and especially the solid products and therefore, a complete mass balance cannot be established.

Table 3. Relative concentration (S(species)/S(nonane)) of various species determined by GC/MS for various concentrations of amine and tert-butyl nitrite (TBN) used for the modification of $LiFePO_4$/C. The concentration of each species relative to that of nonane is given.

	S(species)/S(nonane) (%)			
Species	1.25 mmol amine + 1 eq. TBN	1.25 mmol amine + 2 eq. TBN	5 mmol amine + 1 eq. TBN	5 mmol amine + 2 eq. TBN
***p*-bromoaniline**	76.8	-	260.5	21.7
bromobenzene	2.8	27.0	14.7	100.3
2,4-dibromoaniline	0.4	-	5.5	1.5
1,4-dibromobenzene	0.3	3.5	2.8	11.5
4-bromophenol	-	traces	2.5	7.9
4,4’-dibromo-azobenzene	-	0.9	-	1.9
1-bromo-4-nitrobenzene	-	traces	-	1.2

3.5. Effect of substrate

In earlier studies [31,32], the diazotization reaction was performed in the absence of a substrate onto which grafting can occur. Also, since the oxidation of $LiFePO_4$/C by tert-butyl nitrite was demonstrated (vide supra), the effect of the substrate on the diazotization reaction was evaluated. In addition to nanometric $LiFePO_4$/C discussed above, the modification process was performed with an uncoated $LiFePO_4$ and acetylene black carbon. Acetylene black carbon (AB) was selected to avoid side-reactions with tert-butyl nitrite. In contrast to $LiFePO_4$/C, functionalization did not occur with uncoated $LiFePO_4$ (see thermogravimetric curves of Figure ESI6 in Supplementary Information), a similar observation has been made by Madec *et al.* [24].

Table 4 reports the yield of diazotization and the amount of the various by-products identified in solution after grafting on the different substrates. With the uncoated $LiFePO_4$, only bromobenzene and 1,4-dibromobenzene were formed in low yield. Presumably, tert-butyl nitrite reacted rapidly with the uncoated $LiFePO_4$, leading to its oxidation and a low diazotization yield (28%). This is consistent with the higher diazotization yield and lower concentration of remaining *p*-bromoaniline after reaction with carbon-coated $LiFePO_4$ and highlights the utility of the carbon coating, firstly to enable the surface functionalization and secondly to avoid the oxidation of $LiFePO_4$. Similarly, employing AB as substrate led to a large increase of the diazotization yield that reached 91%, which is much higher than when using $LiFePO_4$/C powder for the modification. Furthermore, the proportion of bromobenzene increased from 2.8% for $LiFePO_4$/C to 9.4% with carbon AB (see Table 4). Due to a higher yield of diazotization, the quantity of by-products generated by degradation of diazonium ions is also increased.

Table 4. Yield of diazotization and GC/MS data for different samples in presence of 1.25 mmol of *p*-bromoaniline and tert-butyl nitrite.

	Nanometric $LiFePO_4$/C	**Uncoated $LiFePO_4$**	**AB**	**No substrate**
Yield of diazotization (%)	40	28	91	99
***p*-bromoaniline**	76.8	91.9	13.0	1.1
bromobenzene	2.8	1.7	9.4	16.9
2,4-dibromoaniline	0.4	-	-	-
1,4-dibromobenzene	0.3	0.4	3.8	2.5
Bis-(4-bromophenyl)-amine	-	-	-	-
4-bromophenol	-	-	4.4	12.2
4,4'-dibromo-azobenzene	-	-	0.9	-
1-bromo-4-nitrobenzene	-	-	0.5	1.6

In smaller proportion, bromo and nitro substituted molecules were also found. It is well known that tert-butyl nitrite is an effective nitrating reagent for phenols, and nitrated by-products have been observed during diazotization reaction of aniline with tert-butyl nitrite [33,34]. This is supported by the observation that an increase of the concentration of tert-butyl nitrite led to a significant increase of the concentration of nitro-compounds and the disappearance of species like 2,4-dibromoaniline, that evidently react with the excess of tert-butyl nitrite. These observations explain why a 100% yielding diazotization reaction is never observed with one equivalent of tert-butyl nitrite [35]. Indeed, reaction of *p*-bromoaniline with tert-butyl nitrite in acetonitrile without substrate gave a yield of 99% for the formation of the bromobenzene diazonium ions. As shown in Table 4, the proportion of by-products in solution is not negligible and the concentration of bromobenzene and 4-bromophenol considerably increased. These results demonstrate, firstly, that the substrate influences the yield of formation of diazonium ions since the diazotization reaction is almost quantitative in absence of substrate, and secondly, that the *in-situ* generated diazonium ions are unstable in acetonitrile.

4. Conclusion

In this paper, the formation of bromobenzene diazonium ions and the grafting of bromobenzene groups on $LiFePO_4/C$ powder were investigated. Analyses of both the modified powder and the reaction solution allowed to get more insight in the grafting reaction. The presence of by-products in solution after grafting demonstrates that only a fraction of the diazonium ions spontaneously reduced by $LiFePO_4/C$ is grafted to its carbon surface. In parallel, the side-reaction between tert-butyl nitrite and $LiFePO_4/C$ particles led to a low yield of diazotization. Surprisingly, the diazotization yield was strongly affected by the nature of substrate and directly related to the contribution of tert-butyl nitrite to the oxidation of $LiFePO_4$. Using 4-bromobenzene diazonium tetrafluoroborate salt resulted in a higher loading of grafted groups but also a higher oxidation of $LiFePO_4/C$. It was shown that the grafting mechanism is very similar using the *in-situ* method or directly by employing the commercial diazonium salt and grafting efficiencies of about 10 and 14% were found for the reaction with *in-situ* generated diazonium ions and the diazonium salt, respectively.

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Graphical and textual abstract

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In-situ formation of bromobenzene diazonium ions and their spontaneous reaction with carbon-coated $LiFePO_4$ in organic media

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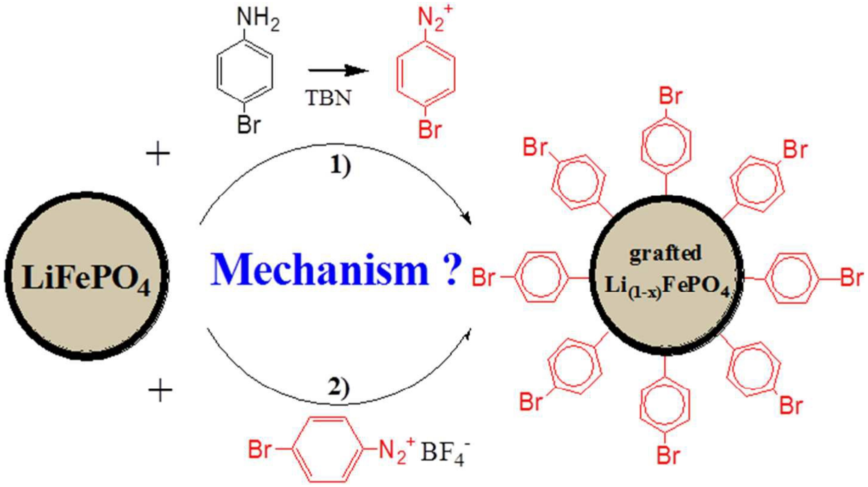

In this study, the diazotization of bromoaniline in presence of carbon-coated $LiFePO_4$ and the grafting of bromobenzene moieties are investigated.