Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information

New Journal of Chemistry

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

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ESI1 - Estimation of the loading of grafted groups

Thermogravimetric analysis (TGA) was used to assess the loading of grafted molecules present at the surface of the modified $LiFePO_4$ [1-3]. The mass gain up to about 400 °C, shown in Figure ESI1, is associated with the formation of $Li_3Fe_2(PO_4)_3$ and Fe_2O_3 during oxidation [2,3]. Despite that oxidation of $LiFePO_4$ occurs up to 600 °C [4], a mass loss is observed above 400 °C due to the burn-off of the carbon coating. The difference at 600 °C between the TGA curves of coated and uncoated $LiFePO_4$ provides the carbon content [2]. As illustrated in Figure ESI1, all the grafted samples present a larger weight loss at 600 °C than unmodified nanometric $LiFePO_4$/C ($LiFePO_4$/C nano), which is associated with the departure of the grafted molecules. It is clear that the method involving the reduction of 4-bromobenzene diazonium tetrafluoroborate salt (△ and ○) is more efficient that the *in-situ* method (▲ and ●), since the weight losses between 400 and 600 °C are higher. Subtracting the weight loss recorded in this range of temperature for the $LiFePO_4$/C nano from that for the different grafted powders allows an estimation of the loading of grafted molecules. The calculated amounts of grafted groups for modified $LiFePO_4$ are reported in Table 1.

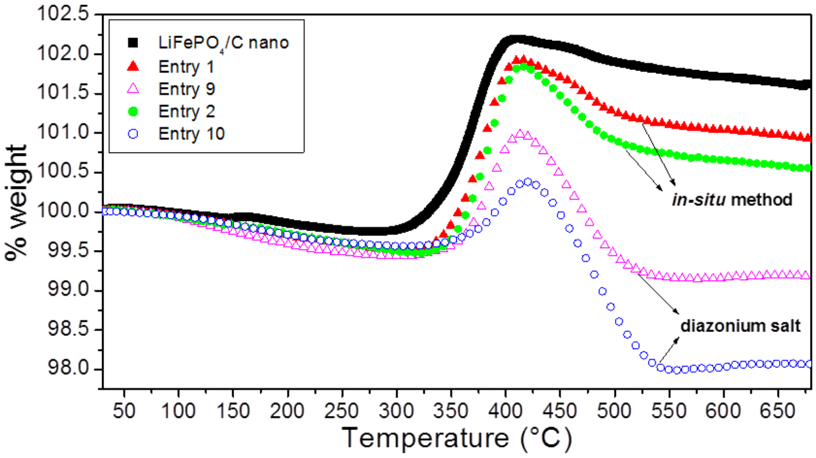


Figure ESI1. Thermogravimetric curves for unmodified (■) and bromophenyl-grafted $LiFePO_4$/C powders by the *in-situ* method (▲ and ●) and reduction of 4-bromobenzene diazonium tetrafluoroborate salt (△ and ○). The data extracted from these curves are presented in Table 1.

ESI2 - Oxidation of nanometric $LiFePO_4/C$ powders by tert-butyl nitrite

$LiFePO_4/C$ was left to react with tert-butyl nitrite alone (without the amine) and the amount of deinserted lithium ions was determined by ICP-AES and consequently the oxidation level of $LiFePO_4/C$. Figure ESI2 shows the linear relation between the level of $LiFePO_4/C$ oxidation (x in $Li_{(1-x)}FePO_4/C$) and the quantity of tert-butyl nitrite used.

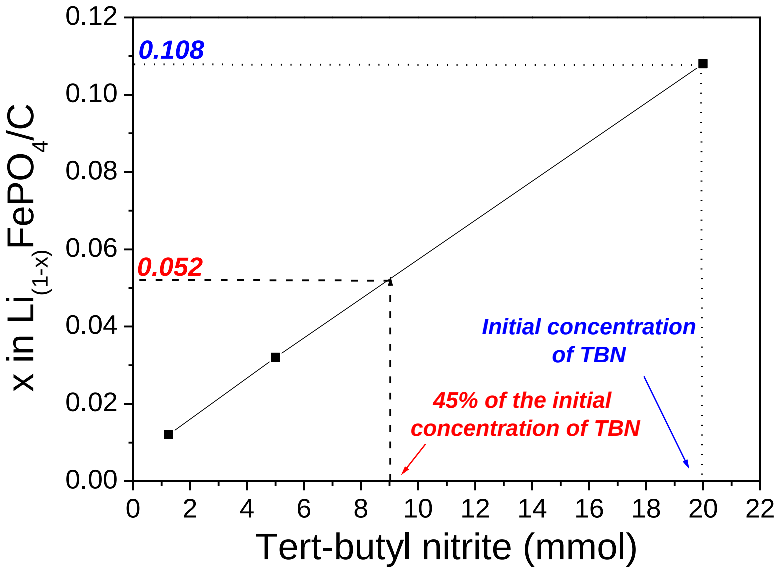
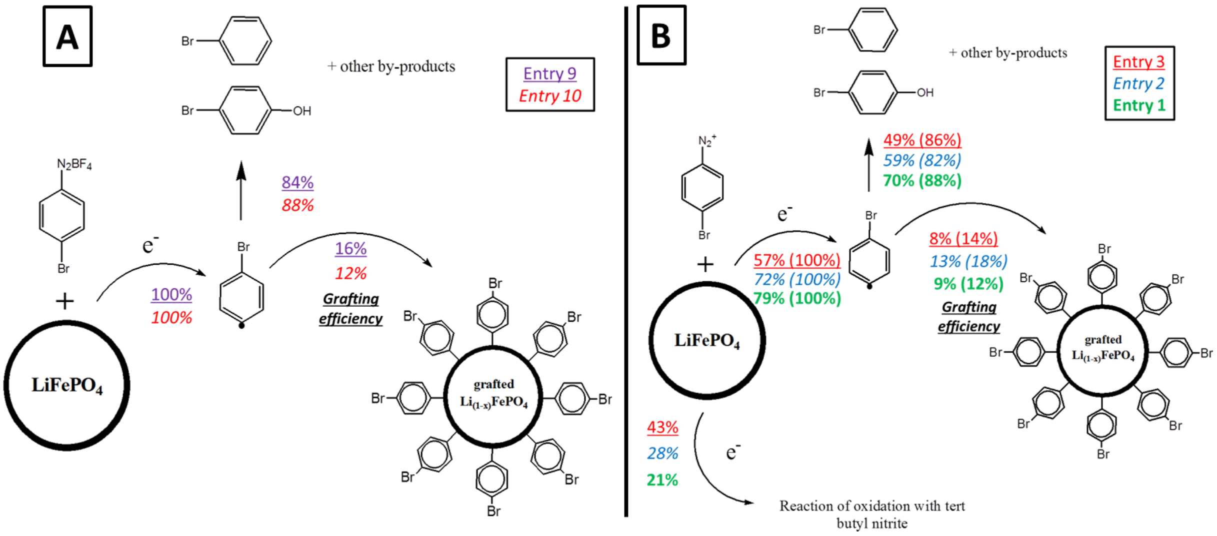


Figure ESI2. Linear relation between the level of $LiFePO_4/C$ oxidation (x in $Li_{(1-x)}FePO_4/C$) and the quantity of tert-butyl nitrite (TBN) used (mmol).

From the data of Figure ESI2, the extent of $LiFePO_4/C$ oxidation by tert-butyl nitrite can be easily found during the grafting reaction by reduction of *in-situ* generated 4-bromobenzene diazonium ions. For instance, employing 20 mmol of *p*-bromoaniline and tert-butyl nitrite for the modification of $LiFePO_4/C$ (entry 3, Table 1 of the manuscript) led to a value of x in $Li_{(1-x)}FePO_4/C$ of 0.121. On the other hand, when $LiFePO_4/C$ reacts with tert-butyl nitrite alone, a value of x in $Li_{(1-x)}FePO_4/C$ of 0.108 is obtained (see Figure ESI2). Thus, 90% of the oxidation of the $LiFePO_4/C$ powder during the grafting reaction is due to the side reaction with tert-butyl nitrite. However, since tert-butyl nitrite also reacts with *p*-bromoaniline to form the corresponding 4-bromobenzene diazonium ions, the quantity of tert-butyl nitrite available to oxidize $LiFePO_4$/C is much lower than 90% in this case. In fact, the yield of diazotization (entry 3, Table 2 of the manuscript) is about 55%, leading to a maximum of 45% of the initial concentration of tert-butyl nitrite involved in the oxidation of $LiFePO_4$/C powder. According to Figure ESI2 and considering that the remaining tert-butyl nitrite reacts entirely with $LiFePO_4$/C, the calculated amount of desinserted lithium ions x in $Li_{(1-x)}FePO_4$/C is about 0.052, corresponding to 43% of the oxidation of the grafted $LiFePO_4$/C powder. Thus, it can deduced that 21, 28 and 43% of the $LiFePO_4$/C oxidation is due to the reaction with TBN, when 1.25, 5 and 20 mmol of precursors (amine + tert-butyl nitrite) were used, respectively. Scheme ESI1 shows the outcome and causes of $LiFePO_4$/C oxidation for different reaction conditions. An average grafting efficiency of 14% was determined for the reaction with 4-bromobenzene diazonium tetrafluoroborate salt (Scheme ESI1A) and the average of 86% of the diazonium ions led to the formation of soluble by-products. For grafting with *in-situ* generated 4-bromobenzene diazonium ions, on average, 10% of the electrons donated by $LiFePO_4$/C are used to form the grafted layer. In contrary to Scheme ESI1A, the oxidation of $LiFePO_4$/C is also due to the reaction with tert-butyl nitrite. Thus, the quantity of electrons that reduced bromobenzene diazonium ions to form the by-products is lower. However, by considering only the actual concentration of diazonium ions being generated, an average grafting efficiency of 15% is found (see values in parentheses in Scheme ESI1B), similar to that found using 4-bromobenzene diazonium tetrafluoroborate salt for the modification. Moreover, in this case, on average, 85% of the electrons led to the formation of by-products in solution, as observed for grafting employing 4-bromobenzene diazonium tetrafluoroborate salt.



Scheme ESI1. Representation of the various contributions to $LiFePO_4$/C oxidation during the reduction of: a) 4-bromobenzene diazonium tetrafluoroborate salt and b) *in-situ* generated 4-bromobenzene diazonium ions. The modification conditions for these grafted $LiFePO_4$/C samples are presented in Table 1. Values in parentheses (right) refer to the oxidation of $LiFePO_4$ when that of tert-butyl nitrite is not taking into account.

ESI3 – Kinetics for the reaction of *p*-bromoaniline with tert-butyl nitrite

Figure ESI3 presents the variation of the concentration of *p*-bromoaniline in presence of 1.25 mmol (1 equivalent) of tert-butyl nitrite in acetonitrile. The kinetics for the disappearance of the amine was slow (second-order rate constant of 4.41 x 10^{-3} $L.mol^{-1}.s^{-1}$ at 22 °C) and only 50% of the amine was consumed after 4 h of reaction and 80% after 10 h. This result explains the higher loading of bromobenzene groups on $LiFePO_4$/C when the 4-bromobenzene diazonium tetrafluoroborate salt was used (compare entries 1-2 with 9-10, Table 1). For the *in-situ* method (Scheme 1, step 1), the diazonium ions are slowly formed during several hours, while with the diazonium salt, 1.25 mmol of diazonium ions are already present in solution at the beginning of the reaction (Scheme 1, step 2).

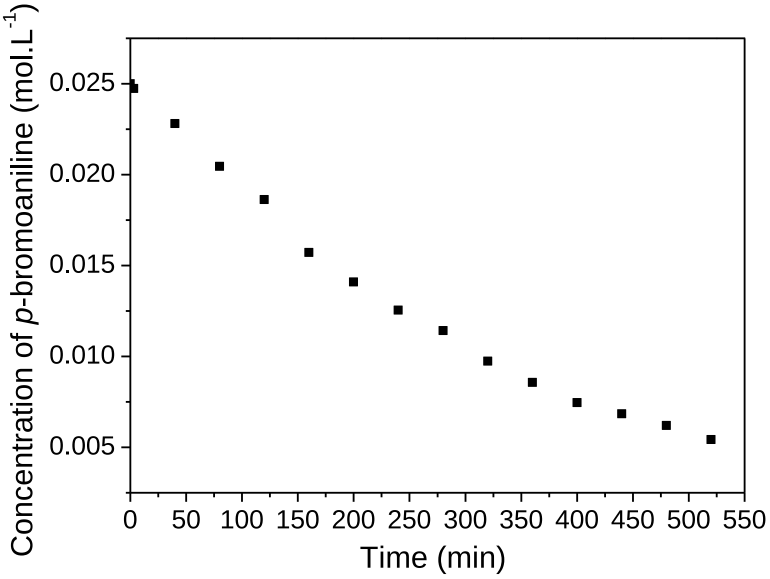


Figure ESI3. Variation of the concentration of *p*-bromoaniline with time after addition of 1.25 mmol (1 equivalent) of tert-butyl nitrite to 1.25 mmol of *p*-bromoaniline in acetonitrile.

ESI4 - Stability of bromobenzene diazonium ions in acetonitrile without $LiFePO_4$

To compare the stability of the bromobenzene diazonium ions in acetonitrile, two different solutions were prepared. The first consists of 1.25 mmol of *p*-bromoaniline and 1.25 mmol (1 equivalent) of tert-butyl nitrite in acetonitrile and the second of 1.25 mmol of 4-bromobenzene diazonium tetrafluoroborate salt in acetonitrile. The solutions were left to react for 24 h and optical photographs of the solutions at different reaction times: 0, 200 min and 24 h were taken (Figure ESI4). Optical photographs show that the solution containing the amine and tert-butyl nitrite became orange after 200 min and dark orange-red after one day. In contrast, the solution containing the diazonium salt remained transparent after 24 h and even after 10 months (Figure ESI5), presumably the diazonium cations are stabilized in the presence of BF_4^- anions. These observations demonstrate the formation of colored by-products in the case of the solution containing *in-situ* generated diazonium ions. Thus, the diazonium salt solution is stable in acetonitrile (slight yellow coloration after 10 months, see Figure ESI5) whereas *in-situ* generated diazonium ions yielded colored degradation products.

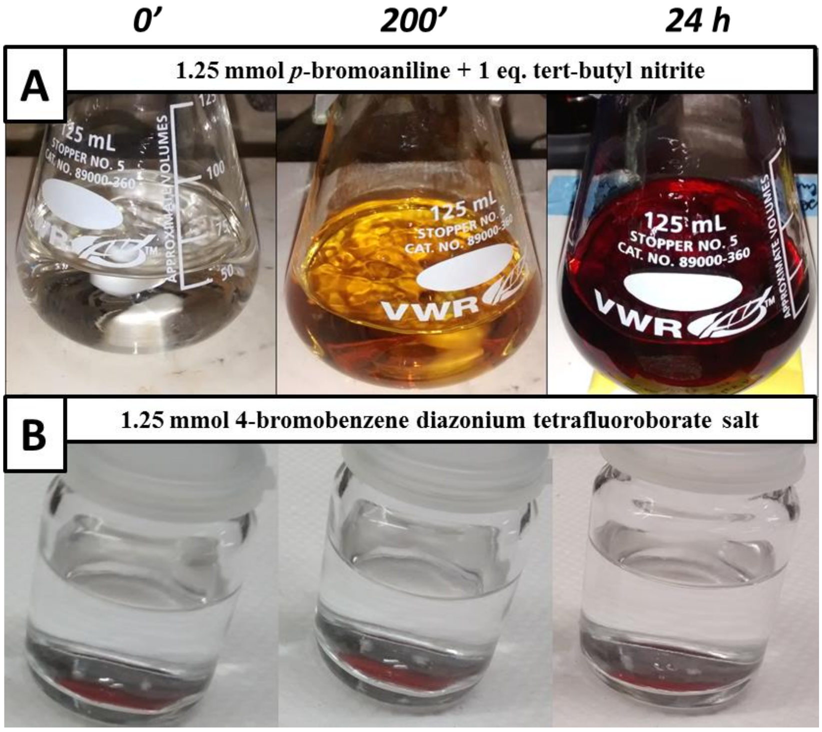


Figure ESI4. Optical images corresponding to: a) a solution of 1.25 mmol of *p*-bromoaniline with 1.25 mmol (1 equivalent) of tert-butyl nitrite in acetonitrile and b) a solution of 1.25 mmol of 4-bromobenzene diazonium tetrafluoroborate salt in acetonitrile at different reaction times: 0, 200 min and 24 h.

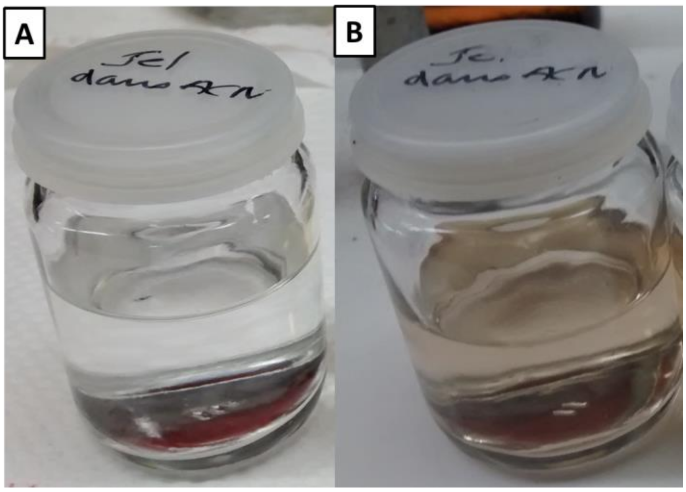


Figure ESI5. Optical images of a solution containing 1.25 mmol of 4-bromobenzene diazonium tetrafluoroborate salt in acetonitrile after: a) 24 h and b) 10 months.

ESI5 - Thermogravimetric curves of uncoated $LiFePO_4$

Thermogravimetric curves of the uncoated $LiFePO_4$ before and after grafting are presented in Figure ESI6. The shape of the thermogram has been explained in previous works [1,5] and detailed above for $LiFePO_4$/C (see Figure ESI1). For the uncoated $LiFePO_4$, no significant weight loss after 450 °C was observed after grafting, suggesting that the functionalization of the surface did not occur, while 0.4 and 0.8 wt. % of grafted groups were obtained following reaction with $LiFePO_4$/C in the same conditions (see Table 1). These results are similar to those reported by Madec *et al.* [6].

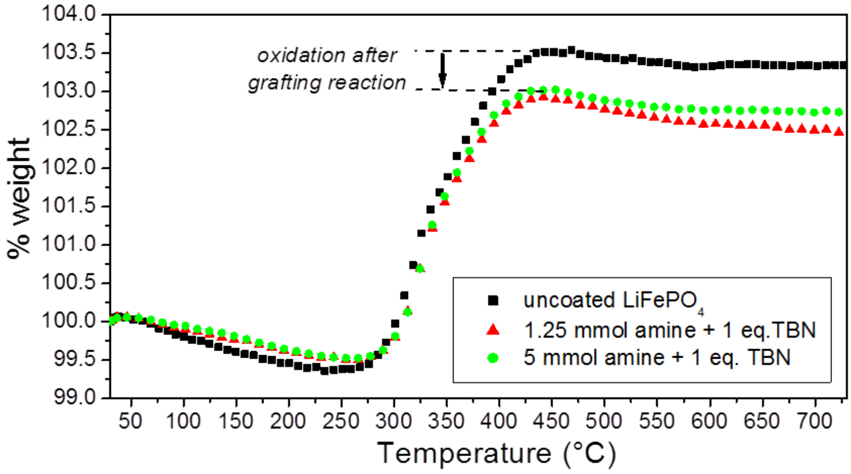


Figure ESI6. Thermogravimetric curves for uncoated (■) and bromophenyl-grafted $LiFePO_4$ powders, modified by employing 1.25 (▲) and 5 mmol (●) of *p*-bromoaniline and tert-butyl nitrite (TBN). Note that the mass gain is lower after grafting reaction.

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