Short communication

# 2,5-Difluoro-1,4-dimethoxybenzene for overcharge protection of secondary lithium batteries

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## Abstract

Based on the voltammetric behaviour of a series of halogen-substituted dimethoxybenzene in 1 M LiPF$_6$/EC:DEC electrolyte, 2,5-difluoro-1,4-dimethoxybenzene (F$_2$DMB) was selected and tested as an electrolyte additive for overcharge protection of Li/Li$_4$Ti$_5$O$_{12}$ cell. From the galvanostatic study of the cells at different overcharge current (C/20, C/50, C/100 and C/200) in the presence of F$_2$DMB, it was found that the shuttle additive can be adsorbed at the cathode surface and form a dense layer which prevents the intercalation of Li$^+$ ion in the positive electrode. At low overcharge current (C/200 rate) the voltage of the cell levelled off at the oxidation potential of the shuttle molecule for more than 50 cycles, but at higher charge rates (C/50 and C/100), the voltage of the cell was levelled off for only 16 cycles. The reason is that the F$_2$DMB molecules remaining in solution after the formation of the layer at the cathode cannot carry the current even at charge rates as low as C/100.
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## 1. Introduction

Space applications of secondary lithium-ion batteries require high voltage power sources which necessitate the fabrication of batteries in which a number of cells are series-connected. The crucial problem for a serial-connected pack is the balance between every elementary cell which is difficult to obtain. As all cells do not have the same capacity nor the same self-discharge characteristics, charging the battery puts in overcharge the elements of lower capacity.

The effects of overcharge may include degradation of electrodes [1,2], currents collectors, electrolytes [3–7] and separators. At present, to prevent the damage causes by the overcharge, each cell is under the control of an external electronic device. This device adds cost, weight and complexity to the battery pack, in particular in the case of space applications. The harmful effects of the overcharge can be avoided by the addition of redox shuttle additives to the electrolyte. These additives must be unreactive until overcharge conditions are reached, but activated once the cut-off voltage of the cell potential is attained.

The oxidized form of the redox shuttle, obtained at the positive electrode in overcharge conditions, diffuses towards the negative electrode where it is normally reduced to the initial form which, in turn, diffuses back to the cathode to be re-oxidized. This constitutes a system of shuttle which transports the overcharge current of at a pre-determined potential. Many factors govern the feasibility of this approach to achieve effective overcharge protection:

(i) the reversibility of the redox reaction is indeed the first pre-requisite to get the above defined electrochemical shuttle effect;
(ii) the oxidation potential of the redox shuttle must be slightly higher than the cut-off potential limit of the cathode;
(iii) the diffusion coefficient and concentration of the redox species should be as high as possible to avoid polarisation concentration effects and hence to carry high currents.

In the past, metallocenes and aromatic molecules have been studied for overcharge protection, operating as a fuse in lithium batteries containing liquid electrolytes [8–12]. More recently Dahn and co-workers [13–18] show the excellent propriety of 2,5 ditertbutyl-1,4-dimethoxybenzene as a shuttle molecule in

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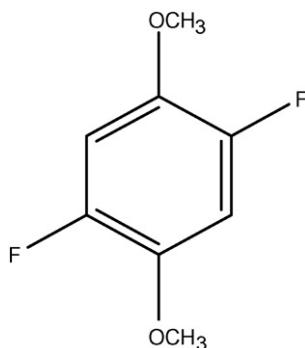  *E-mail address:* tagouguimohamed@lycos.com (M. Taggougui).

Fig. 1. Chemical structure of 2,5-difluoro-1,4-dimethoxybenzene.

LiFePO$_4$/graphite or LiFePO$_4$/Li$_4$Ti$_5$O$_{12}$ cells [13–18]. Nevertheless, the oxidation potential of this molecule is too low for use with cobalt or nickel oxide-based cathodes. In order to reach higher oxidation potential highly electroactive substituents must be added on the benzene ring such as fluorine or –CF$_3$ groups.

We present here the performances of a fluorinated derivative of 1,4-dimethoxybenzene: 2,5-difluoro-1,4-dimethoxybenzene (F$_2$DMB, scheme reported in Fig. 1). This molecule is tested as a possible shuttle additive for high voltage cells using a Li/Li$_4$Ti$_5$O$_{12}$ cell instead of a LiCoO$_2$/Li cell, in order to avoid any interference between the oxidation of the cathode and that of the shuttle molecule which fall in the same potential range.

## 2. Experimental

2,5-Difluoro-1,4-dimethoxybenzene (purity > 99.99%) was obtained from Aldrich and used as received. LiPF$_6$ (99.99%) and all electrolyte grade solvents were obtained from Aldrich. The electrolyte was prepared by dissolving 1.0 M LiPF$_6$ in a mixture of ethylene carbonate (EC) and diethylene carbonate (DEC), 2:3 in volume. The water content of the electrolyte was less than 20 ppm as indicated by the Karl Fischer titration. The F$_2$DMB was dissolved into the electrolyte at a molar concentration of 0.01 or 0.15 M.

Cyclic voltammetry (CV) was performed using a three-electrodes cell and a Radiometer potentiostat (Voltalab PGZ100). A glassy carbon disk (3 mm in diameter) was used as a working electrode, and a strip of metallic lithium was used both as reference and counter electrodes. All potentials are shown in reference to the Li/Li$^+$ system. Potential scanning was run in the range—0.4–4.6 V at a scan rate of 50 mV s$^{-1}$.

Additional voltammograms were run at different scan rate (5, 10, 20 and 30 mV s$^{-1}$) in the aim to determine the diffusion coefficient of the F$_2$DMB molecule in the electrolyte mixture

by exploiting the Randles–Sevcik equation:

$$J_p = 2.69 \times 10^5 n^{3/2} D^{1/2} v^{1/2} C$$

where $J_p$ is the current density, $n$ the number of electrons involved in the redox process (one in our case), $C$ is the F$_2$DMB shuttle concentration (10 mol cm$^{-3}$), $v$ the potential scan rate and $D$ is the diffusion coefficient in units of cm$^2$ s$^{-1}$.

In order to measure $I_{max}$, the limiting current that can be carried by the F$_2$DMB shuttle molecule at a given concentration (0.2 M) in the cell, a chronoamperometric method was used. For this study, the same electrode system than for VC experiments was used and chronoamperograms were recorded at different imposed potentials.

The shuttle molecule was also tested in Li cells using metallic lithium as an anode and Li$_4$Ti$_5$O$_{12}$ as cathode material. Li$_4$Ti$_5$O$_{12}$ was provided by SAFT Company. Two type of separator were used: a CELGARD® 2300 and a polypropylene felt. Li/Li$_4$Ti$_5$O$_{12}$ cells were built using Swagelok connectors and cycled with an Arbin battery cycler. As a Viledon® polypropylene felt was added between the electrode, in order to increase the amount of electrolyte in the cell and hence to avoid any drying during long time experiments, the electrodes are separated by about 1.5 mm. Cells were overcharged at fixed currents corresponding to $C$/20, $C$/50, $C$/100 and $C$/200 rate of charge. The details of the charge–discharge and overcharge program used for each experiment are reported in Table 1.

## 3. Results and discussion

### 3.1. Cyclic voltammetry

A CV voltammogram of the F$_2$DMB molecule, obtained in the EC/DEC electrolyte and recorded at the vitreous carbon electrode, is reported in Fig. 2. F$_2$DMB give a well-defined reversible redox system. The potential of this redox couple, evaluated using the mean of the anodic and cathodic potentials (($E_{p,a} + E_{p,c}$)/2) is 4.2 V versus Li/Li$^+$. In reduction, no signal is observed before the deposition of metallic lithium. On the return sweep, only the oxidation peak of the deposited lithium is observed. This shows that the F$_2$DMB molecule is stable toward oxidation below 4.2 V and toward reduction until lithium deposition.

Fig. 3a shows CV results obtained on the glassy carbon for F$_2$DMB dissolved in the electrolyte at different scan rates. In Fig. 3b, is reported the plot of the peak current density $J_p$ as a function of $v^{1/2}$. From the slope of the straight line, the diffusion coefficient of F$_2$DMB is obtained: $D = 1.85 \times 10^{-5}$ cm$^2$ s$^{-1}$. This value is high as compared to those usually recorded for

Table 1
Charge–discharge programs used for testing F$_2$DMB as shuttle molecule in Li/Li$_4$Ti$_5$O$_{12}$ cells

|  | Step 1: discharge | Step 2: charge | Step 3: overcharge |
|---|---|---|---|
| $C$/20 overcharge | Rate: $D$/20; cut-off: $E = 1.1$ V | Rate: $C$/20; cut-off: $E = 4.5$ V | Rate: $C$/20; overcharge cut-off: 4.5 V |
| $C$/50 overcharge | Rate: $D$/5; cut-off: $E = 1.1$ V | Rate: $C$/5; cut-off: $E = 4$ V | Rate: $C$/50; overcharge stopped after 2.5 h |
| $C$/100 overcharge | Rate: $D$/5; cut-off: $E = 1.1$ V | Rate: $C$/5; cut-off: $E = 4$ V | Rate: $C$/100; overcharge stopped after 5 h |
| $C$/200 overcharge | Rate: $D$/5; cut-off: $E = 1.1$ V | Rate: $C$/5; cut-off: $E = 4$ V | Rate: $C$/200; overcharge stopped after 10 h |
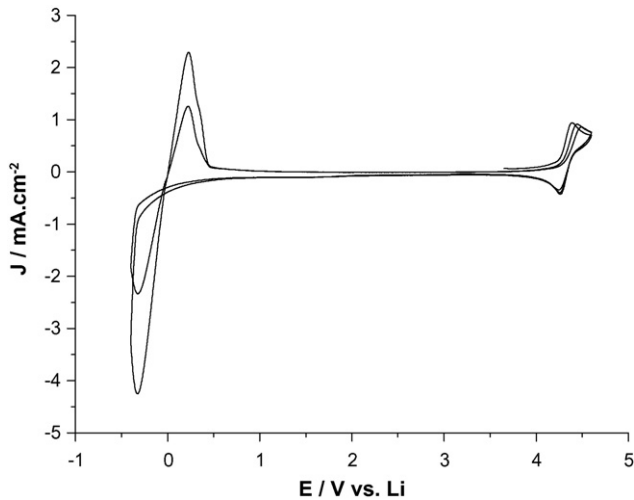
Fig. 2. Cyclic voltammogram of 0.01 M $F_2DMB$ in 1 M $LiPF_6$ in EC/DEC recorded between +4.6 V vs. Li/Li$^+$ and −0.4 V at 50 mV s$^{-1}$.
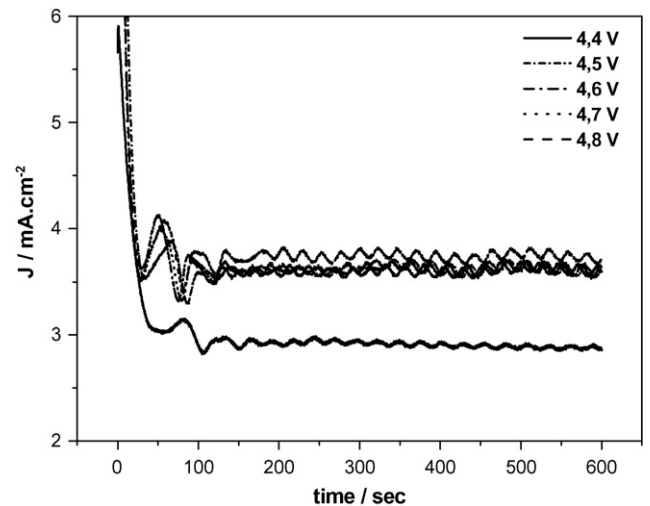


Fig. 4. Chronoamperogram at various imposed potential (4.4–4.8 V) at a vitreous carbon electrode in a cell containing 0.2 M $F_2DMB$ in EC/DEC + $LiPF_6$ 1 M.

ions such as $PF_6{}^-$ or Li$^+$ in same media which means that this molecule is highly mobile.

### 3.2. Chronoamperometry

In Fig. 4 is reported the chronoamperogram of a 0.2 M solution of $F_2DMB$ in the electrolyte at fixed potentials (4.4–4.8 V) obtained at the vitreous carbon working electrode in the three electrodes cell. We can notice that the current density is not represented by a steady line as expected but a wavy curve. The observed oscillations are probably due to diffusion–convection coupling at the vicinity of the electrode interface. The current plateau increases with the applied potential till a limit which is attained for $E = 4.5$ V. Beyond this value no increase in the limiting current is observed. This experiment shows that $F_2DMB$ can play the role of a shuttle molecule and that the maximal current carried is 3.7 mA cm$^{-2}$ which corresponds roughly to 0.27 mA taking into account the geometry of the electrodes.

### 3.3. Cycling experiment using Li/Li$_4$Ti$_5$O$_{12}$ cells

In order to evaluate the influence of $F_2DMB$ on the overcharge behaviour of a Li$_4$Ti$_5$O$_{12}$ electrode, the charge–discharge tests were carried out on Li/Li$_4$Ti$_5$O$_{12}$ cells. $F_2DMB$ is dissolved at a concentration of 0.15 M in the reference electrolyte. The cell is first discharged to 1.1 V at $C/20$, and then charged to 4.5 V cut-off potential at the same rate. In the conditions used, the charge/overcharge current is 0.14 mA. The results for cells with or without addition of $F_2DMB$ are compared in Fig. 5.

The first two plateaux near 1.5 V are due to the standard discharge and charge plateau of the titanate electrode. The plateau recorded at 4.4 V at the end of charge of the titanate electrode corresponds to the $F_2DMB$ shuttle effect. At this potential the $F_2DMB$ molecules carry the entire overcharge current and the cell potential is invariant. At the second cycle, the charge–discharge plateaux of the titanate electrode almost disappear and the same is observed during the following cycles.
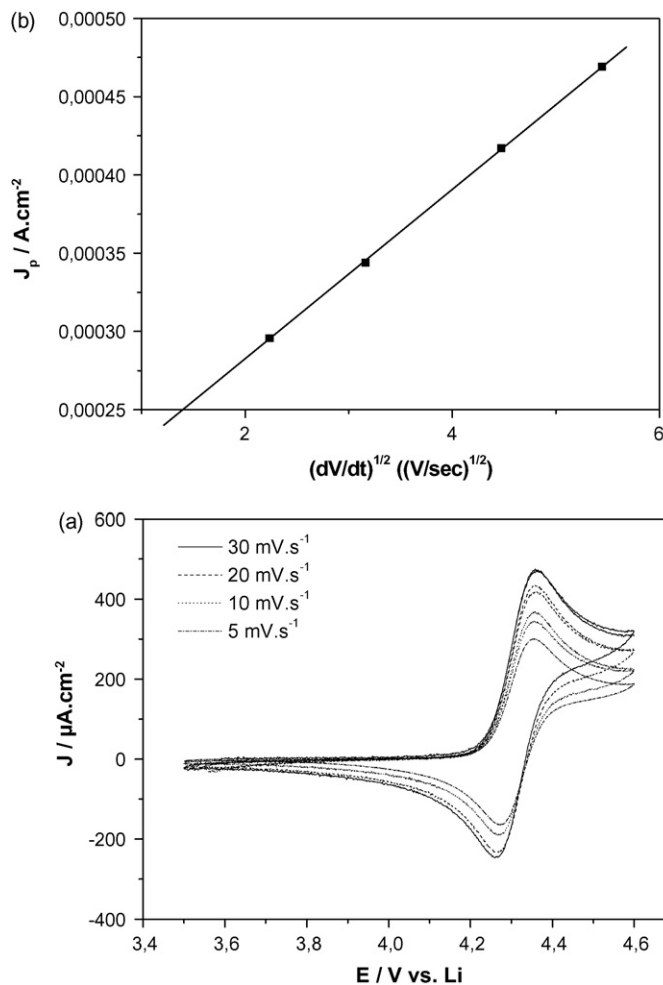


Fig. 3. (a) Cyclic voltammogram of 0.01 M $F_2DMB$ in 1 M $LiPF_6$ in EC/DEC recorded between 3.5 V vs. Li/Li$^+$ and 4.5 V vs. Li/Li$^+$ at for sweep rates. (b) Plot of the peak current density $J_p$ vs. the square root of sweep rate.
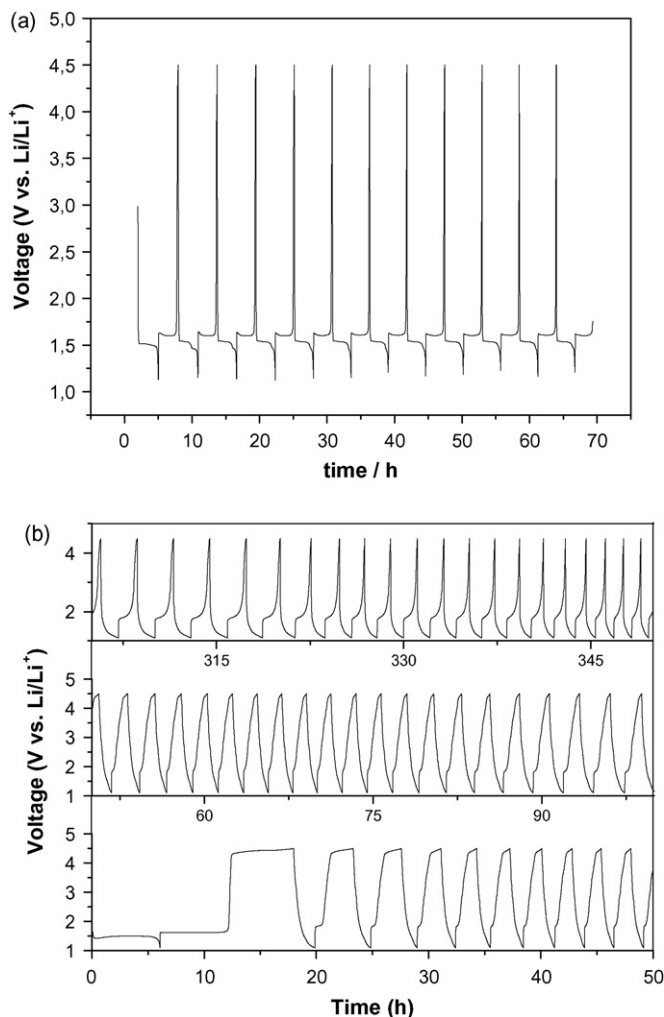
Fig. 5. Li/Li$_4$Ti$_5$O$_{12}$ cell potential vs. time at: (a) C/10 charge–discharge rate without additive and (b) C/20 charge–discharge rate in the presence of 0.15 M F$_2$DMB.

This means that the capacity of the titanate electrode vanished. The plateau at 4.4 V, still remaining for at least 100 of cycles, is decreasing in length. It is inferred that the ability of the shuttle to carry the overcharge current is progressively lost owing to the consumption of F$_2$DMB molecules (oxidized or reduced form) by an unknown reaction.

One possible explanation for both the large capacity loss and the effectiveness of the shuttle effect is that F$_2$DMB molecules (reduced or oxidized form) react at the electrode surface to form a layer which is hardly permeable to lithium ions. The decrease in concentration of the shuttle due to the preceding reaction and possible by side reactions due to its very reactive oxidized form should limit the shuttle effect in duration during the following cycles.

### 3.4. Cycling experiment in Li/Li$_4$Ti$_5$O$_{12}$ cells at low charge rates

The comportment of F$_2$DMB as a redox shuttle has been also tested at lower overcharge rates: C/50 (0.056 mA), C/100 (0.028 mA) and C/200 (0.014 mA), using Li/Li$_4$Ti$_5$O$_{12}$ cells
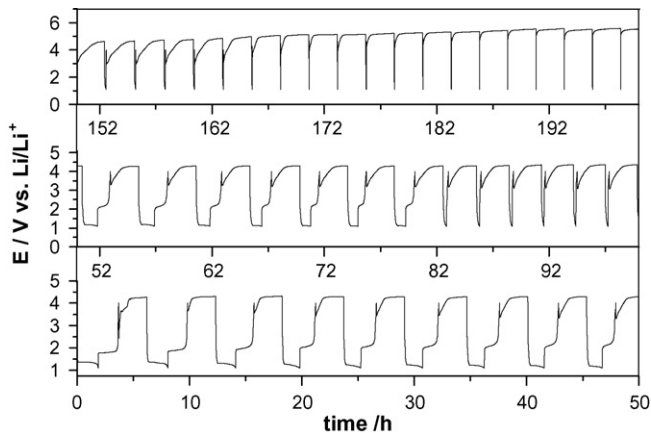


Fig. 6. Li/Li$_4$Ti$_5$O$_{12}$ cell potential vs. time at the C/50 charge–discharge rate in the presence of 0.15 M F$_2$DMB added to the electrolyte.

charged and discharged at C/5 rate to avoid time consuming experiments. Results of cycling experiments at C/50 rate, are reported in Fig. 6. The graph indicates that, the voltage of the cell never exceeds the starting oxidation potential of the shuttle for at least 40 cycles. After about 40 cycles, the voltage of the plateau progressively exceeds the starting oxidation potential of the shuttle. Simultaneously, the charge–discharge capacities of the titanate electrode decrease drastically after ca. 16 cycles. We speculate that the reason for this is that the F$_2$DMB molecules form a layer on the positive electrode which becomes impermeable to lithium ions.

At low overcharge current, the amount of F$_2$DMB in solution remains sufficiently high to carry the current but, as expected, the redox potential increases with the amount of oxidized molecules produced at the cathode. The same trend is noted in Figs. 7 and 8, where the imposed current has been lowered to respectively 0.028 mA (C/100) and 0.014 mA (C/200). The two plateaux correspond nicely to the charge–discharge plateau of the titanate electrode and to the shuttle-protected process. As observed in the preceding experiment, the capacity of the cell is completely lost after 16 charge–discharge cycles. These results confirm the
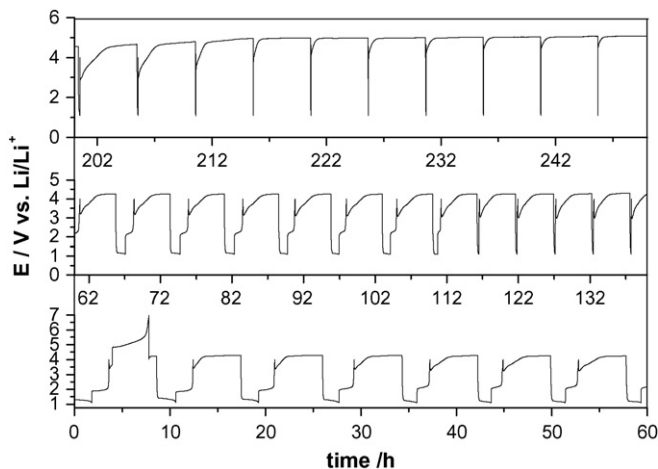


Fig. 7. Potential vs. time variations for Li/Li$_4$Ti$_5$O$_{12}$ cell containing 0.15 M F$_2$DMB in EC/DEC + LiPF$_6$ 1 M; charge and discharge are operated at C/5 rate and overcharge current corresponds to C/100 rate.
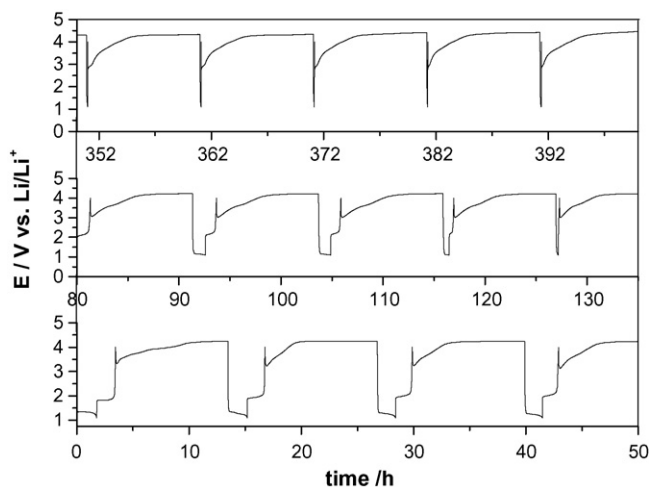
Fig. 8. Potential vs. time for $Li/Li_4Ti_5O_{12}$ cell containing 0.15 M $F_2$DMB in EC/DEC + LiPF$_6$ 1 M; charge and discharge are operated at $C$/5 and overcharge at $C$/200.

hypothesis of the formation of a compact layer on the electrode. The shuttle effect remains for more than 50 cycles at the lowest rate with practically no drift in the oxidation potential of the shuttle which is probably linked to the amount of oxidized form in solution. As the degradation of the molecule is slow down at low overcharge rates, it is not surprising to notice that the shuttle effect remains for a longer time.

## 4. Conclusion

Possible use of 2,5-difluoro-1,4-dimethoxybenzene as a shuttle additive for overcharge protection has been investigated. In spite of the fact that cyclic voltammetry experiments show that this molecule exhibit a nice reversible comportment at a vitreous carbon electrode, cycling experiments using a $Li/Li_4Ti_5O_{12}$ cells, containing $F_2$DMB dissolved in the electrolyte, reveal that the positive electrode capacity is drastically affected. It is sug-

gested that the main cause of this capacity loss is the reaction of the $F_2$DMB molecule or its oxidized form, in solution or at the cathode surface. This reaction will provoke the formation of a blocking layer at the cathode surface which impedes intercalation. Further work is needed to analyse this layer and to determine the nature of the unknown reaction.

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