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Poly(benzoquinonyldisulfide) as organic positive electrode for Mg and Li batteries

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Abstract

The study of innovative solutions to replace current lithium technology is being carried out at a rapid pace. One of the proposed solution is the development of magnesium batteries, especially organic positive electrode which can exhibit high capacity and capacity retention. In this field, the electrochemical responses of poly(benzoquinonyldisulfide) (PBQDS) in lithium and magnesium cells were investigated in diglyme and sulfolane based electrolytes. Using cavity micro-electrode, similar response was obtained by cyclic voltammetry with the presence of a reversible redox system at 3.5 V vs. Li\textsuperscript{+}/Li or 2.2 V vs. Mg\textsuperscript{2+}/Mg. Using sulfolane + LiTFSI (bis(trifluoromethane)sulfonamide lithium salt) electrolyte, the PBQDS active material achieves a stable capacity of 140 mAh g\textsuperscript{-1} at C/20. In Mg cell, even if the starting capacity is high, a capacity decrease is noticed along time presumably due to the progressive Mg\textsuperscript{2+} trapping within the quinone structure. The addition of solvating additive permits to partially mitigate this drawback.

Keywords: Organic cathode material, magnesium battery, rechargeable batteries, polymer active materials, designed electrolyte
Introduction

The undeniable benefit of lithium-ion (LIB) batteries for a more environmentally friendly future was recognized by the 2019 Nobel Prize in Chemistry. However, relying only on LIBs for energy storage will put considerable strain on lithium and cobalt resources.[1] To prevent resource shortages, alternative battery technologies are desirable to satisfy the energy demand.[2] In which, magnesium battery offers many distinct advantages, including its high earth-abundance, high energy density and reversible dendrite-free Mg deposition.[3–5] One of the important challenge is to develop positive electrodes which permit a reversible insertion/de-insertion of multivalent cations. Despite numerous studies, the performances obtained with inorganic materials remain very poor and, to date, one of the best result shows, using the Chevrel phase Mo₆T₈ (T = S, Se ou Te) and TiO₂ [6,7] as cathode, a capacity of about 70 mAh g⁻¹ and a cyclability (> 2000 cycles) with a very low cell potential (< 1 V). For inorganic materials including V₂O₅, MoS₂ and Olivine compounds [8–12] promising capacities can only be obtained in the presence of water, which allows to lower the Mg²⁺-oxide electrostatic interaction, but which is not compatible with metallic Mg [13]. In parallel, alternative approaches that seem to be promising concern redox-active organic materials in which intermolecular forces can be considered weaker than those involved in inorganic materials [14,15]. One of the key drawbacks of redox-active organic materials is their poor volumetric power [16] and their solubility which can significantly reduce the performance and the cycle life of these materials [17–20]. In order to overcome the drawback of dissolution of small organic molecules, many researches were focused on the immobilization of redox function by polymerization or using selective separators [21–28]. The most studied organic positive electrodes are dimethylbenzoquinone (DMBQ) and polyanthraquinone (PAQ) [26,29,30]. DMBQ [17] was a promising candidate in Mg system with capacity over 200 mAh
g\textsuperscript{-1}, whereas PDI–EDA (Perylene diimide-ethylene diamine) [31] showed a more impressive performance in term of cyclability with more than 2000 cycles with capacity near the theoretical value 54 mAh g\textsuperscript{-1}. Another interesting material for organic electrode was the PAQ, which exhibits stable performances after one hundred cycles with a capacity of 100 mAh g\textsuperscript{-1} with MgCl\textsubscript{2}–Mg(TFSI)\textsubscript{2} in a mixture of THF and glyme as electrolyte between 0.5 and 2.5 V vs. Mg\textsuperscript{2+}/Mg [27,31]. However, the capacity drops along cycling to reach only 70 mAh g\textsuperscript{-1} after 30 cycles. It is necessary to stress that this result was obtained with 0.5 M Mg(TFSI)\textsubscript{2} + 1 M MgCl\textsubscript{2} in DME as electrolyte. Without MgCl\textsubscript{2}, the starting capacity i.e. 110 mAh g\textsuperscript{-1}, quickly decreases after few cycles up to 25 mAh g\textsuperscript{-1}. In this context, H. Dong et al. [20] proved that in presence of MgCl\textsubscript{2}, the intercalation of MgCl\textsuperscript{+} occurs instead of Mg\textsuperscript{2+} in organic material. This leads to decrease the specific energy as the salt of the electrolyte is involved in the electrochemical process. Moreover, it is important to note that addition of MgCl\textsubscript{2} in the electrolyte induces some corrosion issue.

Here, we study for the first time, PBQDS as positive active material. The material was obtained using a low-cost, 3-steps synthesis. Its electrochemical properties are investigated in lithium and magnesium batteries, allowing a comparison between the two systems, in terms of electrochemical processes. To avoid the MgCl\textsuperscript{-} intercalation and to prevent corrosion phenomenon Mg(TFSI)\textsubscript{2} alone was used in diglyme or sulfolane in this study.

**Experimental part**

*PBQDS Synthesis and material characterizations*

Synthesis of PBQDS : to tetrachlorobenzoquinone (TCBQ, 6.150 g, 0.025 mol) dissolved in 100 mL 1-methyl-2-pyrrolidone (NMP) inside a glove box, anhydrous Li\textsubscript{2}S (Sigma-Aldrich 99.98%, 2.875 g, 0.0625 mol) was added. After stirring and heating at 160 °C overnight in Ar flow, the mixture was cooled down to room temperature and transferred into 400 mL of 0.1 M
HCl solution for 48 hours which led to the precipitation of the product. The solid was filtered and washed with deionized water until the post-filtration liquor became colorless. For purification, the crude product was dissolved into 300 mL 1 M LiOH solution. After that, concentrated HCl was added dropwise into the solution until pH reaches around 1. A large amount of solid was formed in this step. The viscous mixture is centrifuged at 5000 rpm for several times during 10 minutes and washed between two centrifugation steps with 0.1 M HCl aqueous solution and at the end by 0.1 M HCl in ethanol, the final washing solution becoming nearly colorless. Poly(hydroxybenzoquinonyldisulfide) (PHBQDS) product was dried at 80 °C under vacuum to obtain a black powder. In order to get the final product, the oxidation of hydroquinone function in PHBQDS to quinone need to be done in the last step. To achieve this, 2.0 g of PHBQDS is homogeneously dispersed in 200 mL anhydrous tetrahydrofuran (THF) in sonication bath before 4.0 g of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was added at room temperature. After two days of reaction, the mixture was centrifuged several times at 5000 rpm during 10 minutes and washed with THF between two centrifugation steps until the solution become nearly colorless. PBQDS, obtained in a quantitative yield, is dried at 80 °C for 48 hours under vacuum, then stored in Ar glove box.

FTIR measurements were performed with IR spectrometer (BRUKER, VERTEX 70V) from 4000 to 400 cm⁻¹ using 32 accumulations and a resolution of 4 cm⁻¹ under N₂ flow. Raman scattering was measured using a Renishaw Invia spectrometer. The 785 nm excitation line of a laser diode was used for the measurements. The morphology of the redox polymers is mainly characterized by scanning electronic microscopy (SEM) using an Ultra 55 (Zeiss) microscope with a voltage of 5 kV and a SE detector. Mapping EDX analysis was performed on the same instrument with SDD detector (BRUKER AXS-30 mm²). ImageJ is used for post-treatment and analyse the collected image. The coupled plasma mass spectrometry (ICP-MS) measurement was performed using a NexION 2000 instrument of PerkinElmer. The
electrodes were carefully cleaned prior the ICP-MS measurement. Thermogravimetric measurement was performed by using TGA 1 STArE instrument of METTLER TOLEDO under air flux at 50 mL min⁻¹ from 25 °C up to 1000 °C with a heating rate of 10 °C per minute.

**Electrochemical characterizations**

Cyclic voltammetry (CV) is carried out by a VMP3 potentiostat from Biologic. A 3-electrodes configuration is used with a platinum cavity electrode diameter 100 µm. The counter and reference electrodes are Mg or Li foil in a protected cell containing electrolyte. The Mg electrode were prepared from Mg disk foil (99.9%, 0.25 mm, Goodfellow) after polishing by abrasive grinding paper from P360 to P2400. The potential of the Mg reference electrode was checked after each experiment by ferrocenium/ferrocene redox couple, and correction of the potential was performed if needed. The scan rate was fixed at 1 mV.s⁻¹.

For the CV performed in the cavity electrode, the samples were prepared by mixing 70% active material and 30% carbon black (SuperP®, 99%) in weight. The mixtures were ground with THF two times in glove box, after that the solvent was evaporated.

Cycling tests were performed using Galvanostatic Cycling with Potentiostat Limitation (GCPL) (VMP3 potentiostat – Biologic) in two or three-electrode Swagelok cells for Li and Mg tests, respectively. The cells were assembled in glove box (Campus, Jacomex) with sub-ppm values of oxygen and water. The cells were taken out of the glove box, placed in an oven (UN30, Memmert) held at 25 °C or 40 °C depending of the solvent used. Coulombic efficiency was determined as a capacity ratio of (n+1) discharge/(n) charge, as experiments started with a discharge. GITT was applied with a pulse duration of 20 minutes with a current 3.83 µA (corresponding to C/20). Then, the cells were relaxed for three hours and this progress was repeated until the cut-off potential was reached.

The active material was mixed with carbon black and polyvinylidene difluoride (PVdF, Solef 5130, Solvay 12 wt.% in NMP Alfa Aesar) as binder in the ratio 60:30:10 (active
material/Super P®/PVdF). The ink casted onto an aluminium current collector was dried overnight at 60 °C and several hours at 80 °C under vacuum before being stored in a glove box.

The different solvents used (Sigma-Aldrich, 99.5% for diglyme and 99% for sulfolane) were dried three times successively using molecular sieves for one week. All of the electrolytes are obtained using the same protocol with two steps. In dried solvents, 0.5 M Mg(TFSI)$_2$, previously dried at 150 °C, was added, the obtained electrolyte was dried again on molecular sieves (3 Å) until the water content was below 2 ppm. Celgard®3401 was used as separator.

**Results and discussion**

Linking active organic units with thioether bonds, which was previously proposed by Song et al. [32], is a simple strategy to synthesize polymer electrode materials. After a three steps reaction summarized in **scheme 1**, the poly(hydroxybenzoquinonyldisulfide) PBQDS, presented two sulfur links between monomer units. In the first step, the lithiated polymer was obtained through a polycondensation reaction, and two remaining steps were used to form the quinone structure. PBQDS was obtained in a high yield, more than 95%.
**Scheme 1.** PBQDS synthesis starting from TCBQ.

To check the complete oxidation of the PHBQDS hydroquinone groups into quinone ones, the products were characterized by FT-IR. In the FT-IR spectra (Fig. S1), the oxidation of hydroquinone moieties was observed with the disappearances of the strong and broad O-H stretching mode (between 2100 and 3600 cm\(^{-1}\)) and of the C-O stretching band at 1190 cm\(^{-1}\) characteristic of PHBQDS. Signatures at 1623 cm\(^{-1}\) for C=O stretching and 692 cm\(^{-1}\) for C-S stretching were obtained in the intermediate and final products.

Thermogravimetric analysis (TGA) is used to analyze the thermal stability of PBQDS. The polymer is stable up to 200 °C, with a weak weight loss at 75 °C associated with water removal (Fig. S2a). The derivative time dependent weight loss indicates a degradation process in two steps weakly separated in temperature where the first step corresponds to the first sulfide-bridge broken and the second step is the total degradation of the polymer at high temperature.

The PBQDS elemental analysis is shown in Fig. S2b. The presence of H (1.42%) and the excess of O may be associated with some water absorption, as no OH group was observed in PBQDS compounds by the FT-IR investigation. The relative low S percentage may indicate the presence of some monosulfide bridges in the polymer.

Energy-dispersive X-ray spectroscopy (EDX) was used to complete the elemental analysis to evaluate the presence of chloride element (Fig. S2c). The peaks of the different elements such as S, C, O are observed. Only a small amount of Cl is detected at 2.6 keV, showing that the chloride substitution by sulfide moieties is effective. However, this weak amount could be due to chloride terminal function in the polymer chain presumably due to the fact that moderate molecular weight of the polymer is reached. No other elements are detected.
Based on literature data [33], the particle size has a large impact on the electrochemical cell capacity as the diffusion process in large solid particles can be the limiting process. Pristine synthesized PBQDS particle sizes are in the range of dozens µm or even higher. Thus, a manual grinding method (MGM) and ball milling technique (BMT) were used to reduce the particle diameters. Several BMT speeds and experiment times were investigated. A compromise between particle size, aggregate formation and polymer degradation was found with grinding at 550 rpm during 30 minutes. The size of the polymer particles dropped to around 10 µm for the largest particles (Fig. 1). In addition to SEM characterization, the specific surface area was measured by Brunauer–Emmett–Teller (BET) method, whereas the pristine material exhibits a surface of 3 m² g⁻¹, after 30 minutes at 550 rpm MBT, the BET value increases up to 15 m² g⁻¹. This value is comparable to the one obtained from PAQS [34]. Using these conditions, no degradation of the polymer can be checked by Raman spectroscopy (Fig. S3).

**Fig. 1.** SEM of PBQDS before and after using BMT.

*Electrolyte properties*

To evaluate the impact of the electrolyte composition on the electrochemical performances, both sulfolane and diglyme were used as solvent. Indeed, the solvent polarity and donor number could have a large impact on the organic material solubility during the cycling test and the solvating ability towards Mg²⁺. These solvents were selected for their high stability in
reduction as observed when there are used in the lithium battery [35–47]. The properties of the two solvents are given in Table 1.

Table 1. Physical and electrochemical properties of the solvents and the magnesium, lithium electrolytes based on diglyme and sulfolane solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>DN/kcal mol⁻¹</th>
<th>AN/kcal mol⁻¹</th>
<th>Permittivity 25 °C</th>
<th>Viscosity /mPa s</th>
<th>Conductivity /mS cm⁻¹ 25 °C Mg(TFSI)_2</th>
<th>Conductivity /mS cm⁻¹ 25 °C 1 M Li(TFSI)_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfolane*</td>
<td>14.8</td>
<td>19.2</td>
<td>44</td>
<td>10.3</td>
<td>1.5 (30 °C)</td>
<td>2.4 (0.4 M)</td>
</tr>
<tr>
<td>Diglyme</td>
<td>18</td>
<td>10.5</td>
<td>7.6</td>
<td>1.14</td>
<td>4.3 (20 °C)</td>
<td>8.3 (0.5 M)</td>
</tr>
</tbody>
</table>

*Mg(TFSI)_2 solubility in sulfolane is limited to 0.4 M.

The diglyme exhibits a lower polarity and a higher solvation ability vs. Mg^{2+} than sulfolane (Table 1), whereas the viscosity of sulfolane is significantly higher. The conductivities for both lithium and magnesium-based electrolytes, obtained by the dissolution of LiTFSI or Mg(TFSI)_2 in the solvent, are plotted vs. temperature in Fig. S4.

As expected, due to the high viscosity of sulfolane, the conductivities obtained in this medium for both lithium and magnesium salts are lower than the ones obtained in diglyme at low temperature. However, at 60 °C, these values are very close with 6 \times 10^{-3} S cm⁻¹ and 3.6 \times 10^{-3} S cm⁻¹ for 0.5 M Mg(TFSI)_2 in diglyme and 0.4 M Mg(TFSI)_2 in sulfolane, respectively while these values recorded for lithium-based solutions are 13 \times 10^{-3} S cm⁻¹ and 5.3 \times 10^{-3} S cm⁻¹, respectively. In lithium-based electrolyte, a classical VTF law is observed, with a pseudo-activation process, which is not the case for 0.5 M Mg(TFSI)_2 in diglyme. The weak activation of the conductivity vs. temperature in diglyme may be related to a decrease of Mg^{2+} salt dissociation in diglyme with the temperature increase, as observed in Ca^{2+} based
electrolyte [48]. Such behaviour is not observed in the sulfolane solvent due to its high dielectric constant which enhances salt dissociation.

**Electrochemical performance in Li batteries**

The polymer was firstly tested by cyclic voltammetry in both diglyme and sulfolane lithium electrolytes at 1 mV.s$^{-1}$. The CV curves show some reversibility of the oxidation/reduction centred on the carbonyl groups in presence of Li$^+$, with $E_{1/2} = 2.8$ V vs. Li$^+$/Li and $\Delta E = 1.2$ V and 0.8 V in sulfolane and diglyme solution, respectively, and a ratio $I_{\text{peak ox}}/I_{\text{peak red}} = 1.4$ (**Fig. 2a**). One can suggest that regarding the $\Delta E$ values, the kinetic of the redox process is slower in sulfolane than in diglyme. These values are quite similar to the $E_{1/2}$ and $\Delta E$ obtained from polybenzoquinonesulfide (PBQS) [32] in good agreement with the similarity of the redox centers.

**Fig. 2.** (a) Cyclic voltammetry of manual grinding PBQDS as active material in glyme and sulfolane based electrolytes at 25 °C and 1 mV.s$^{-1}$. (b) Discharge capacity and Coulombic efficiency of Li system with manual grinding PBQDS in sulfolane electrolyte at 40 °C including 3 cycles at C/50 and 40 cycles at C/20. (c) Discharge capacity and Coulombic
efficiency of Li system with manual grinding PBQDS in diglyme electrolyte at 25 °C including 3 cycles at C/50 and 40 cycles at C/20.

Moreover, whereas the oxidation process seems to occur in one step in both solvents, the two successive steps observed in the cathodic region are more distinguishable in the sulfolane electrolyte compared to the diglyme based one. In addition, while the response is stable along cycling in sulfolane based electrolyte, a weak decrease of the current is observed cycle per cycle in diglyme-based electrolyte (Fig. S5).

The electrochemical performance of manual grinding PBQDS electrode has been evaluated at C/20 in presence of the different electrolytes (Fig. 2b and 2c). In diglyme, the capacity of the cell increases the first cycles and reaches 110 mAh g⁻¹ for the 3rd cycle, a value far from the theoretical one i.e. 319 mAh g⁻¹, (value determined based on a two-electron redox reaction). In addition, along cycling, the capacity decreases notably to reach 85 mAh g⁻¹ after 50 cycles. The capacity decrease, which is in accordance with the current evolution observed in CV measurement, may be associated with the progressive dissolution of the reduced form of PBQDS in diglyme based electrolyte. This could explain, as well, the fact that the maximum of capacity is far from the expected one. The use of sulfolane as solvent avoids the solubility of the PBQDS and the capacity increases with the cycle number. However, the capacities obtained are lower than those in diglyme which may be associated with the high viscosity of the electrolyte (which limits the mass transport through the electrolyte) in addition to the large sizes of the PBQDS particles.

In order to improve the capacity of this system through a better electrolyte accessibility, active material was ground using ball-milling technique in view to reduce the particle size. The electrochemical performance of the new electrodes was investigated only in a sulfolane based electrolyte at 40 °C due to the solubility problem observed in the diglyme.
One can observe the beneficial impact of the lowest particle sizes since during the first cycles, the discharge capacity reaches 180 mAh g\(^{-1}\), with a stable capacity up to 50 cycles around 140 mAh g\(^{-1}\) (Fig. 3b), with a coulombic efficiency of about 97%. However, the maximum capacity is rather low and corresponds of about the half of the theoretical one. This may be explained by several aspects, i) the presence of some particles or aggregates with size of few microns even after ball milling (Fig. 1), which can limit the overall accessibility of the material, ii) or in the potential range used, the difficulty to access to the two quinone centred redox processes.

Fig. 3. (a) Galvanostatic charge/discharge curves in sulfolane electrolyte with ground PBQDS. (b) Discharge capacity and Coulombic efficiency of Li system with PBQDS ground by the ball-milling technique in sulfolane electrolyte at 40 °C including 3 cycles at C/50 followed by 40 cycles at C/20. (c) Power test and Coulombic efficiency of the Li cell in various scan rates from C/10 to 1C and come back to C/10 at 40 °C.

A power test was performed between C/20 to 2 C (Fig. 3c). The capacity values slowly decrease while increasing the current density from C/20 to 2 C, the main decrease is observed
at C, with respectively 80 mAh g\(^{-1}\) at C and 60 mAh g\(^{-1}\) at 2 C. It has to be outlined that by returning to a moderate C-rate, C/20, the initial capacity is almost restored which shows that a high C rate does not involve any degradation of the material. Regarding the coulombic efficiency, it increases with the C-rate, with 98% at C/20, 99% at C/10, and higher than 99.5% for the high C-rates. Based on the large capacity improvement observed with the decrease of the particle size, some optimization of the BMT protocol should be efficient to increase the capacity obtained especially at high C-rate.

_Electrochemical performance in Mg batteries_

Electrochemical characterization in the Mg batteries was investigated with Cyclic Voltammetry and Galvanostatic tests with 0.5 M Mg(TFSI)\(_2\) in diglyme or 0.4 M Mg(TFSI)\(_2\) in sulfolane. The CV analysis was performed at 1 mV.s\(^{-1}\) using a cavity microelectrode. For the first cycle, the CV curves share the same shape in both diglyme (Fig. 4a) and sulfolane (Fig. 4b) and exhibit an overall reversible system. Meanwhile, for further cycles, the CV curves are significantly different. While no degradation process is observed in sulfolane electrolyte as evidenced by the absence of any change in the CV curve along cycling, the CV shape is deeply modified in the diglyme until no redox signatures are observed from the third cycle. As previously observed, this fading is due to the progressive dissolution of the reduced form of the redox material. Surprisingly, the use of a divalent cation doesn’t avoid the problem of solubility, on the contrary, the process is amplified. Thus, for galvanostatic test, only sulfolane-based electrolyte was investigated.
Fig. 4. Cyclic voltammetry of PBQDS ground by ball-milling technique as active material in two different electrolytes: (a) diglyme solvent and (b) sulfolane solvent in Mg battery systems at 25 °C and 1 mV.s⁻¹. (c) Galvanostatic charge/discharge curves in sulfolane electrolyte (d) Discharge capacity and Coulombic efficiency in sulfolane electrolyte at 40 °C.

The shape of the galvanostatic curves obtained in Mg-based electrolyte is close to those obtained in the lithium-based one. The potential derivative is extracted from the 4th cycle (Figure 5) for galvanostatic tests in both Li and Mg cells carried out under similar conditions. The potential and width of the peak can give information on the polarization phenomenon associated with the insertion/de-insertion of ions (Li⁺, Mg²⁺). While in the lithium configuration, very fine peaks at the same potential are obtained for charge and discharge (at 3.45 V vs. Li⁺/Li), in the case of the Mg cell, wide peaks separated by 200 mV are observed (2.7 V and 2.5 V vs. Mg²+/Mg for charge and discharge respectively). From the thermodynamic point of view, a shift of 668 mV would be expected in correlation with the E⁰ Mg²+/Mg vs. E⁰ Li⁺/Li. The observed offset of 900 mV is about 230 mV higher than expected, this may be associated with polarization phenomena as discussed above, showing that the insertion/de-insertion of Mg²⁺ seems to be more difficult and slower than that of Li⁺.
Fig. 5. Superimposition of the potential vs. differential capacity curves (4th cycle) for PBQDS in Li and Mg cells in the sulfolane-based electrolyte.

Regarding capacity retention after over 40 cycles in sulfolane-based electrolyte, a large difference can be noticed between Mg and Li systems. Whereas at the first cycles, the same capacity is reached in both systems, i.e. 180 mAh g\(^{-1}\), in lithium cell a stabilization of the capacity value is observed while in Mg system the capacity regularly decreases cycle per cycle. Concerning the coulombic efficiency (determined by \(D_{n+1}/C_n\)), values higher than 98% were obtained throughout the cycling test, while the ratio \(C_n/D_n\) is close to 95% leading to the observed capacity decrease. This behavior may be attributed to some solubility problem during the reduction step or to some diffusion process limitation. The cycling tests were performed also at low C-rate i.e. C/50, and at high temperature \(T = 60 \, ^\circ\text{C}\) and C/20. However, no improvement of the performance of the material can be obtained whatever the experimental conditions. Similar capacity evolution was obtained with an increase of the capacity during the first cycles and a continuous capacity decrease. The nature of the anion was also investigated and Mg(ClO\(_4\))\(_2\) was used instead of Mg(TFSI)\(_2\), the same evolution is noticed at both 60 °C and 40 °C.

In Mg battery, one of the key parameters governing the overall reaction rate, and therefore the possibility of quickly charging or discharging the battery, is the diffusion coefficient of the
Mg$^{2+}$ inside the active material. The galvanostatic intermittent titration technique (GITT) is widely used to study cation diffusion in both anode and cathode materials [49,50]. GITT tests were performed on the PBQDS electrode at 40 °C in both lithium and magnesium-based configuration.

The apparent diffusion coefficient evolution in discharge for Li and Mg cells are shown in Fig. S6. The average Li$^+$ diffusion coefficient value is $6 \times 10^{-13}$ cm$^2$ s$^{-1}$ which is 20 times higher than Mg$^{2+}$ value at $3 \times 10^{-14}$ cm$^2$ s$^{-1}$ for discharge. In addition, the polarization observed, in the GITT measurement, for the Mg cell is much higher than the one in the Li cell.

In addition, to explain the continuous decrease of the capacity in Mg cell, the amount of Mg$^{2+}$ trapped in PBQDS at the end of the charge (after the complete oxidation of PBQDS), after a long cycling test has been determined, using ICP-MS. Whereas after the charge process, no Mg$^{2+}$ is expected inside the positive electrode as the quinone should be in its neutral state, the amount of magnesium corresponds to 0.51 Mg per monomer unit after the end of the charge (count 3% error). This result shows unambiguously that Mg$^{2+}$ remains trapped within the redox polymer.

In a brief summarize, the GITT investigation indicates that the mobile species Mg$^{2+}$ diffuse more slowly than Li$^+$ and a large part of Mg$^{2+}$ is trapped into the material. This could be due to the strong Mg$^{2+}$/O interaction, which could induce a weak diffusion up to no diffusion of Mg$^{2+}$ cation during the oxidation process.

The discrepancy observed for Mg and Li cells could be associated with the charge of the cation. To reduce the cationic character of Mg(II) some anion (e.g. Cl$^-$) can be added in order to build up in situ MgCl$^+$. This is well illustrated by the work of H. Dong et al. [20] which prove the active role of the chloride ion, the insertion/de-insertion of Mg (II) is less efficient in quinone-based materials without the possibility of forming MgCl$^+$ which mitigates the O/Mg(II) interaction. Nevertheless, in this study MgCl$_2$ cannot be added, the presence of the
chlorine anion contributing to corrosion phenomenon observed on the Al current collector in the potential range studied.

3.4. The impact of crown-ether as an additive

Recently, crown ether has been used as an additive in order to improve the Mg plating/stripping [51] [52]. As the crown ether has a high solvation property vs. cation due to the presence of chelating oxygen [55], we investigated the impact of crown ether addition onto the Mg$^{2+}$ insertion/de-insertion process from the PBQDS positive electrode. As the complex formed between Mg$^{2+}$ and 18-crown-6 (18C6) is a 1/1 complex based on Raman investigation [54], an equimolar ratio Mg$^{2+}$/18C6 was performed in sulfolane based electrolyte.

**Fig. 6.** (a) Charge/discharge profile of PBQDS in 0.4 M Mg(TFSI)$_2$ + 0.4 M 18C6 sulfolane electrolyte at 40 °C. (b) Discharge capacity vs. cycle number of PBQDS in 0.4 M Mg(TFSI)$_2$ + 0.4 M 18C6 in sulfolane at 40 °C. (c) Comparison plots of the ratio between charge and discharge versus cycles on galvanostatic test on an electrolyte with and without 18C6.
The presence of 18C6 does not have a great effect on the shape of the galvanostatic curves (Fig. 6a), as far as capacity retention is concerned (Fig. 6b), an almost identical evolution can be observed with first an increase in capacity followed by a continuous decrease. However, regarding the evolution of the charge and discharge capacities, some differences can be mentioned. The ratios \( D_{n+1}/C_n \) and \( C_n/D_n \) obtained for PBQDS in the presence or the absence of 18C6 were plotted vs. the cycle number, after the 10th cycle i.e. in the capacity decrease part (Fig. 6c).

While without additive the ratio \( C_n/D_n \) is close to 0.95 (indicating that close to 5% of the Mg\(^{2+}\) inserted in the material cannot be de-inserted), in the presence of 18C6, the ratio \( C_n/D_n \) is close to 1, indicating that 18C6 seems help the Mg\(^{2+}\) de-insertion. However, while \( D_{n+1}/C_n \) is close to 1 without additive, the presence of 18C6 induces a decrease of this value i.e. 0.95. This decrease in capacity may be associated with some active material dissolution or with the interaction of 18C6/Mg\(^{2+}\) which required a high desolvation energy before its insertion. To verify our hypothesis, the amount of Mg\(^{2+}\) inside the electrode after charging was determined by ICP-MS analysis. The amount of magnesium determined corresponds to 0.2 Mg\(^{2+}\) per quinone, a significant lower value with respect to the one obtained without 18C6 i.e. 0.51. The data from ICP-MS measurement and the charge/discharge ratio indicate that crown ether plays an important role in the process. It seems to help to extract Mg\(^{2+}\) with a reduction of more than half of the Mg\(^{2+}\) trapping side reaction. However, this reduction is not total presumably due to the 18C6 size which is not the more suitable for Mg\(^{2+}\) solvation. The electrolyte was also checked by cyclic voltammetry to assess the presence or absence of soluble active material in the cell. However, no electrochemical signal was obtained, this may be due to the fact that since the amount of active material is weak, the concentration of the soluble active material is too low to be detected.
Conclusion

In this study, a new quinone sulfide based polymer, PBQDS, was synthesized with a high yield from commercially available materials. The electrochemical properties of this polymer were investigated for both Li and Mg cells, allowing performance comparisons to be made. The PBQDS exhibits good electrochemical properties in a lithium battery system with a sulfolane- based electrolyte, with a stable capacity of 140 mA.h g⁻¹. Lowering the particle size significantly improves the achieved capacity; however, some optimization is still required to move towards the theoretical capacity. For the Mg system, a limitation by diffusion has been observed, part of the Mg²⁺ is trapped in the material due to the Mg²⁺/O interaction. This could be mitigated by reducing the particle size, using more solvating solvent and/or using an additive such as crown ether. The results obtained with the addition of crown-ether seems to be very promising and deserve further study.

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