Chemical reactivity of aprotic electrolytes on a solid Li$_2$O$_2$ surface: screening solvents for Li–air batteries

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Abstract. Nowadays, simulation techniques are routinely used to generate accurate models of the structures of crystalline and amorphous solids, to study surfaces, defects and the properties of complex systems, and to screen possible candidate materials for the most diverse types of technological applications. The screening of novel molecular structures has been so far pursued by calculation of intrinsic properties with first-principle methods. Still, the use of intrinsic properties as scoring functions may not always be optimal for systems of high complexity. In these cases, increasingly detailed and realistic simulations that take into account the interaction with the surrounding molecules are of crucial importance. In this paper, we present an effective way to screen different solvents with respect to their chemical stability versus Li$_2$O$_2$ solid particles. To achieve this, the minimum energy paths for different types of reactions of a series of aprotic solvents (acetonitrile and pivalonitrile, dimethyl sulphoxide, N-methyl-2-pyrrolidone and some of its derivatives, penta ethylene glycol (PEG-5) and a fluorinated derivative) with solid Li$_2$O$_2$ are computed and reported. From these data, we can extract the reaction energy barriers, which compare extremely well with the available experimental data and offer a convenient way for screening and designing suitable solvents for Li–air batteries from first-principle calculations.
Lithium–air (oxygen) batteries offer one of the highest theoretical specific energy among electrochemical energy-storage devices [1–3]. Schematically, they comprise a lithium anode in combination with an oxygen cathode, which ideally operate in ambient air. During the Li–air battery discharge process, oxygen from the surrounding environment diffuses into the battery and is chemically reduced at the surface of the air electrode (cathode). In aprotic electrolytes, the peroxide and possibly oxide anions, generated during discharge, react further with lithium ions to form lithium peroxide (Li$_2$O$_2$) and potentially lithium oxide (Li$_2$O), which are insoluble and deposit in the porous structure of the cathode. While the formation of Li$_2$O$_2$ upon cell discharge has been confirmed by many independent experiments [1, 4–6], the concurrent production of Li$_2$O was never really proved [4, 7, 8], and for this reason Li$_2$O did not attract a lot of attention in the past few years.

Since the first pioneering work of Abraham [1], different groups worldwide redirected their research interests to this potentially breakthrough technology, trying to address many of the open scientific issues for designing the ultimate Li–air cell, including new materials for the anode, cathode and electrolyte. Finding a suitable solvent remains one of the most elusive challenges in rechargeable Li–air battery technology. In fact, besides low viscosity, low volatility and high oxygen solubility, the desired properties of a suitable electrolyte are anodic stability at high potentials, formation of a stable solid electrolyte interface (SEI) at the metallic lithium anode, and stability against oxygen-reduced intermediates (LiO$_2$) and final discharge product (Li$_2$O$_2$).

For non-aqueous Li–air batteries, aprotic electrolytes play a critical role in the performance of the cell [4]. In fact, the highly reactive nature of the discharged species (Li$_2$O$_2$) demands the design of organic electrolytes that are highly stable and that are not degraded during the charge–discharge process. Among the aprotic solvents, carbonate-based ones, such as propylene carbonate (PC), have been widely used for Li–air batteries [4, 7, 9, 10] since the early years of this technology. However, carbonate-based solvents decompose during the discharge of the battery to form lithium and alkyl carbonates. Their presence in the white...
solid forming at the cathode upon battery discharge has been unambiguously determined by in situ differential electrochemical mass spectrometry (DEMS) [4, 9], by in situ surface-enhanced Raman spectroscopy [7], by x-ray diffraction powder analysis [11] and by theoretical investigations [12].

Although there is a fundamental lack of understanding of the decomposition mechanisms of carbonate solvents by oxygen reduction products, two hypotheses emerged in literature for the carbonate formation, differing in the reactive species that triggers the electrolyte degradation: (a) O₂ radicals (mainly superoxide ion, LiO₂) formed in the transient stage of the discharge process; and (b) solid Li₂O₂ formed upon discharging of the cell.

Inspired by a theoretical work [13], several groups [7, 9, 11] proposed the superoxide ion, O₂⁻, as the species responsible for electrolyte degradation. In fact, while O₂⁻ is the primary reduction product of oxygen in non-aqueous electrolyte [14, 15], the half-life of the superoxide depends on the nature of the supporting electrolyte cation present in the electrolyte solution [14]: large organic cations, such as tetrabutylammonium (Bu₄N⁺) in acetonitrile solutions, stabilize the superoxide, Bu₄NO₂, protecting the di-oxygen from further reduction to O₂⁻ or O₂²⁻. In contrast, the presence of lithium ions (Li⁺) renders the superoxide, LiO₂, unstable with a very short half-life, triggering its decomposition into Li₂O₂ and O₂. The LiO₂ surviving decomposition can either be reduced to Li₂O₂ or decompose the organic solvents, depending on the kinetics of the two processes.

Surprisingly, the chemical reactivity of Li₂O₂, which is the desired discharge product, was ignored in the early development of Li–air cells, and only recently was its crucial importance highlighted in both theoretical [12] and experimental studies [16–19]. In a recent paper of ours [12], the problem of whether the peroxide, O₂²⁻, can be considered a pivotal discharge product for the decomposition of carbonate-based electrolytes was addressed by using large scale simulations to model the reactivity of a surface of Li₂O₂ in contact with liquid PC (electrolyte thickness approximate 2 nm and a total system size of approximate 1000 atoms), with ab initio molecular dynamics techniques. Also, given the level of accuracy required, all results obtained with standard-gradient corrected density functional theory were refined by means of a hybrid-exchange correlation functional using a novel scalable implementation [20]. We suggested that Li₂O₂ acts as a primary degradation agent to decompose PC to alkyl carbonates by hydrogen abstraction and by nucleophilic addition followed by ring opening. Most important, we reported, for the first time, the impact that solid Li₂O₂ particles may have on the electrolyte decomposition. In fact, compared with Li₂O₂ units in solution, PC degrades with a barrier-less reaction on a surface of Li₂O₂. Several experiments performed afterwards confirmed the proposed theoretical picture. Younesi et al [19] presented a detailed study on how different electrolytes react when exposed to Li₂O₂. By using x-ray photoelectron spectroscopy (XPS), they found that both carbonate solvents (PC and ethyl carbonate (EC)/diethyl carbonate (DEC)) and ether solvents (tetraethylene glycol dimethyl ether (TEGDME)), in contact with a surface of Li₂O₂, decompose to a large extent by forming alkyl carbonates and carboxylates [19]. In another study, the degradation of ether solvents (dimethoxyethane (DME)) on a surface of Li₂O₂ was presented in a isotopically labelled DEMS and XPS experiment [16], where McCloskey et al report quantitative evidence of the reaction between Li₂O₂ and the ether electrolyte, suggesting the formation of a single passivation layer of Li₂CO₃ on the surface of Li₂O₂. The observed decomposition of DME in the presence of Li₂O₂ was later also the subject of a theoretical investigation [21].
Because the formation of Li$_2$O$_2$ upon cell discharge is beyond doubt, having been confirmed by different research groups worldwide [1, 4–6], the stability of any electrolyte versus Li$_2$O$_2$ is a key property. In fact, similar to other alkali-metal peroxides, Li$_2$O$_2$ is a very strong oxidizing agent, and for this reason it should be equally important to screen novel electrolytes not only for the stability against reduced oxygen species but also against solid Li$_2$O$_2$ particles and autoxidation. The example of glyme based electrolytes (DME) should be considered like a case study. In fact, DME was reported to be extremely stable versus the superoxide anion [22–24] and extremely resilient to autoxidation [25]. Nonetheless, different works [16, 19] clearly demonstrated how DME undergoes degradation upon cell discharging.

In this effort, molecular simulations offer an important service for addressing material discovery challenges. In fact, simulation techniques are now routinely used to generate accurate models of the structures of crystalline and amorphous solids, to study surfaces, defects and properties of complex systems, and to screen possible candidate materials for the most diverse types of technological applications. While most of these applications call for modelling physical and chemical properties of extremely complex systems, material discovery developed in the last years mainly relied on screening novel molecular structures based on the calculation of intrinsic properties by first-principle calculations. Still, the ranking of individual intrinsic properties, like the redox potential, or the evaluation of reaction barriers in conditions far from a realistic experimental setup could compromise the final outcome of material screening. In these cases, increasingly detailed and realistic simulations that take into account the interaction with the surrounding molecules is of crucial importance. In this paper, we present an effective way to screen different solvents with respect to their chemical stability versus Li$_2$O$_2$ solid particles. To achieve this, the minimum energy paths for different types of reactions of a series of aprotic solvents (acetonitrile and pivalonitrile, dimethyl sulphoxide (DMSO), N-methyl-2-pyrroldione (NMP) and some of its fluorinated derivatives, penta ethylene glycol (PEG-5) and a fluorinated derivative—see figure 1 for their chemical structure) with solid Li$_2$O$_2$ are computed and reported. From these data, we can extract reaction energy barriers that offer important guidelines for the screening and design of novel electrolyte systems for Li–air batteries. The paper is organized as follows: in section 2 the computational methods are described. The results and discussion are presented in section 3, and the conclusions in section 4.

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2. Computational methods

The first critical step to inspect the chemical stability of several electrolytes in the presence of solid lithium peroxide (Li$_2$O$_2$) was to set up a realistic representation of the cathodic environment of discharged Li–air batteries. All calculations reported below have been performed either with CPMD$^1$, which offers optimal scalability on IBM® BlueGene®/Q, or with CP2K$^2$, best suited for medium-scale computational infrastructures. In particular, we used CPMD to refine the calculations with the PBE0 [26] parameter-free exchange-correlation functional. For all other results based on generalized gradient approximation (GGA) (Perdew–Burke–Ernerhof (PBE) [27–29]) functional, we used CP2K.

2.1. CP2K and CPMD setup

The CP2K package adopts a hybrid basis set formalism known as Gaussian and plane wave method (GPW) [30], where the Kohn–Sham orbitals are expanded in terms of contracted Gaussian-type orbitals (GTO), whereas an auxiliary plane-wave basis set is used to expand the electronic charge density. When using a reciprocal space representation of the electron density, the computational time required to calculate the Hartree potential scales linearly with the dimension of the system. The GPW formalism requires the use of pseudo-potentials (PP) to describe the interaction of the valence electrons with the frozen atomic cores. In our investigation, norm-conserving Goedecker, Teter and Hutter (GTH) PPs [31] were used for all atomic species. The GTO basis sets used in CP2K are typically optimized for the specific PP. Here, double valence basis sets with polarization functions (DZVP) have been used for all atomic species. The auxiliary plane wave (PW) basis set was defined by the energy cutoff of 300 Ryd. All calculations are spin-polarized to describe the formation of any radical species properly, and performed using the generalized gradient-corrected PBE functional [27–29] empirically corrected for long-range dispersion interactions [32]. Low spin states (singlet) are used in all calculations. Triplet wave function calculations were performed only for selected points. The structures have been optimized (both for geometry and for minimum energy path optimizations) until the atomic forces were lower than $10^{-3}$ Ha Bohr$^{-1}$.

The refinement of the minimum energy paths at the PBE0 [26] level was performed using the CPMD software (see footnote 1), with three-dimensional periodic boundary conditions and plane-wave basis sets as the expansion of electronic wave functions. In these calculations, a plane-wave energy cutoff of 100 Ryd was used combined with GTH PPs [31], and the cell in the non-periodic dimension was enlarged to 40 Å.

2.2. Surface

The electrolyte decomposition on the Li$_2$O$_2$ surface was modelled by using a slab of Li$_2$O$_2$, created from a Li$_2$O$_2$ crystallographic cell [33], exposing the $\{10\overline{1}0\}$ crystallographic plane, with 2D periodic boundary conditions [34]. The slab used in the simulations is shown in figure 2. It consists of a orthorhombic box defined by vectors of length 19.0936 and 23.178 Å in the $x$ and the $z$ Cartesian direction, respectively. In the $y$-direction, perpendicular to the surface, a length of 25.00 Å is used to leave a sufficient amount of empty space between the slab and the box.

$^1$ CPMD Developers CPMD www.cpmd.org.

$^2$ CP2K Developers CP2K www.cp2k.org.

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boundary, so that a negligible electron density is present at the box surface of the non-periodic dimension [34]. The large supercell for the Li$_2$O$_2$ slab used during the calculations avoids the need for doing any k-point sampling. We considered the stoichiometric $\{10\bar{1}0\}$ surface since this structure was reported to be one of the most stable [35] surfaces for lithium peroxide. Recently, more exhaustive studies [36] on the stability of Li$_2$O$_2$ surfaces identified several Li$_2$O$_2$ surface terminations that are more stable than the stoichiometric one, revealing that an oxygen-rich surface may constitute the majority of the Li$_2$O$_2$ crystallite surface area. It is interesting to note that, although the difference in the stoichiometry of the entire surface slab, our surface exposes many oxygen atoms similarly to the topological features described for the oxygen rich surfaces [36].

Another important aspect is the spin state of the surface. In fact, all oxygen-rich surfaces have been described as half-metallic [36], whereas there is no information concerning the surface magnetization for stoichiometric surfaces. The only data accessible in literature is about small Li$_2$O$_2$ nano-clusters [21], in which the high spin states were found to be more favourable than low spin states. Still, in the same paper [21], the authors report on a CPMD study for both the singlet and triplet state, from which it is possible to see that the energy fluctuations of the singlet and the triplet overlap in several points at 300 K. Therefore, it is reasonable to expect an equipartition of high and low spin states at room temperature. For sake of completeness, we also computed energy barriers in a high spin state whenever a comparison with other theoretical values was possible, and we did not observe any major difference in the type of reactivity or the magnitude of the barriers.

2.3. Characterizing reactive paths

The reactivity of the electrolytes on the Li$_2$O$_2$ surface were investigated using the metadynamics algorithm with bond distances as collective variables [12]. In contrast to standard quantum-chemical approaches, where the results strongly depend on the chemical intuition used in building the model, metadynamics simulations [37] sample the potential energy space with respect to a set of internal (collective) variables in a more unbiased way. Therefore, it can be considered a useful exploratory tool, having the advantage of providing reactive trajectories which are close to the minimum free-energy path projected in the space of collective variables.
Reactive trajectories were then optimized using a climbing image nudged elastic band (NEB) [38, 39] approach with an optimal number of images sampling the reactive path. These calculations were performed using the CP2K code (see footnote 2) with an ab initio computational setup identical to the one reported above. Finite-temperature contributions were not included in the minimum energy profiles.

To improve the accuracy in the evaluation of the energy barriers, we recomputed the minimum energy paths, optimized at the PBE level, using the PBE0 [40] functional. Calculations were performed with a development version of CPMD using a novel parallelization for the evaluation of the exact Hartree–Fock exchange [20], which ensures a practically perfect scaling up to approximately 6 million BG/Q threads. The overall computational cost involving all the PBE calculations (CP2K) was of 2 millions CPU hours, while the one involving the PBE0 calculations (CPMD) was of 4 millions CPU hours. This research activity is part of the INCITE proposal (2013) on lithium–air battery acknowledged by the US Department of Energy (DOE) and with computing time on the BG/Q at the ALCF—Argonne National Laboratory (ANL).

3. Results and discussion

In this work, we used density functional theory calculations (PBE and PBE0) to predict the reactivity of aprotic solvents on a surface of Li$_2$O$_2$. All systems contain around 300 atoms and more than 650 occupied molecular states. To reduce the complexity, we investigated the reactivity of isolated molecules on Li$_2$O$_2$ surface, leaving the study of the correct electrolyte–Li$_2$O$_2$ interface and the impact that additional lithium ions and solvent molecules may have on the barriers reported below to a subsequent work. For this reason the magnitude of the reaction energies we reports below are in general quite large, while we expect that in the presence of a complete electrolyte–Li$_2$O$_2$ interface these values should decrease sensibly. Nonetheless, the impact that surfaces may have on reaction barriers is crucial and despite the lack of additional solvent molecules and a proper interface on the Li$_2$O$_2$ material, the present work provides the most realistic theoretical framework for computational screening and material design of stable aprotic solvents for Li–air batteries at the moment. We selected a few organic electrolytes, pre-screening between different solvents with a large dielectric constant grouped into classes with similar functional organic group, such as aliphatic nitrile, sulphoxide, glyme and lactam groups. The analysis described in the following sections is restricted to the initial reactive step of the degradation process for each solvent molecule. For a few compounds, metadynamics explorations suggested more than a single reaction pathway, which we optimized and report accordingly below. For clarity, each class of electrolyte will be discussed in a separate section. In figure 3, we show some of the characteristic geometries for few representative compounds.

3.1. Nitrile group

Acetonitrile is widely used in battery applications because of its relatively high dielectric constant (37.5) and its ability to dissolve electrolytes. While it was found to be relatively stable to superoxide anions [22], no information is available in literature regarding its stability versus solid Li$_2$O$_2$. Undoubtedly, acetonitrile cannot be used in a single electrolyte Li–air cell because of its reactivity with metallic lithium. In fact, lithium reacts with acetonitrile to produce lithium cyanide (LiCN), which in turn can react with weak acids to produce toxic hydrocyanic gas.
Figure 3. Characteristic geometries for a few representative compounds (acetonitrile, DMSO, NMP and PEG-5). In detail: (a1) frame 1 of the optimized minimum energy path for acetonitrile; (a2) frame 32 of the optimized minimum energy path for acetonitrile; (b1) frame 1 of the optimized minimum energy path for DMSO; (b2) frame 32 of the optimized minimum energy path for DMSO; (c1) frame 1 of the optimized minimum energy path for NMP; (c2) frame 32 of the optimized minimum energy path for NMP; (d1) frame 1 of the optimized minimum energy path for PEG-5; (d2) frame 32 of the optimized minimum energy path for PEG-5.
Figure 4. Minimum energy path (eV) for the nucleophilic addition of $\text{O}_2^-$ to the nitrile group of $\text{CH}_3\text{CN}$.

Nonetheless, it is interesting to investigate its reactivity versus $\text{Li}_2\text{O}_2$ as a possible electrolyte for the cathode chamber of a dual electrolyte Li–air battery.

Placed on the surface of $\text{Li}_2\text{O}_2$, an isolated acetonitrile is physically adsorbed with an energy of 2.70 eV, interacting strongly with the exposed lithium ions on the $\text{Li}_2\text{O}_2$ surface. In this configuration, the nitrile group is in a favourable position for a nucleophilic attack by the peroxide anion $\text{O}_2^-$, because the distance that separates the oxygen of the peroxy group and the carbon of the nitrile group is only 2.458 Å (see figure 3(a1)). We observe that acetonitrile undergoes a strong chemical adsorption by mild nucleophilic interaction between the carbon of the nitrile group and the oxygen of the peroxy rather than a complete nucleophilic addition at the CN carbon. The reaction is exergonic ($-0.120$ eV) and proceeds with an activation energy of 0.035 eV. At the minimum of the interaction, the distance between the carbon and the oxygen is 1.910 Å while the transition state is characterized by an initial bending of the C–CN bond (see figure 3(a2)). The minimum energy profile is reported in figure 4.

Regarding the aliphatic group, it is well-known that acetonitrile is an extremely weak acid. This is confirmed by our calculations, which characterize the proton abstraction as an extremely endergonic process with a barrier of 0.734 eV. By looking at the minimum energy path of the hydrogen abstraction process (see figure 5), it is clear that the product is only a kind of metastable state and that in ambient conditions its formation, unless stabilized by the presence of cations, may be less important.

Because the nucleophilic addition on the nitrile group is promoted by the close contact between the peroxide and acetonitrile, we decided to investigate a relatively bulkier aliphatic nitrile, i.e. pivalonitrile (2,2-dimethylpropanenitrile or tBut-CN). Pivalonitrile is absorbed on the $\text{Li}_2\text{O}_2$ surface with an interaction energy of 2.48 eV, and at the minimum of this interaction the carbon of the nitrile group is only marginally further away from the oxygen of the peroxy group (2.521 Å), exposing the bulkier t-buthyl towards the open space. Like acetonitrile, pivalonitrile also exhibits a second interaction with the $\text{Li}_2\text{O}_2$ surface that is isoenergetic with the physically absorbed one, in which the oxygen atom of the peroxy group is at 1.986 Å away from the carbon of the nitrile group, a distance larger than that achieved by acetonitrile. In figure 6 we report the minimum energy path of the nucleophilic interaction, which is characterized, as expected,
by a larger barrier than acetonitrile (0.121 eV). Similarly to acetonitrile, the transition state is characterized by the initial bending of the linear C–CN bond.

In general, we observe that the aliphatic nitriles are potentially good candidates as possible electrolytes when comparing their stability versus Li$_2$O$_2$. In fact, in contrast to the other electrolytes described below, acetonitrile and pivalonitrile do not undergo any molecular degradation, despite showing a strong interaction with the surface. This interaction may not necessarily be seen as a negative aspect. In fact, similarly to what happens at the anode with the formation of a SEI layer, the possibility of forming a strong interaction while preserving the chemical nature of the molecules may allow a stabilized growth of Li$_2$O$_2$, owing to the formation of a stable interface. By chemical manipulation and design, it is possible to tune a certain property with a quite good accuracy but at the price of changing other chemical and physical properties. For instance, pivalonitrile may exhibit a weaker interaction with the Li$_2$O$_2$ surface than acetonitrile, as expected from the presence of the bulkier group, but many of its
physical and chemical properties, like its dielectric constant and ability to dissolve lithium salts, may have been dramatically changed in going from acetonitrile to pivalonitrile. In this specific case, for example, we may expect a lower ability of pivalonitrile to dissolve lithium salts, given the large apolar t-buthyl group as compared with the smaller methyl.

3.2. Sulphoxide group

DMSO is an organo-sulphur compound with the formula \((\text{CH}_3)_2\text{SO}\). It is an important polar aprotic solvent that dissolves both polar and non-polar compounds and is miscible with a wide range of organic solvents. Because of these important properties, it has been used in recent Li–air research activities \[5\]. We decided to investigate the stability of DMSO and the type of reactivity, if any, that this molecule may have when combined with a surface of \(\text{Li}_2\text{O}_2\).

Placed on the surface of \(\text{Li}_2\text{O}_2\), DMSO is physically adsorbed with an energy of 2.25 eV, with the oxygen of the sulphoxide group and the lithium ions on \(\text{Li}_2\text{O}_2\) surface interacting at close distance (2.069 Å) (see figure 3(b1)). Because of the strong interaction with the lithium atoms, the sulphur is also in relatively close contact with the oxygen atom of the peroxy group (2.685 Å). The nucleophilic attack of the oxygen proceeds with a low barrier (0.237 eV), and the overall reaction is extremely exergonic (−2.37 eV). In figure 7 we report the optimized minimum energy path for the decomposition of DMSO. Compared to what we observed in previous studies on PC \[12\], the degradation of DMSO is a concerted reaction in which the oxygen-sulphur distance reaches a value of 1.738 Å at the transition state, while the oxygen-oxygen distance extends to 1.738 Å. Following the transition state, we observe the formation of an oxide anion (O\(^2\)\(^–\)) and of the oxidized DMSO (methylsulphonylmethane) along the minimum energy path, see the first shoulder at −1.2 eV. The close contact of methylsulphonylmethane with the oxide anion (O\(^2\)\(^–\)) and the lack of additional lithium ions and solvent molecules at the \(\text{Li}_2\text{O}_2\)-electrolyte interface promote the subsequent proton abstraction from one of the methyl groups, with the formation of OH\(^–\) and the anion of methylsulphonylmethane (see figure 3(b2)). Because of the lack of a proper interface description between the \(\text{Li}_2\text{O}_2\) surface and the electrolyte in the theoretical model, DMSO in experiments may not necessarily degrade further to the anion stage, like we observed in our simulations, and

**Figure 7.** Minimum energy path (eV) for the oxidation of DMSO by \(\text{Li}_2\text{O}_2\).
instead proceeds only as far as the formation of the sulphone and oxide anion, which could be immediately stabilized by the excess lithium ions present at the interface.

Compared with PC, where a solid alkyl-carbonate layer forms on the top of Li$_2$O$_2$ [12, 19], DMSO is oxidized to a sulphone when reacting with the surface of Li$_2$O$_2$. Although the corresponding methylsulphonylmethane is solid at room temperature, it is plausible to expect its dissolution into DMSO. Therefore, unless the electrolyte is specifically screened with sensitive analytical techniques for oxidation products after discharge/recharge, the use of DMSO may be documented as a stable electrolyte for Li–air. In a recent publication, Peng et al [5] have indeed reported the successful use of DMSO with a gold nano-porous (NPG) cathode. They documented the formation of Li$_2$O$_2$, but as no analytical examination of the solvent (after cell discharge/recharge) was performed, no definitive statement can be made about its stability.

3.3. Glyme group

Depending on the chain length, glymes exhibit different physical properties, like the melting and the boiling points. From a molecular point of view, they tend to form chelate complexes with cations (like Li$^+$) acting as bidentate ligands. The ones routinely used in industrial processes are dimethoxyethane (DME) and tetraethylene glycol dimethyl ether (TEGDME), which are clear, colourless, aprotic, highly used as polar solvents, and have excellent chemical and thermal stability. Together with a high-permittivity solvent (like PC), DME is used as the low-viscosity component of lithium–ion batteries electrolytes. The idea of using DME for Li–air technology was therefore a natural choice, similarly to what happened for PC in the past decades.

While initially promising and certainly more stable to reduced O$_2$ species than organic carbonates, ethers exhibit increasing electrolyte decomposition upon cycling [4, 5, 10, 41, 42]. These data show that glymes are increasingly unstable upon cycling, and their side-reaction products can be difficult to detect by x-ray diffraction because of their poor crystallinity. These results demonstrate that ethers do not support the necessary reversible Li$_2$O$_2$ formation/decomposition upon cycling that is essential for operation of the Li–air cell. This poor behaviour was related to their ease in forming peroxides. Regarding the possible mechanisms for forming peroxides, one can hypothesize on two different nucleophilic attacks to the ether carbon by either peroxide or superoxide. Two independent studies reported that the C–O bond breaking of ethers by a singlet Li$_2$O$_2$ monomer or tetramer required activation barriers in excess of 1 eV [6]. Further investigation on Li$_2$O$_2$ tetramer triplet reported activation barriers for the nucleophilic substitution of 2.0 eV [21]. Also a possible attack by the superoxide anion (OO$^-$) was rejected by Bryantsev et al [22], because of its barrier in excess of 1.35 eV. The outcome of these theoretical investigations, limited to cluster calculations including an implicit solvent description, would identify DME as a stable solvent, in contrast to the experimental evidence that undoubtedly show its decomposition. For sake of completeness, we also need to report that a very recent experimental paper [43] comes to a different conclusion concerning the stability of tetraglyme in Li–air batteries than the experimental works cited above.

We therefore decided to investigate the stability of pentaethylene glycol dimethyl ether (PEGDME, very similar to TEGDME) on a surface of Li$_2$O$_2$ in an environment more realistic to the one present in Li–air electrochemical cells. Because of the large number of rotational degrees of freedom of the ether chain, PEGDME exhibits multiple minima when interacting with the surface of Li$_2$O$_2$. The minimum interaction we found from our sampling was of 3.8 eV, in which the oxygen atoms of PEGDME interact with multiple lithium ions on the surface of
Li$_2$O$_2$ (see figure 3(c1)). The solvation of the superficial lithium ions places both the hydrogen and the carbon atoms of the ethers in a favourable position for reacting with the peroxide moieties.

The first type of reactivity we investigated was the hydrogen abstraction from the aliphatic CH$_2$ group. In figure 8, we report the minimum energy path. Similarly to what we observed for DMSO, the hydrogen abstraction involves a concurrent C–H and O–O bond breaking, with the formation of an oxide anion (O$_2^-$), an hydroxide radical and a carbon radical, stabilized by the interaction with the superficial lithium atoms (see figure 3(c2)). The reaction is exergonic (−2.33 eV), with a barrier of 0.901 eV.

This value should be compared with the one reported by a recent work [44], where lithium peroxide tetramer clusters were used to compute the activation energy for the C–H bond breaking reaction. In this paper, Assary et al [44] report a barrier of 1.21 eV for the hydrogen abstraction in solution and at the B3LYP level of theory using a singlet wave function and a value of 1.42 eV using a triplet wave function. Also, they report a lower barrier (0.66 eV at the B3LYP level) for the hydrogen abstraction by a defective site of a Li$_2$O$_2$ tetramer in a triplet state. Compared with the value reported for singlet calculations (1.21 eV), our value of 0.901 eV, which is still at the GGA level of theory (see the section below for PBE0 results) and for a singlet wave function, is smaller. We performed a similar calculation using a high spin (triplet) wave function and did not notice big differences between the singlet and the triplet values for the reaction barrier (high spin wave function (triplet) energy barrier: 0.849 eV). Nonetheless the corrected barrier at the PBE0 level (1.102 eV, see section below), allows us to perform a direct comparison with the B3LYP value and clearly to pinpoint our lower barrier for the hydrogen abstraction to a surface effect. This effect is also mentioned by Assary et al [44], who report a decrease in their reaction barrier by 0.2 eV when using a larger (Li$_2$O$_2$)$_{16}$ cluster for their surface model.

This behaviour resembles very much the one of PC, whose degradation is barrier-less and spontaneous on a surface of Li$_2$O$_2$, in contrast to the same type of degradation in solution by a single Li$_2$O$_2$ unit [12].

The hydrogen abstraction process alone cannot justify the number of degradation products documented in different experiments [4, 5, 10, 41, 42]. Therefore, we extended the sampling
of the reaction space to find subsequent steps in the degradation process that would allow us to rationalize and propose key changes in the aliphatic chain that would lead to an increase of the glyme stability.

After the first hydrogen abstraction, we found that a subsequent abstraction in a neighbouring CH₂ group may lead to the formation of an olefine, which in strongly oxidizing conditions may degrade further into carboxylate containing species. In figure 9, we report the minimum energy path for the formation of the olefine starting from the PEGDME radical (after the first hydrogen abstraction). The process is highly exergonic (−2.76 eV) because of the reduction of two peroxides to oxides anions; the reaction barrier is 1.149 eV.

Immediately after hydrogen abstraction, PEGDME can undergo a nucleophilic attack by the newly formed hydroxyl group. Even in this case the reaction is a concerted one, in which the O–H bond, formed during the hydrogen abstraction, breaks to restore the CH₂ moiety while concurrently the oxygen is attacking the CH₂ carbon in a SN₂-type reaction. The final products are alkoxides, which can degrade further to carboxylates in these highly oxidizing conditions. The reaction is exergonic (−1.84 eV), and the reaction barrier is 1.071 eV, which is still easily accessible at room temperature.

Because the type of reactivity involving glymes goes through the hydrogen abstraction process, we thought of modifying the aliphatic chain so as to ideally prevent degradation. An interesting class of organic ethers are the fluorocarbon ethers, famous for having a high oxygen solubility [45], which generally is a desirable property for a battery in which oxygen plays an active role. While screening for possible reaction products involving the abstraction of fluorine, we could not identify any stable O–F compound, similar to what happens with the hydrogen abstraction. Therefore, the presence of a fully fluorinated aliphatic chain may be the key in preventing the degradation of glymes. Still, because of the low polarity of such solvents, fully fluorinated ethers may be impossible to use as solvents, because lithium salts may probably not reach a sufficiently high concentration for use in battery electrolytes. For this reason we decided to screen the stability of partially fluorinated PEGDME.

On a single −CH₂ group, undergoing first hydrogen abstraction and immediately after nucleophilic attack, we substituted one hydrogen atom with a fluorine atom. For the hydrogen
abstraction process, we did not notice any relevant difference compared with the non-fluorinated ether, finding a barrier of 0.9 eV (comparable to the one reported for PEGDME). However, on the subsequent nucleophilic attack, the fluorinated ether has a barrier of 1.178 eV, larger by 0.1 eV than the non-fluorinated glyme. In figure 11, we report the minimum energy path for the fluorinated glyme, to be compared with that of the non-fluorinated glyme reported in figure 10.

By combining a suitable ratio of fluorine atoms on the aliphatic backbone of the ether it may be possible to increase the stability of glymes, while preserving the good polar aprotic characteristics.

3.4. Lactam group

In this section, we focus our discussion on NMP and some of its derivates. NMP is a chemical compound with a five membered-lactam structure. It belongs to the class of dipolar aprotic
solvents, which includes also dimethylformamide, dimethylacetamide and DMSO. Because of its good solvency properties, NMP is used to dissolve a wide range of chemicals, from ionic salts to apolar solvents, and accordingly attracted attention as a possible solvent for Li–air batteries. N,N-dialkyl amides, such as N,N-dimethylacetamide and N-alkyl Lactams, such as NMP, have been reported to be significantly more stable to superoxide than organic carbonates and glymes [22, 24], although a recent investigation [46] using dimethylformamide (DMF) as the basis for the electrolyte, confirmed that there is indeed electrolyte decomposition, which increases on cycling, and that the stability of DMF to oxygen-reduced species is insufficient for practical applications in non-aqueous Li–air batteries. Chen et al [46] also report that the first discharge cycle when using DMF is dominated by reversible Li$_2$O$_2$ formation. Interestingly enough, theoretical calculations [22] for NMP (with similar functional group) show a barrier in excess of 1.5 eV for the reaction with superoxide, which is therefore unlikely to proceed at room temperature. Still, superoxide is called upon to justify the amide and lactam degradation when interpreting experimental works [46]. As Li$_2$O$_2$ formation occurs and the degradation is observed only when cycling, we believe that it is crucial to understand the NMP stability versus a surface of Li$_2$O$_2$ and, eventually, also how one can increase this stability.

Placed on the surface of Li$_2$O$_2$, NMP is physically adsorbed with an energy of 3.15 eV, with the oxygen of the lactam group and two lithium ions on Li$_2$O$_2$ surface interacting at close distance (1.868 and 1.910 Å, see figure 3(d1)). In this minimum configuration, the carbon of the lactam group is in close contact with the oxygen of the peroxy group, the distance between them being of 2.346 Å. With a barrier of 0.310 eV, NMP reacts with the peroxy in a similar way to what we reported for the barrier-less process of PC [12]. The oxygen–oxygen bond weakens while the carbon–oxygen bond forms. Compared with PC, in which ring opening led to alkyl carbonates, in this case the ring opening is followed by an immediate loss of H$^-$ from the CH$_2$ group next to the nitrogen atom and the formation of a secondary aldime. Aldimines in presence of oxyding species can easily undergo further decomposition to NO and carboxylic anions. In figure 12, we report the minimum energy path of the complete degradation to aldime (see figure 3(d2)).
As the reactivity is driven by the close contact of the peroxo group with the carbon of the lactam, we decided to investigate the stability of NMP-modified molecules. The first one is \( N \)-methyl-3-dimethyl-2-pyrrolidone (NMDP) and the second is the \( N \)-t-buthyl-2-pyrrolidone (NTP). Both molecules have bulkier groups, which should prevent the close contact of the amide group with the peroxo group. In fact, the absorption energy for NMDP and NTP is 2.81 and 2.93 eV, respectively, and the equilibrium distances between the oxygen of the peroxo and the carbon of the lactam group are 2.958 Å for NMDP and 2.756 Å for NTP. As expected, both molecules exhibit a higher stability than NMP, and while the degradation process follows an identical pathway, the barriers characterizing the nucleophilic attack followed by the aldimine formation are 0.548 eV for NMDP and 0.638 eV for NTP. Figures 13 and 14 report the minimum energy paths for these two decomposition pathways.

From what we were able to rationalize from the NMP molecular modifications proposed above, a key role for NMP stability is played by the hydrogens positioned on the \(-\text{CH}_2\) group.
next to the nitrogen atom whose elimination allows the ring opening followed by aldimine formation. It was therefore a natural consequence to model an NMP molecule with fluorine instead of hydrogen atoms on the aliphatic ring. We tested 3,4,5-difluoro-NMP on the surface of Li$_2$O$_2$, and with great surprise we noticed that the molecule undergoes a nucleophilic addition by the peroxo group, characterized by a barrier of 0.290 eV. Moreover, in contrast to NMP, the presence of the fluorine atoms does not allow ring opening. The minimum energy path is reported in figure 15.

It is also plausible to conjecture that in presence of an excess of Li ions, one of the fluorine atoms next to the nitrogen atoms may still be eliminated to form an aldimine. An explicit modelling of the electrolyte layer in contact with the Li$_2$O$_2$ surface could provide further insight into possible further degradation steps. On the basis of this computational evidence, we conclude that the bare Li$_2$O$_2$ surface reacts almost instantaneously with fluorinated NMP solvents to form products, that undergo further degradation less easily. This could potentially play a critical role for protecting the Li$_2$O$_2$ surface, in a very similar way as to what happens with SEIs at the lithium anode. Therefore, fluorinated lactams, although not easy to synthesize, may be of some interest for experimental testing.

3.5. Impact of the use of PBE0 on the electrolyte degradation barriers

To improve the accuracy in the evaluation of the energy barriers, we refined the barriers computed with the GGA (PBE) functional for the several electrolytes using the hybrid functional PBE0 [40], obtaining the results reported in table 1. Calculations were performed with a development version of CPMD with a novel parallelization of the exact Hartree–Fock exchange part [20], which ensured a practically perfect scaling up to approximately 6 millions BG®/Q threads. The energy differences between the use of PBE and PBE0 on transition state geometries are smaller than 1.0 eV, which is the maximum error between all transition state geometries, detected for the degradation reaction. In general, the electrolytes analysed in this work, are all more stable than PC, which was decomposing with a barrier-less process [12]. DMSO, NMP, with a barrier of approximately 0.8 eV can be still considered extremely vulnerable to chemical degradation. PEG-5, instead shows larger barriers at the PBE0. Hypothesizing a self-sustained
Table 1. Differences in the energies at the PBE0 and PBE level (for the chemical degradation processes of different electrolytes by Li$_2$O$_2$) for transition state geometries as optimized with NEB.

| Electrolyte   | PBE E (eV) | PBE0 E (eV) | $\Delta$E$_{PBE0-PBE}$ (eV) |
|---------------|------------|-------------|------------------------------|
| CH3CN (NA)    | 0.035      | 0.045       | 0.010                        |
| CH3CN (HA)    | 0.734      | 0.867       | 0.133                        |
| tBut3CN       | 0.121      | 0.129       | 0.008                        |
| DMSO          | 0.237      | 0.738       | 0.501                        |
| PEG-5 (HA)    | 0.901      | 1.102       | 0.201                        |
| PEG-5 (2-HA)  | 1.149      | 2.013       | 0.864                        |
| PEG-5 (NS)    | 1.071      | 1.496       | 0.425                        |
| PEG-5F (NS)   | 1.178      | 1.744       | 0.566                        |
| NMP (NA)      | 0.310      | 0.798       | 0.488                        |
| NMDP (NA)     | 0.548      | 1.469       | 0.921                        |
| NTP (NA)      | 0.638      | 1.699       | 1.061                        |
| NMP-F (NA)    | 0.290      | 0.807       | 0.517                        |

chain reaction, even such high barrier could easily lead to molecular degradation in short times. Finally, PBE0 calculations confirm the outcome of the PBE ones for the proposed novel NMP molecules and the fluorinated PEG-5, having all larger barriers than the corresponding pristine structures. Further experimental investigations are required to provide information on the impact of this molecular design exercise on the original physical–chemical properties of both NMP and PEG-5.

4. Summary and conclusions

In this work, we presented an effective way to screen different solvents with respect to their intrinsic chemical stability against Li$_2$O$_2$ solid particles. To achieve this, the minimum energy paths for different types of reactions of a series of aprotic solvents (acetonitrile and pivalonitrile, DMSO, NMP and some of its fluorinated derivatives, PEG-5 and a fluorinated derivative) with solid Li$_2$O$_2$ have been computed. In contrast to the state of the art in material discovery, where the screening of novel molecular structures is mainly based on the calculation of intrinsic properties by first-principle calculations, we increased the complexity of the model, leading to more realistic simulations. In fact, the ranking of individual intrinsic properties, such as the redox potential, or the evaluation of reaction barriers in conditions far from a realistic experimental setup may compromise the final outcome of material screening.

This work serves also as a validation of the computational setup for screening and designing suitable electrolytes for Li–air batteries. In fact, we refined our understanding of solvent stability in Li–air batteries, as we have been able to characterize some of the chemical features that increase stability against solid Li$_2$O$_2$ particles. We find that aliphatic nitriles are potentially good candidates, especially in dual-electrolyte Li–air setups when comparing their stability versus Li$_2$O$_2$. Sulphoxides easily undergo oxidation to sulphones which are particularly stable to further oxidation, and therefore potentially useful as Li–air battery electrolytes.
We find glyme groups relatively stable to Li$_2$O$_2$ surface degradation, although the barrier for their degradation may still be accessible at room temperature. For this reason, it is not possible to exclude a priori the possibility of ethers to undergo hydrogen abstraction with a subsequent self-sustained chain degradation process. Finally, we find lactams unstable when exposed to Li$_2$O$_2$ particles, although a few key chain modifications may lead to an increase of their stability. We would like to stress, that any conclusion in this paper is strictly related to the chemical stability of the electrolyte on Li$_2$O$_2$. We proposed few different chemical structures, that allowed us to tune a certain property with a quite good accuracy while potentially changing, on the other side, other chemical and physical properties. Therefore, it is a strict requirement to involve in the final evaluation of optimal electrolytes, not only the chemical stability versus Li$_2$O$_2$, which is a necessary condition, but also other key properties in a multi-objective optimization process.

In conclusion, in this paper we have shown that with current computer simulations, it is possible to perform reliable screening based on complex reactivity indicators.

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