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## Text mining assisted review of the literature on Li-O2 batteries

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## PAPER

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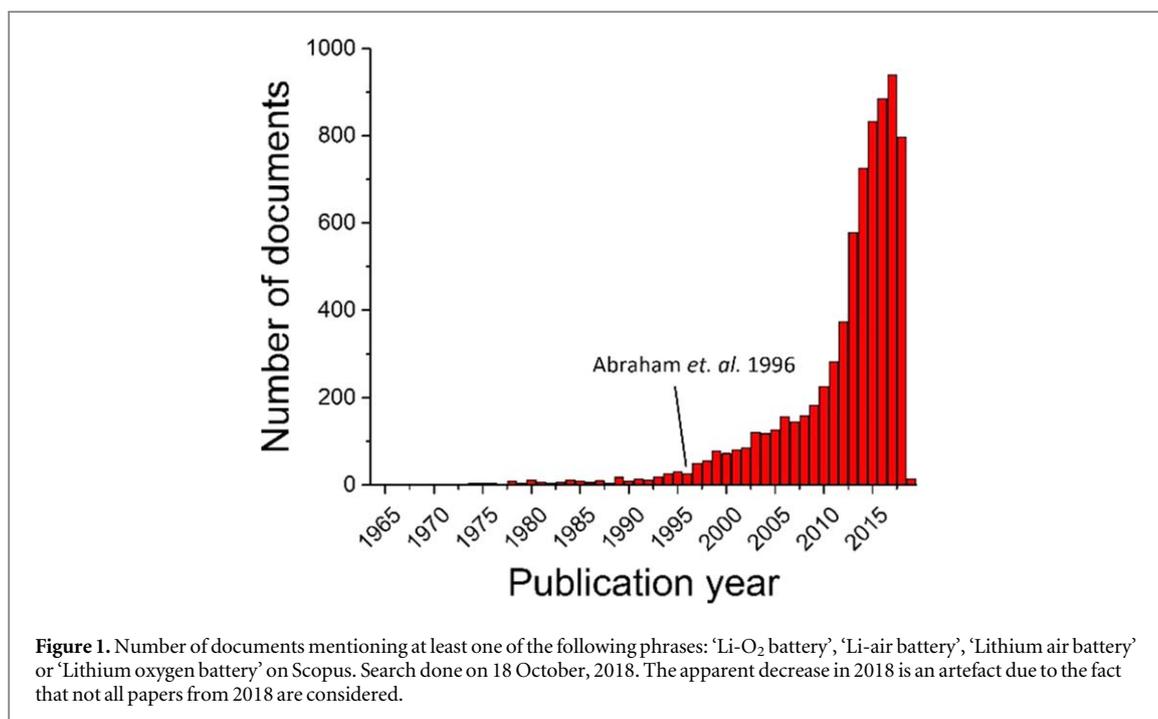
Keywords: text mining, machine learning, lithium oxygen batteries

**Abstract**

The high theoretical capacity of Li-O<sub>2</sub> batteries attracts a lot of attention and this field has expanded significantly in the last two decades. In a more general way, the large number of articles being published daily makes it difficult for researchers to keep track of the progress in science. Here we develop a text mining program in an attempt to facilitate the process of reviewing the literature published in a scientific field and apply it to Li-O<sub>2</sub> batteries. We analyze over 1800 articles and use the text mining program to extract reported discharge capacities, for the first time, which allows us to show the clear progress made in recent years. In this paper, we focus on three main challenges of Li-O<sub>2</sub> batteries, namely the stability-cyclability, the low practical capacity and the rate capability. Indeed, according to our text mining program, articles dealing with these issues represent 86% of the literature published in the field. For each topic, we provide a bibliometric analysis of the literature before focusing on a few key articles which allow us to get insights into the physics and chemistry of such systems. We believe that text mining can help readers find breakthrough papers in a field (e.g. by identifying papers reporting much higher performances) and follow the developments made at the state of the art (e.g. by showing trends in the numbers of papers published—a decline in a given topic probably being the sign of limitations). With the progress of text mining algorithms in the future, the process of reviewing a scientific field is likely to become more and more automated, making it easier for researchers to get the 'big picture' in an unfamiliar scientific field.

**1. Introduction**

To reduce our dependence on fossil fuels, it is crucial to develop adequate energy storage systems, so that the electricity generated from renewable energy sources can be used. Transportation is a key application of energy storage in which we also need high energy density systems. Lithium oxygen (Li-O<sub>2</sub>) batteries are a good candidate for such applications thanks to their high theoretical discharge capacity of 1168 mAh g<sub>Li<sub>2</sub>O<sub>2</sub></sub><sup>-1</sup>, 3–7 times higher than typical Li-ion batteries, and the low cost of their constituent materials [1]. The high theoretical gravimetric capacity of Li-O<sub>2</sub> batteries comes from the conversion type electrochemistry it follows under operation. A typical Li-ion battery works with two intercalation electrodes, e.g. graphite [2] and LiCoO<sub>2</sub> [3]. In these systems, lithium ions intercalate into a crystal structure and occupy interstitial sites. The number of lithium ions stored per number of host atoms is thus relatively low, and these materials provide limited capacities. For Li-O<sub>2</sub> batteries, the active material at the cathode side is not stored in the battery at the charged state. During the discharge, lithium ions migrate to the cathode and react with oxygen atoms dissolved into the electrolyte either from air or an oxygen gas tank. The lightweight nature of both lithium and oxygen atoms lead



to the high capacity. However, there are several challenges to overcome before the industrial use of Li-O<sub>2</sub> batteries becomes a reality. As we will show below, stability [4, 5], cyclability [6, 7], low practical capacity [8], rate capability [9], discharge and charge overpotentials [10], are major problems with such batteries.

Significant research efforts have been put into these systems aiming at bringing Li-O<sub>2</sub> batteries closer to practical applications. The intensity of the research in this field can be illustrated by a simple search on *Scopus* [11] using the keywords ‘Li-O<sub>2</sub> battery’, ‘Li-air battery’, ‘lithium air battery’ and ‘lithium oxygen battery’. With this search, any article or document containing at least one of these strings is extracted from the database. Figure 1 shows the increasing number of publications year-by-year, totaling 7323 documents (search done on 18 October, 2018). The same search on the *Web of Science* [12] database shows a number of documents close to 10 000. This first simple search confirms that the research field on Li-O<sub>2</sub> batteries has become immense. The apparent decrease in 2018 is an artefact due to the fact that not all papers from 2018 are considered. To read all of the documents in the literature is a daunting task: assuming a researcher reads 100 papers per year, he/she will need more than 70 years to read all the papers mentioning Li-O<sub>2</sub> batteries. We clearly need to develop efficient methods to extract the literature relevant to us. Furthermore, the classical preparation of reviews may be biased by the expertise or views of the writers: text mining has the potential to be a formidable complementary or an alternative tool towards the preparation of transdisciplinary reviews. Here, we explore the potential of such an approach.

Text mining is a method to extract *useful information* from a text with the aid of a computer program. The term *useful information* may refer to a wide variety of information depending on the intended use of the method. Text classification, clustering, numerical value extraction, document summarization are some of the many sub-branches of the method. A typical text mining method uses one or a combination of statistical pattern analysis, lexical analysis, occurrence frequency analysis, tagging etc.

There are many recent reports on the developments and applications of text and data mining techniques for automatic extraction of data and meaning from textual and/or numerical data. Kajikawa *et al* [13] analyzed emerging technologies in energy research using a citation network analysis. They generated clusters by analyzing citation networks, each cluster having a specific topic such as fuel cells, solar cells. Then, they analyzed the title and abstract of thousands of articles to obtain insights into the emerging research fields and technologies. In a different study, Gomila *et al* [14] used a combination of tech-mining and semantic-TRIZ (Teoriya Resheniya Izobreatatelskikh Zadatch—Theory of Inventive Problem Solving). The former is suited for highlighting trends and weak signals while the latter can identify the use of a technology, or a battery, and the functional relationships between its components. Following their new approach, they analyzed trends in Li-ion battery cathodes (LiMn<sub>2</sub>O<sub>4</sub>, LiCoO<sub>2</sub>, LiFePO<sub>4</sub>) and the use of graphene in Li-O<sub>2</sub> batteries. They showed a sharp rise of the number of articles using graphene in Li-O<sub>2</sub> batteries after 2010. Kay *et al* [15] focused on the use of graphene in various applications between 2000 and 2013. They exploited text mining, visualization tools and mapping kits to create scientific and patent activity maps. These maps show that the graphene research was conducted mainly

in the fields of materials science, physical chemistry and engineering and 18 macro-disciplines and 35 macro-patent categories were identified.

Going beyond bibliometric analyzes, Ghadbeigi *et al* [16] developed a data-driven approach to design battery materials. They considered resources and performance of materials, and created a database containing over 16 000 data points gathered from over 200 articles. They investigated energy density, power density and scarcity of several intercalation and conversion materials. They observe that intercalation based cathode materials with a similar structure type exhibit a comparable property-based tendency, and that the alloys show less voltage hysteresis than conversion-based materials. With a similar objective, Jain *et al* [17] discussed several data mining techniques such as clustering, linear models, and tree-based regression. They present the use of such techniques in various materials applications including Li-ion battery design, piezoelectric materials and compound prediction. They demonstrate a way for analyzing the properties of valence and conduction bands in materials. This method is linked with the Materials Project [18] database through its API [19] (Application Programming Interface) to use data for over 2500 compounds. Sohn *et al* [20] investigated critical parameters affecting energy density and capacity retention in 38 layered and 33 spinel cathode materials. Existing experimental data was mined using a confirmatory factor analysis based on a structural equation model; and the usefulness of such a technique to pinpoint critical parameters was demonstrated.

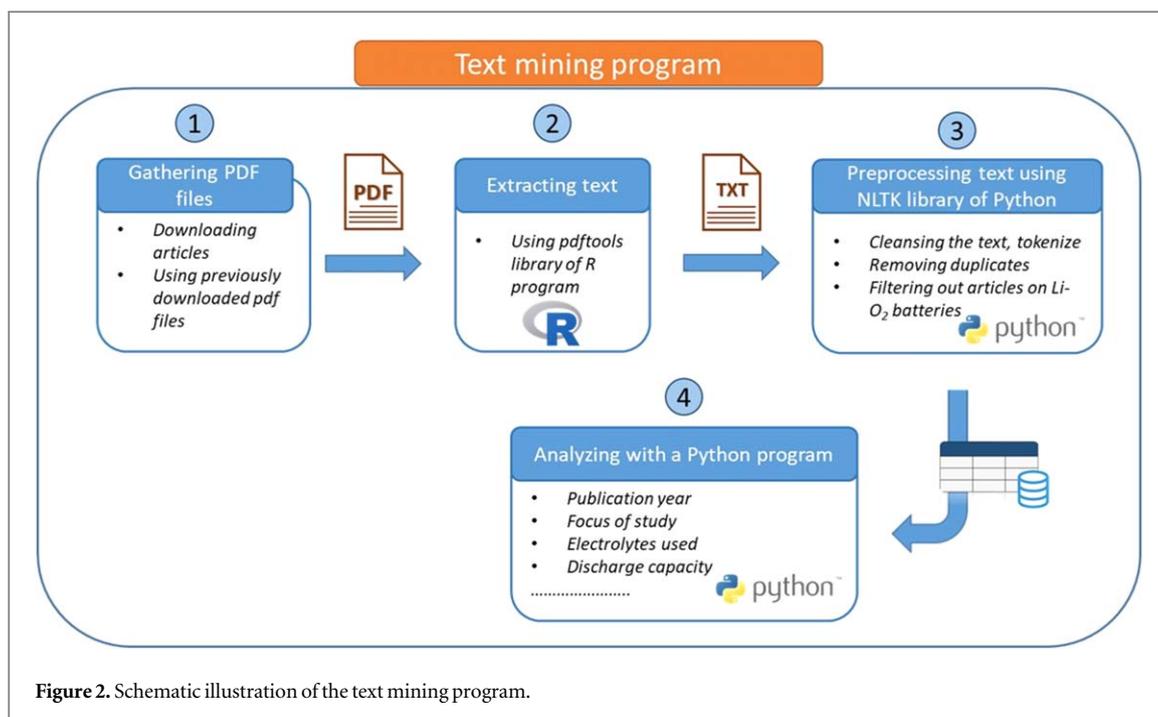
Very recently, Schnell *et al* [21] developed a data mining approach that they applied to a real battery production line. In that work, the authors showed, for the first time, the systematic acquisition, processing and analysis of data from a battery production line along the whole process of the cell production chain. The work aimed at analyzing and improving the production process for the Li-ion battery manufacturing line. They used various data mining and machine learning methods to single out key quality drivers and predict the quality of the cells. This could replace or reduce the need for costly formation and aging procedure. Electrode fabrication processes and electrolyte filling process were identified as key quality drivers.

In this work, we use machine learning-based text mining tools to study global trends in Li-O<sub>2</sub> battery research field. In the next section, we describe the tools and methods we use. We then report on the outputs of this text mining program, i.e. the data extracted from about 1800 articles on Li-O<sub>2</sub> batteries. This work should be seen as an attempt to produce a semi-automated review of the Li-O<sub>2</sub> batteries field, completed by comments on specific papers to provide deeper insights into the systems in a more traditional way.

## 2. Methodology

We developed a text mining program using a combination of Python and R programming languages. The general scheme is shown in figure 2.

- (1) We gather articles. This is done in two ways. First, we realize a search on Scopus with the keywords ‘*Li-O<sub>2</sub> battery*’, ‘*Li-air battery*’, ‘*lithium air battery*’ and ‘*lithium oxygen battery*’. This search led to 7323 documents (on 18 October, 2018). Then, we manually read the title and abstract of these documents and downloaded all of the articles on aprotic Li-O<sub>2</sub> batteries in PDF format (1797 articles). In principle, this step can be done automatically in a much faster way through APIs. However, most of the journals’ API systems limit the number of articles that can be downloaded or sometimes even block the whole university access. Secondly, we gathered previously downloaded articles in PDF format which are not necessarily all on aprotic Li-O<sub>2</sub> batteries. This collection consists of about 2300 articles downloaded in the last few years. Normally the first step should cover almost all of the articles published to date, however, we carry out the second step to make the text mining flexible to add new articles later on and to assess the efficiency of our filtering process. Then we give the collection of PDF files gathered through these two methods (4092 articles) as an input to an R code.
- (2) The R code opens up the PDF files using the *pdftools* library, extracts their text content and saves it as text files. We have tried to do this text extraction using the *PyPDF2* library of Python, but we found out that the library of R is more accurate. The text files created by the R code are given as inputs to a *preprocessing code* written in Python using the Natural Language Toolkit (NLTK) library, and carrying out the data curation.
- (3) In the preprocessing code, we clean the text data (deletion of spaces and extra characters; conversion of the text to lowercase, except for acronyms and special names) and tokenize it (conversion of the raw text to a list of words). Then, we check for duplicate documents and too short files and remove them. Too short files are in general conference abstracts or files for which extracting text is not possible (e.g. the text is saved as photos). The final stage of preprocessing is to filter out the articles actually focusing on Li-O<sub>2</sub> batteries. To select articles studying Li-O<sub>2</sub> batteries, we use a machine learning algorithm, the Naïve Bayes’ classification



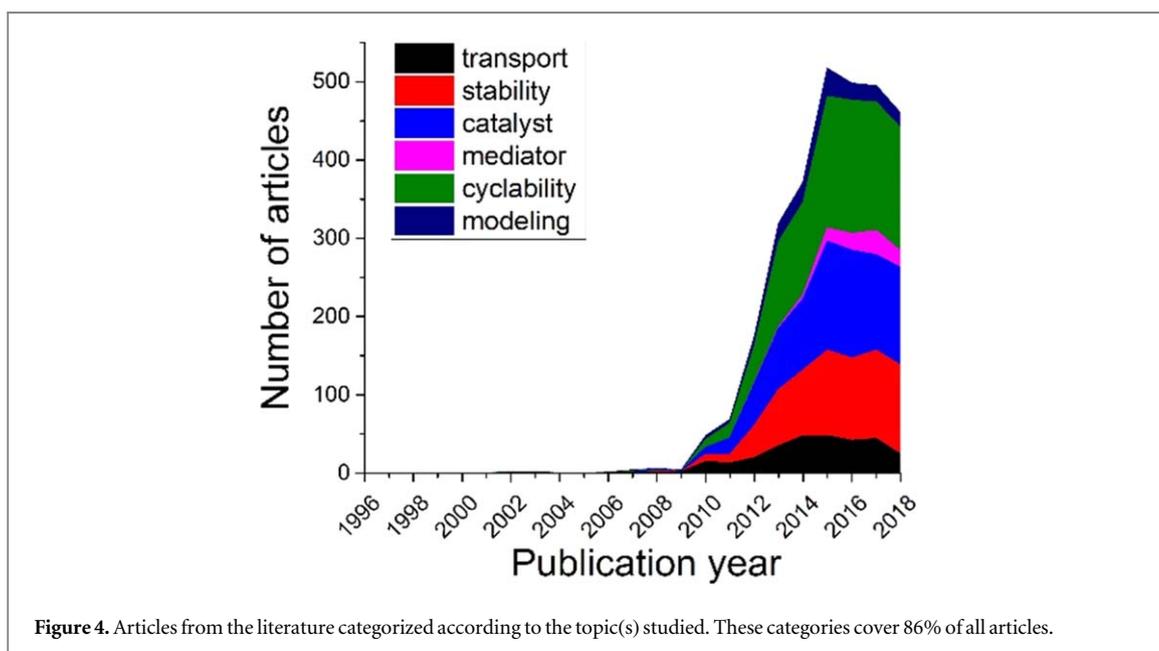
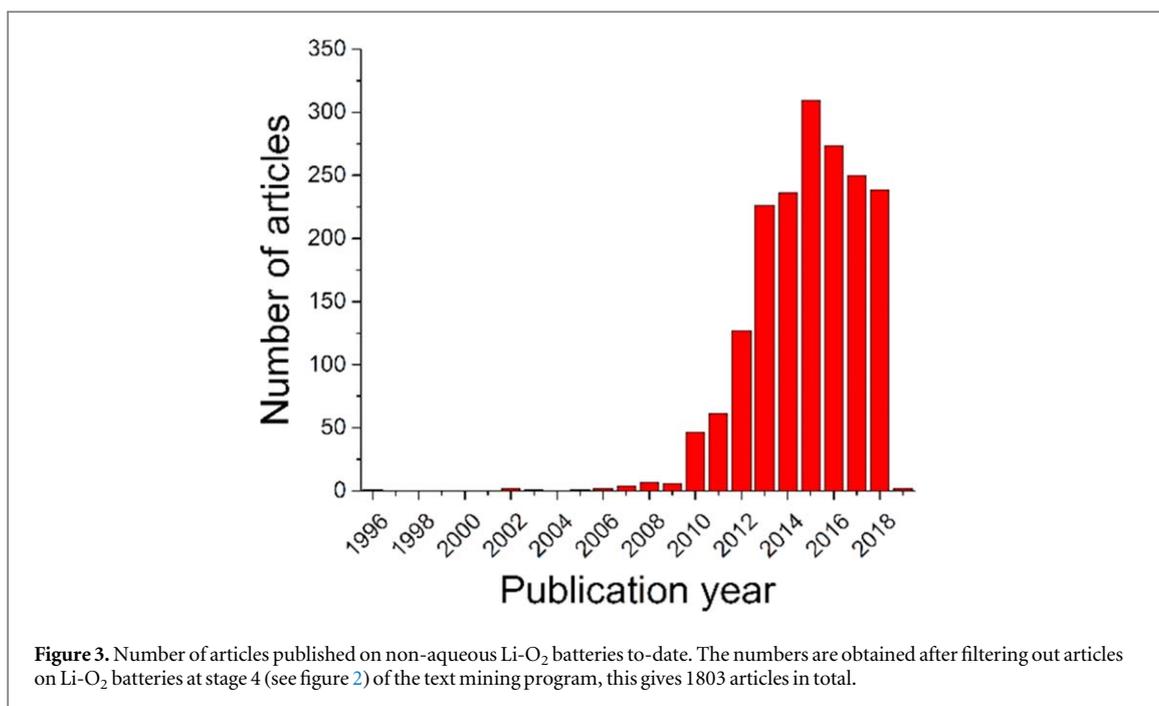
method, implemented in the NLTK library. We choose this method as it is fast and it can be trained on a small training set. Furthermore, we found it gives satisfactory results for the goal of our manuscript. The assumption of independent features in the Bayes theorem is a downside of this method. However, other classification techniques that includes the dependence of features such as the LSTM method (long short term memory, a class of recurrent neural networks) may require much larger training data sets than the ones than can be established from the specific field of Li-O<sub>2</sub> batteries. We used 200 Li-O<sub>2</sub> battery and 200 non-Li-O<sub>2</sub> battery articles as a training set for this algorithm.

Then the 1803 Li-O<sub>2</sub> articles preprocessed and filtered are passed to the fourth stage.

- (4) In this stage, we carry out the bibliometric analysis: we extract the publication year of the articles, the type of electrolytes used, the discharge capacities and other information described in the remainder of this article. When analyzing these articles, to figure out the focus of the study, the text mining program searches for the number of occurrences of some keywords in an article (for instance, for 'stability' it looks for the use of words such as *stability*, *stabilized*, *unstable* and its synonyms and antonyms such as *parasitic reaction*). If these keywords are used in an article more than ten times, then it is considered that the article studies that topic. For classifying the articles according to the electrolytes used, it is considered that the article studies an electrolyte if the electrolyte name appears more than 4 times in the text. These numbers of occurrences are optimized manually based on a training set consisting 50 articles, split as 25 articles in the correct class and 25 articles out of that class. Needless to say, an article can belong to several categories. For example if the authors study lithium and oxygen transport in porous electrodes through modeling [22], the article is counted in both *modeling* and *transport* categories. We would like to underline here that the topics are currently chosen by the user of the text mining program. In the future, it would be better if the text mining could identify key challenges on its own, for example using clustering techniques. This is however much more difficult to implement as, in an article, there are many words which are repeated more than ten times.

### 3. Results and discussion

The Scopus search introduced in figure 1 is commonly used to get a rough idea of the number of publications in a field but actually has many drawbacks. Indeed, when reading some of the search results, one quickly realizes that there are many documents not related with lithium oxygen batteries. To get a better estimation of the actual number of publications on non-aqueous Li-O<sub>2</sub> batteries, the whole search result was filtered manually by checking the title and abstract. As described in the Methodology section, this filtering can be done automatically on a set of PDF files if these are already downloaded; in our case we were limited by the journals' API systems.



The filtered group includes all the derivatives of non-aqueous Li-O<sub>2</sub> batteries such as Li-ion oxygen battery, Li-air battery, Li-O<sub>2</sub> flow battery, Li-O<sub>2</sub> batteries with trace amounts of water as an additive but not aqueous Li-O<sub>2</sub> batteries. Figure 3 shows the number of articles after the filtering, totaling 1803 articles. This collection of articles is much smaller than the 7323 initially extracted from the Scopus database. Actually, most of the articles shown in the Scopus search focus on oxide cathodes for Li-ion batteries, and some articles are on catalysts for oxygen reduction reaction in the context of fuel cells. Li-O<sub>2</sub> batteries are just cited in these articles as alternative energy related systems.

To get a clearer idea of the topics studied in the literature, the articles were categorized according to the aspect of a battery they study (figure 4). Such a classification gives a good indication of the main challenges faced in a specific field of research. While in this case the topics were chosen by the authors, they cover 86% of all articles which confirms the importance of these issues in the field of Li-O<sub>2</sub> batteries. This classification can make literature searching and reading much easier since one can automatically filter out documents studying a particular aspect of Li-O<sub>2</sub> batteries. It would be possible to help prioritise which articles should be read first by intersecting the articles dealing with different fields, e.g. ‘catalyst’ and ‘cyclability’ and ‘published after 2015’.

The article categories shown in figure 4 can be grouped into three main challenges of Li-O<sub>2</sub> batteries. The cyclability and stability categories are mainly focused on making the battery components stable and pointing out if any parasitic reactions and degradation process are occurring. The other three categories (transport, catalysts and mediators) are mainly related to the low practical discharge capacity and rate capability issues. These two challenges are not independent from each other, yet the use of mediators mainly affects the discharge capacity and the catalysts enhance the rate capability; the transport of reactants influences both discharge capacity and rate capability. In the following, we focus on these three challenging aspects of Li-O<sub>2</sub> batteries.

### 3.1. Stability and cyclability

For any type of secondary battery, stability is a key issue. To be used in a commercial application, a battery should be stable for at least several hundreds of discharge-charge cycles. Achieving this with Li-O<sub>2</sub> batteries remains extremely challenging.

In most systems, a Li anode is used to fully benefit from the high capacity of the air cathode. However, Li metal can react with the electrolyte and oxygen coming from the cathode side. Several researchers tried to design solid-state Li-O<sub>2</sub> batteries to tackle this issue [23, 24], but the solid state electrolyte brought more problems than it solved. Low ionic conductivity, poor interface wettability and large resistance are some of the problems encountered with solid-state Li-O<sub>2</sub> batteries. In addition, there are still parasitic reactions occurring in the cathode.

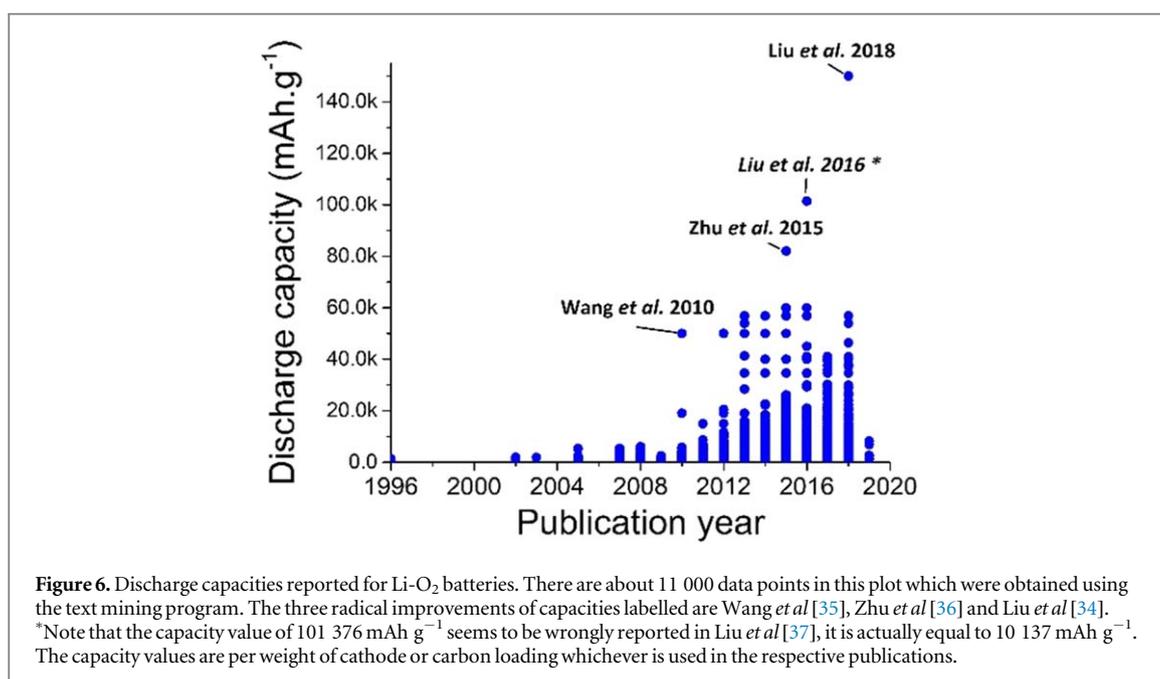
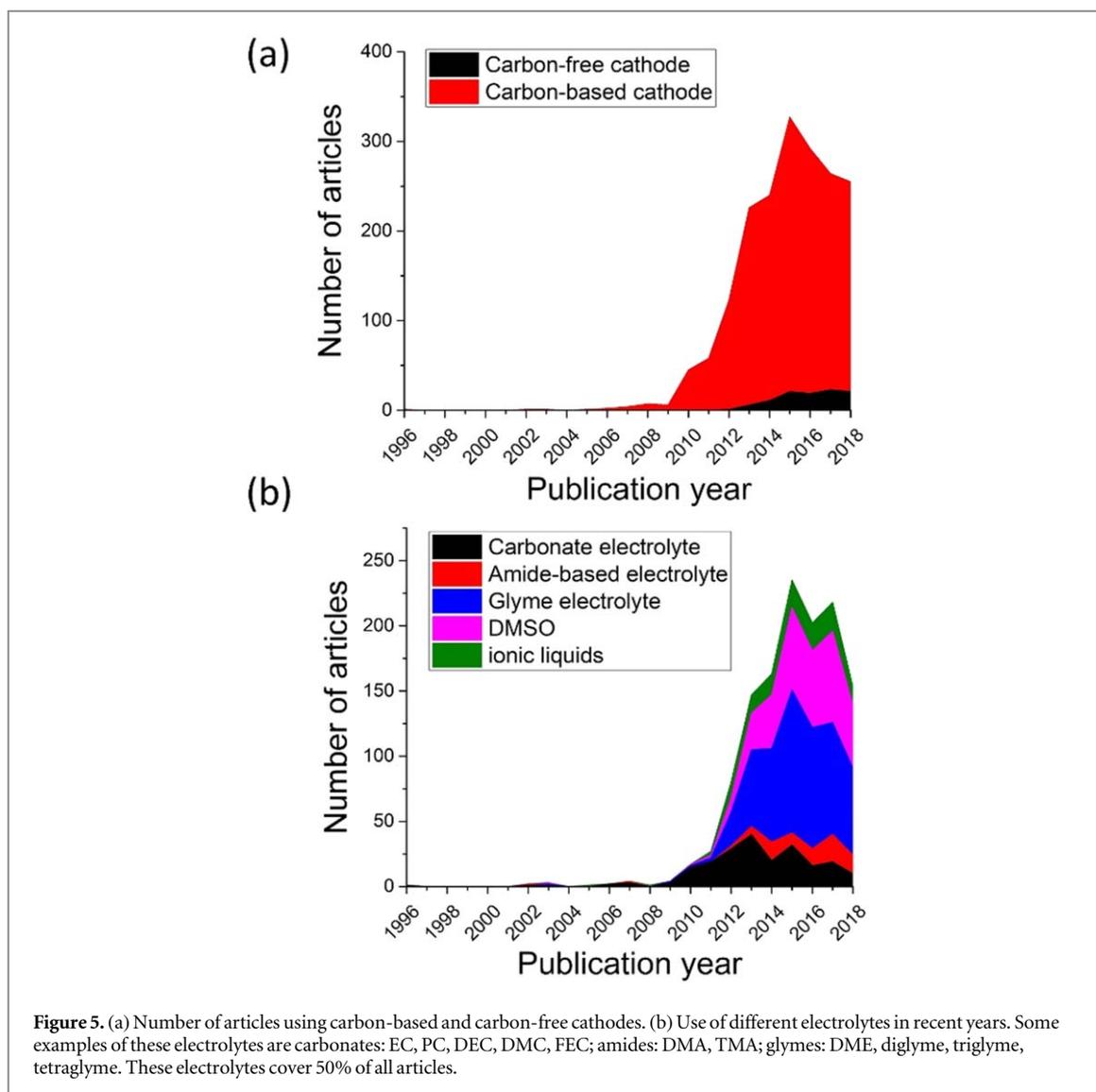
Li metal protection is another approach for increasing the stability. Kim *et al* coated the Li anode with a conductive polymer and AlF<sub>3</sub> particles and achieved an improved stability in line with a suppressed growth of dendrites on the anode [25]. As dendrites lead to short circuiting and end of the battery life, suppressing them is a good strategy to promote the stability of Li-O<sub>2</sub> batteries. Nevertheless, Kim *et al* still observe degradations of the electrolyte and cathode. Such degradations are difficult to avoid as the intermediate species in a Li-O<sub>2</sub> battery are quite reactive. The LiO<sub>2</sub><sup>\*</sup> radical can attack the electrolyte and the carbon cathode which leads to the formation of lithium carbonates. This was demonstrated by Leskes *et al* who studied the end of discharge products of a Li-O<sub>2</sub> battery using <sup>17</sup>O and <sup>13</sup>C solid state NMR spectroscopy [26]. They showed the formation of Li<sub>2</sub>CO<sub>3</sub> and small amounts of LiOH and HCO<sub>2</sub>Li side products. McCloskey *et al* also worked on this topic. They prepared a 99% <sup>13</sup>C labelled cathode and analyzed the CO<sub>2</sub> gas release during the battery operation by differential electrochemical mass spectrometry (DEMS). They could show that the electrolyte and carbon cathode both contribute in similar amounts to the CO<sub>2</sub> evolution [27]. There has also been some work on using more stable electrolytes and cathodes. Some carbon-free cathodes have been synthesized and tested [28], e.g. Cui *et al* grew Co<sub>3</sub>O<sub>4</sub> nanorods on Ni foam and reported discharge capacities above 4000 mAh g<sup>-1</sup>, with a good capacity retention [29].

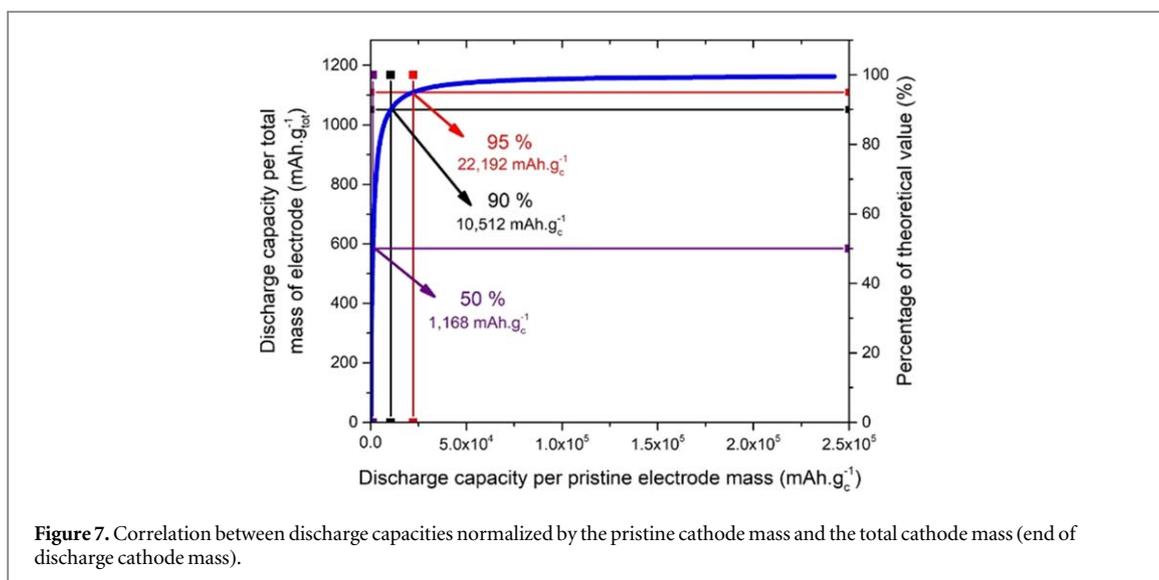
While the carbon cathodes are not the best in terms of stability, the scientific community seems to still prefer this alternative (figure 5(a)). This is mainly because of their low cost and easy production. Over the years, researchers have explored various carbon materials going from carbon blacks in the early times to nano-structured cathodes such as graphene based materials [30, 31] or templated electrodes [32] in more recent works.

Unlike the limited changes on the carbon cathode side, the Li-O<sub>2</sub> battery field has seen an evolution for the electrolytes. Figure 5(b) shows a classification of the text mined articles according to the electrolytes investigated. From this figure, it is clear that carbonate electrolytes, which were almost exclusively used until 2011, now represent a small fraction of the projects. In fact, the field moved to much more stable electrolytes such as ether, amide based electrolytes or ionic liquids. While the current text mining approach does not provide the reason for a loss of interest in carbonates, it provides a hint that there are limitations with such electrolytes which can then be confirmed by reading recent papers on the topic.

### 3.2. Low practical discharge capacity

Another problem of Li-O<sub>2</sub> batteries is the low practical capacity compared to the theoretical one. This low capacity is the result of two main aspects. The first one is the inefficient use of the pore volume, and the second one is the fact that the reaction rate is too slow for applying high discharge currents. We used our text mining program to extract capacities reported in the filtered set of 1803 papers, these values are given in figure 6. This graph clearly shows the recent progress in achieving higher and higher discharge capacities, starting from 1410 mAh g<sup>-1</sup> for Chevron acetylene black carbon electrodes with polyacrylonitrile-based polymer electrolyte discharged at 0.1 mA cm<sup>-2</sup> in the work of Abraham *et al* [33]. In 1996, to about 150 000 mAh g<sup>-1</sup> for reduced graphene oxide (rGO) electrodes with dimethoxyethane (DME) electrolyte with 10 mM of 2,5-di-tert-butyl-1,4-benzoquinone and 20 000 ppm of H<sub>2</sub>O electrolyte additives discharged at 0.1 mA cm<sup>-2</sup> in the work of Liu *et al* [34] in 2018. The text mining approach proposed here thus allows one to identify quickly the key breakthrough papers reporting the largest capacities achieved in the Li-O<sub>2</sub> batteries field. We note that a similar extraction





could be made for other relevant quantities such as the number of cycles, the discharge current or the material loading.

These capacity values might seem extremely large compared to the typical capacities obtained in Li-ion battery cathodes ( $150\text{--}400\text{ mAh g}^{-1}$ ) [38] and the  $1168\text{ mAh g}^{-1}$  theoretical capacity. In fact, one should pay attention to the common way in which the capacity in Li-O<sub>2</sub> battery is normalized in the literature. Typically, the gravimetric discharge capacity of a Li-ion battery is normalized by the mass of active material and any inactive components in the cathode such as the binder and the conductive carbon. However, for Li-O<sub>2</sub> batteries, the active material is oxygen which is eventually expected to come from air, even though at the development stage most researchers work with pure oxygen gas. Therefore, the gravimetric capacities are normalized by the mass of the pristine cathode (mass of the carbon in the cathode + mass of the binder if used) or sometimes just the mass of carbon in the cathode, which is the inactive part of the cell. In principle, the values should be normalized by the mass of the cathode at the end of discharge in order to compare them with Li-ion batteries capacities. In practice, this normalization is rarely adopted because of the difficulty to measure the mass of the cathode after discharge (presence of residual electrolyte, difficulty of detaching the cathode and the separator, etc...). Because of the normalization approach preferred by many, it is quite common to see reports of very large discharge capacities in the order of several tens of thousands  $\text{mAh g}^{-1}$  whereas the theoretical capacity for Li-O<sub>2</sub> batteries is  $1168\text{ mAh g}^{-1}\text{Li}_2\text{O}_2$ .

Using adequate metrics for measuring performances is important in order to optimize the systems, we would thus like to examine this in more detail here. When we assume that the only discharge product is Li<sub>2</sub>O<sub>2</sub>, there is a direct way to renormalize the capacity (equation (4)).

$$Q_{tot} = \frac{Q}{m_{tot}} = \frac{Q}{m_{\text{Li}_2\text{O}_2} + m_c}, \quad (1)$$

$$\frac{1}{Q_{tot}} = \frac{m_{\text{Li}_2\text{O}_2} + m_c}{Q} = \frac{m_{\text{Li}_2\text{O}_2}}{Q} + \frac{m_c}{Q}, \quad (2)$$

$$\frac{1}{Q_{tot}} = \frac{1}{Q_{\text{Li}_2\text{O}_2}} + \frac{1}{Q_c}, \quad (3)$$

$$Q_{tot} = \frac{1}{\frac{1}{Q_{\text{Li}_2\text{O}_2}} + \frac{1}{Q_c}}, \quad (4)$$

where  $m_c$  is the mass of the pristine cathode (carbon + binder),  $m_{\text{Li}_2\text{O}_2}$  is the mass of the produced Li<sub>2</sub>O<sub>2</sub>,  $m_{tot}$  is the total mass of the cathode ( $m_c + m_{\text{Li}_2\text{O}_2}$ ),  $Q_c$  is the capacity normalized by the pristine cathode mass,  $Q_{\text{Li}_2\text{O}_2}$  is the capacity normalized by the mass of Li<sub>2</sub>O<sub>2</sub> ( $1168\text{ mAh g}^{-1}$ ) and  $Q_{tot}$  is the capacity normalized by the total cathode mass.

Figure 7 shows the relation between the capacities normalized by the mass of the pristine cathode, which is the typical way used to report capacities, and the capacity normalized by the mass of the cathode at the end of discharge. If Li<sub>2</sub>O<sub>2</sub> is the only discharge product, then its mass can be inferred from the current measured through the electrochemical setup. With this renormalization, we see that, indeed, the capacity normalized by

the mass at the end of discharge does not exceed the theoretical capacity. We also notice that, interestingly, above 20 000 mAh g<sup>-1</sup> for the typical normalization, the capacities normalized by the mass at the end of discharge do not change much. Finally, one should keep in mind that it is the values normalized by the mass of the cathode at the end of discharge which should be compared to Li-ion batteries. As such, the typical capacities obtained for Li-O<sub>2</sub> batteries are not orders of magnitude larger than the capacities of Li-ion batteries [39, 40].

We note here that our current text mining program does not identify the type of normalization used for the capacity. In general, clearer rules for reporting the properties of interest for a given type of system would make text mining processes easier.

Coming back to the capacity limiting phenomena, the inefficient use of the porous volume is related to the fact that Li<sub>2</sub>O<sub>2</sub> discharge products are not filling up all the pore volume in the electrode. This phenomenon is strongly linked to the electrode mesostructure and the size of the Li<sub>2</sub>O<sub>2</sub> discharge products. The insulating nature of Li<sub>2</sub>O<sub>2</sub> implies that electrochemical reactions cannot occur far from the cathode surface, unless a redox mediator is used.

There have been several works on studying the role of electrode mesostructure on the discharge capacity and which of its properties are the most important. Kuboki *et al* compared the performance of four carbon based electrodes, and realized that having large mesoporous volume will lead to high discharge capacities [41]. Meini *et al* have studied several carbon electrodes (Timcal Super C65, Vulcan XC72, Ketjen black EC600JD, Black Pearls 2000) and observed that the electrodes with larger carbon surface area (CSA) lead to large discharge capacities [42]. At other studies, where more than ten different electrode mesostructures are tested, neither the surface area, nor the pore volume turned out to be important, but the pore size was the key electrode parameter for achieving large discharge capacities [43, 44]. Torayev *et al* investigated the electrode mesostructure role using a pore network model, and showed that the relative importance of the electrode mesostructural parameters can alter depending on the type of discharge particle growth [45]. For instance, when there is formation of thin Li<sub>2</sub>O<sub>2</sub> films, then the CSA becomes an important parameter, or when there is formation of large discharge particles, then the pore size plays a capacity determining role.

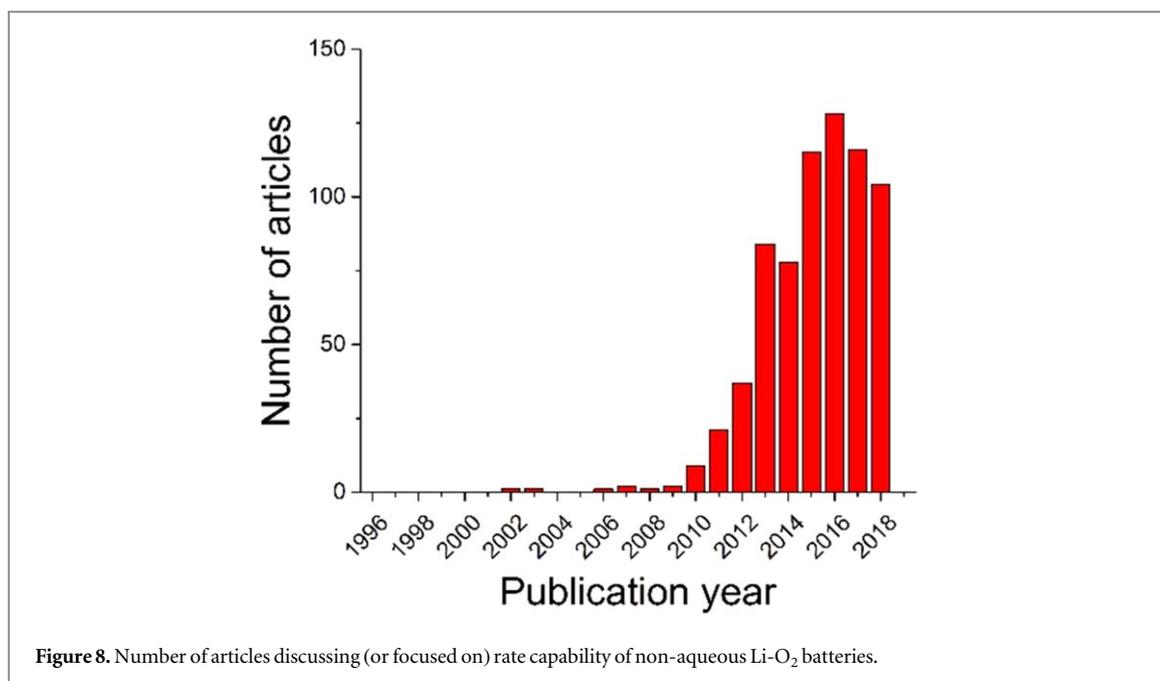
Several new electrode architectures have been designed and studied to enhance the Li-O<sub>2</sub> battery capacity such as carbon aerogels [46], graphene based electrodes [44, 47] and carbon nanotubes [48].

Along with testing new electrode designs, there is another approach to use the pore volume more efficiently, which is preferentially growing large discharge particles. The growth of discharge products follows several steps. After the initial nucleation of a Li<sub>2</sub>O<sub>2</sub> particle, the particle can grow through both electrochemical and chemical reactions.

The growth of a Li<sub>2</sub>O<sub>2</sub> particle follows a combination of electrochemical and chemical reactions. Once a nuclei is formed, when its size is small, the particle can grow through electrochemical reactions, taking up electrons from the carbon support. However, once the particle reaches a certain size, the insulating nature of Li<sub>2</sub>O<sub>2</sub> hinders the electron transport and the electrochemical growth. The growth of the particle beyond this size depends heavily on the chemical route, which includes electrochemical reactions such as formation of LiO<sub>2</sub> [49]. In this so called chemical route, O<sub>2</sub> and Li<sup>+</sup> react and form LiO<sub>2</sub> close to the cathode surface where charge transfer can occur. The lithium superoxide then dissolves in the electrolyte and consequently adsorbs on Li<sub>2</sub>O<sub>2</sub> particles. The adsorbed LiO<sub>2</sub> can disproportionate and form Li<sub>2</sub>O<sub>2</sub>, leading to the particle growth.

The relative importance of this solution growth mechanism with respect to the film growth or the end of discharge strongly depends on the solubility and stability of LiO<sub>2</sub> in the electrolyte. Laoire *et al* showed for the first time the role of the solvent properties, particularly the donor number (DN), and its stabilization effect on dissolved lithium superoxide [50]. High DN solvents stabilize the lithium superoxide molecules in the electrolyte and facilitate the growth of large particles. Johnson *et al* investigated four solvents, 1-methylimidazole (Me-Im), dimethyl sulfoxide (DMSO), DME, acetonitrile, with different DNs and proposed a model mechanism for the discharge particle growth [51]. They showed that high DN solvents (Me-Im and DMSO) give much higher capacities than the low DN solvents (DME, acetonitrile). The solution mechanism occurring in high-DN solvents would delay the surface passivation mechanism.

Another way of growing large discharge particles is to use redox mediators. Lacey *et al* introduced this concept by using a 1 mM concentration of ethyl viologen ditriflate in their electrolyte and showing the viologen-promoted formation of Li<sub>2</sub>O<sub>2</sub> [52]. Since 2012 there has been a growing interest in using redox mediators to promote formation of large discharge products (figure 4). There were about 98 articles published on mediators in the last 7 years, including review articles discussing it. Several mediators have been tested and demonstrated to promote the solution mechanism. For example, Lim *et al* analyzed several redox mediators including tetrathiafulvalene, N,N,N',N'-tetramethyl-p-phenylenediamine and lithium iodide [53]. Gao *et al* showed that using 2,5-di-tert-butyl-1,4-benzoquinone, the discharge capacity of gas diffusion layer electrodes can increase by one to two orders of magnitude [54]. Aetukuri *et al* and Liu *et al* reported that introducing trace amounts of H<sub>2</sub>O in the electrolyte results in larger Li<sub>2</sub>O<sub>2</sub> particle sizes and hence higher discharge capacities can be achieved [34, 55]. Liu *et al*



showed that using redox mediators coupled with trace amounts of water as additive can lead to Li<sub>2</sub>O<sub>2</sub> particles as large as 30  $\mu\text{m}$ .

### 3.3. Rate capability

The rate capability limitation, the second reason for low practical capacity, occurs when the reaction rate cannot keep up with the discharge current. Improving the rate capability has been one of the most studied aspect of Li-O<sub>2</sub> batteries (figure 8).

To understand this limitation, it is useful to write down the net current equation in its general form

$$J = nFAk \left[ C_{\text{Ox}} e^{\frac{-\beta nF(U-U_0)}{RT}} - C_{\text{Red}} e^{\frac{(1-\beta)nF(U-U_0)}{RT}} \right], \quad (5)$$

where  $J$  is the net current,  $n$  is the number of electrons exchanged in the electrochemical reaction,  $F$  is the Faraday constant,  $A$  is the active cathode surface area,  $k$  is the reaction rate constant,  $C_{\text{Ox}}$  and  $C_{\text{Red}}$  are the concentrations of the oxidized and reduced species respectively,  $\beta$  is the charge transfer coefficient,  $U$  is the electrostatic potential of the electrode,  $U_0$  is the standard potential of the reaction,  $R$  is the gas constant and  $T$  is the temperature. From equation, it is clear that three parameters can affect the current: the active surface area, the reaction rate constant and the concentration of reactants.

The role of the active surface area on the rate capability can be quite significant. Along the discharge of a Li-O<sub>2</sub> cell, the active cathode surface area can be progressively reduced by the formation of solid discharge products on the cathode surface. This effect is not significant at low current densities because at slow discharge the discharge products grow as large particles [56]. As such, they do not cover large areas of the cathode surface. However, when the discharge current density is increased, there is a preferential formation of Li<sub>2</sub>O<sub>2</sub> as small discharge particles or as a thin film. This leads to a coverage of larger amounts of the cathode surface area per volume of discharge product. The relation between the discharge product size and the current density has been studied in the work of Adams *et al* [57]. They show that increasing the discharge current leads to a decrease in the discharge product size. Discharging at high currents gives less time for LiO<sub>2</sub> intermediates to dissolve in the electrolyte and contribute to the growth of large particles. The higher overpotential occurring at higher currents also leads to the fast reduction of LiO<sub>2</sub> into Li<sub>2</sub>O<sub>2</sub> and hence the formation of smaller discharge products. The effect of the active surface area on the rate capability can be reduced by using electrolytes that favor large discharge product formation such as electrolytes with additives and mediators as explained previously.

Apart from acting on the active surface area or promoting the solution phase mechanism, one can try to increase the reaction rate constant in order to be able to apply larger currents. The reaction rate constant is a function of the activation energy [58], which can in principle be lowered by oxygen reduction reaction catalysts. Since the early years of Li-O<sub>2</sub> batteries, there has been an avalanche of articles on catalysts (figure 4). Wu *et al* compared discharge capacities of electrodes: Ketjen Black (KB) electrode without a catalyst, carbon electrode with platinum catalyst, KB electrode with pyridinic nitrogen–cobalt catalysts and multi-walled-nanotubes electrode with pyridinic nitrogen–cobalt catalysts [59]. They observed that the multi-walled-nanotubes

electrode containing the pyridinic nitrogen–cobalt catalysts gave the highest discharge capacity,  $\sim 3700 \text{ mAh g}^{-1}$  among all. Rate capability tests with a discharge current increasing from 50 to  $800 \text{ mA g}^{-1}$  also showed an improved rate capability. In particular, the discharge capacity of this electrode at  $800 \text{ mA g}^{-1}$  provides a discharge capacity similar to the KB electrode at  $50 \text{ mA g}^{-1}$ . Lim *et al* reported that adding a  $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$  catalyst into the KB electrode increases the discharge capacity of the cell by three times [60].

While catalysts are shown to improve the discharge capacities, there is a risk that they also catalyze parasitic reactions. McCloskey *et al* measured  $\text{O}_2$  and  $\text{CO}_2$  gas emissions with DEMS on charge for cells with carbon electrodes without any catalyst, and with gold,  $\text{MnO}_2$  and platinum catalysts [61]. They observed that the electrodes with catalysts released less oxygen and much more carbon dioxide than the electrode without any catalyst. This work clearly shows that catalysts foster parasitic reactions, probably involving the decomposition of some cell components, when present.

The last factor contributing to poor rate capability is the lack of reactants. The two primary reactants in a Li- $\text{O}_2$  battery are  $\text{Li}^+$  and  $\text{O}_2$ . The concentration of  $\text{Li}^+$  ions can be modified easily by changing the amount of lithium salt added into the electrolyte. The typical range of lithium salt concentration is between 0.1 and 1 M. The concentration of oxygen is much more difficult to change and strongly depends on the electrolyte solvent. Typical oxygen solubilities in commonly used electrolytes are just a few milli-molars, e.g. 2.10 mM, 4.43 mM and 9.57 mM for DMSO, tetraglyme and DME respectively [50]. Because of this low oxygen concentration, about two orders of magnitude lower than the lithium ion concentration, oxygen is the limiting reactant. There are two ways of tackling this issue.

The first way is to increase the solubility of oxygen in the electrolyte by using electrolytes that have a high oxygen solubility. For instance, triglyme has a superior oxygen solubility compared to tetraglyme, and Wu *et al* have observed a better performance for the triglyme based electrolyte [62, 63]. Chen *et al* used octamethylcyclotetrasiloxane as an additive to tetraglyme-based electrolyte [64]. They showed that by increasing the additive content from 0 to 10 volume percent, the oxygen solubility, the discharge capacity and the capacity retention improved. However, this way of improvement is quite challenging since changing the electrolyte can generate stability and reaction rate issues.

The second way is to increase oxygen diffusion. This can be done by moving to electrolytes that have high oxygen diffusion coefficients or by choosing electrode mesostructures with lower tortuosities. Modifying the electrode mesostructure is probably a less risky approach since it does not change the whole electrochemistry of the system. When using carbon materials, we can prepare cathodes with a very large variety of mesostructures. The number of papers working on this approach can be seen in the *transport* category of figure 4. As described previously, electrodes can be tailored towards achieving some target property, e.g. a high surface area [65, 66] or large pores [67], or synthesized in a more controlled fashion to obtain templated electrodes with specific mesostructures [44, 68].

## 4. Conclusions

In this review article, we analyzed the Li- $\text{O}_2$  battery literature via an *in house* developed text mining program. The program was written using the R and Python programming languages and the pdftools and NLTK libraries. We carried out an analysis of over 1,803 articles, which we believe cover almost all the articles published about Li- $\text{O}_2$  batteries in English language.

The text mining results show a shift from carbonate based electrolytes towards glymes and DMSO. The analysis also demonstrates that a large portion of the literature is focused on cyclability, stability and catalysis. We pointed out several studies trying to tackle these key limitations of Li- $\text{O}_2$  batteries. To improve the stability of these batteries, solid-state electrolytes, Li-metal anode coating, and non-carbon cathode materials have been tested. The low practical capacity is partly overcome by favoring the growth of large discharge products, either by selecting specific electrolytes or by adding redox mediators to common electrolytes. Improving the electrode architecture also helps to increase the discharge capacity. The low rate capability is partly mitigated using specific electrode designs and electrolytes with higher oxygen solubility and diffusion.

Regarding the biases related to writers who are not native English speakers, we believe that we deal with this to some extent by checking for several words for each of the topics. As a final comment, we would like to underline that our semi-automated approach still involves a relatively large input from the user as our study included manual filtering and the choice of topics for the classification of the articles. With the improvement of text mining algorithms and the move towards open access articles, more automated approaches should be available soon. Such tools will be very valuable for researchers who want to keep track of the state of the art in various fields.

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