Short communication

Influence of the cathode porosity on the discharge performance of the lithium–oxygen battery

S. Reza Younesi [*], Sigita Urbonaite [1], Fredrik Björefors, Kristina Edström

Department of Materials Chemistry, The Ångström Laboratory, Uppsala University, Box 538, SE-75121 Uppsala, Sweden

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ABSTRACT

By varying the ratio between the amount of carbon and Kynar binder in the cathode of a lithium–oxygen battery, it could be shown that an increasing amount of binder resulted in a decrease in the discharge capacity, mainly as a result of the decrease in the cathode porosity. It was shown that the Kynar binder blocked the majority of the pores with a width below 300 Å as determined by studying the pore volume and pore size distribution by nitrogen adsorption. Three carbonate based electrolytes (PC, PC:DEC (1:1), and EC:DEC (2:1) with 1 M LiPF$_6$) were tested with the various cathode film compositions. Generally, the PC:DEC and EC:DEC based electrolytes provided higher capacities than PC. The results indicated that the air electrode composition and its effect on the porosity of the cathode, as well as electrolyte properties, are important when optimizing the discharge capacity.

1. Introduction

The lithium–oxygen (Li–O$_2$) battery (often referred as lithium–air (Li–air)) is a very attractive energy storage system because of its active cathode material – oxygen – which is not present in the cathode but continuously taken from the surrounding [1,2]. This results in a battery with higher energy density, well beyond that of common lithium-ion batteries. Reversibility of a Li–air battery with a high theoretical specific energy density of 11.5 kWh kg^{-1} excluding oxygen, and 5.2 kWh kg^{-1} including oxygen, was first identified by Abraham and Jiang [3]. The whole research area attracted a renewed interest when it was shown that a Li–O$_2$ battery could be cycled at least 50 times [4]. However, despite the advantage of superior energy density, Li–air batteries are still in the early stage of their development. Still, many different aspects of this complex system need to be studied in detail.

Two main types of Li–air batteries are recognized based on the choice of electrolyte; aqueous and non-aqueous. One of the most important differences is the solubility of the reaction products during the discharge, which are soluble in water based electrolytes while regarded insoluble in organic ones. In the Li–O$_2$ battery with an organic electrolyte, the discharge reaction products, commonly considered to be lithium oxides (Li$_2$O$_2$ and Li$_2$O), need space in the cathode part to be accommodated [3]. Several studies have paid

attention to the porosity of the air electrode and have identified a number of favourable factors for an improved capacity [5–14]. It has been concluded that the porosity of the carbon itself [5–14], the electrode thickness [6,7,12], and the carbon loading [6,15] influence the performance and discharge capacity. The amount of the electrolyte in the air electrode [6] and wetability of the electrolyte [7] also have been reported as important parameters. Today, it is mostly agreed that the surface area of the carbon is not the only parameter to affect the capacity of the Li–air battery as earlier suggested. The surface area has lately also been considered in combination with the pore size distribution (PSD) and pore volume in the cathode. Kuboki et al. [5] demonstrated that the mesopore volume of carbon, not the surface area, was the main parameter affecting the discharge capacity. Xiao et al. [6] also showed that the discharge capacity of a Li–air battery was affected by the mesopore volume of carbon. The relation between the discharge capacity, the carbon loading and the electrode thickness was also discussed. Read [7] studied different types of carbon black with a number of electrolytes and suggested that the discharge capacity was related to the surface area wetted by electrolyte, not to the total surface area of the carbon. Mirzaeian et al. [8] further reported that a carbon with higher pore volume and larger pore diameter increased the discharge capacity. Yang et al. [9] also confirmed that the surface area was not the only parameter affecting the discharge capacity. According to their results, Super P, as an example, with a small surface area possessed higher capacity compared to some other carbons with higher surface area. Finally, Tran et al. showed [10] that the capacity of the air electrode depended on the surface area of large pores, not the surface area of all pores. They concluded that the micropores and some parts of the mesopores did not play a

* Corresponding author. Tel.: +46 18 471 3769; fax: +46 18 513548.
  E-mail address: reza.younesi@mkem.uu.se (S.R. Younesi).
[1] Present address: Electrochemistry Laboratory, Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland.

large role to increase the capacity because they would be blocked by products produced during the discharge reaction.

Despite the fact that the influence of the carbon surface area, pore volume, and PSD on the capacity of the Li–air battery have been studied before, there has not been any systematic study on the impact of these on cast cathode films. It is plausible to expect that also the polymeric binder can have an impact on the porosity by blocking pores in the carbon particles. The pore volume of the cast cathode film is both originated from the pores of the carbon particles and from the pores formed when carbon particles stick to carbon or to Kynar. This study was performed to investigate how the carbon to binder ratio changes the morphology, surface area, pore volume, and PSD of the cathode, and how this affect the discharge capacity of the Li–O_2 battery. The comparison between the different cathode films was established by using scanning electron microscopy (SEM), gas adsorption, and electrochemical experiments in combination with three carbonate based electrolytes.

2. Experimental

Porous cathode films were produced by casting slurries consisting of the carbon Super P (Lithium battery grade, Erachem Comilog) as active material and Kynar 2801 (Arkema) as binder, using propylene carbonate (PC) as plasticizer. All thicknesses of the prepared cathode films were similar (~40 μm), enabling their comparison. All films were processed as self-standing cast films. Battery cells with four different carbon to Kynar weight ratios using three different electrolytes were tested. Propylene carbonate (PC), ethylene carbonate (EC), and diethyl carbonate (DEC) were used as solvents in the electrolytes, also containing 1 M $LiPF_6$ (Ferro). All the solvents were purchased from Ferro, Purolyte®. $LiPF_6$ was dried at 60 °C over night in a vacuum furnace within an Argon-filled glove box (H_2O and O_2 < 1 ppm) before the electrolyte preparation. The water content in the electrolyte was <10 ppm as measured via Karl Fischer titration. A typical Li–O_2 battery was assembled in a glove box using the Swagelok^{TM} configuration with an opening allowing oxygen to access the cell. Lithium foil was used as the negative electrode, and glass–fibre (Whatman) as the separator. The cells were connected to a Digatron BTS-600 and cycled at 30 °C with a current density of 80 mA g^{-1} of carbon with a lower cut-off voltage of 1.2 V.

Gas adsorption experiments were performed on a Micromeritics ASAP 2020 surface area and porosity analyzer equipped with the ASAP 2020 V3.04 E software. The samples were first degassed for at least 2 h and then analyzed at 77 K using nitrogen gas. The morphologies of the electrodes were examined by a scanning electron microscope (SEM) LEO 1550 operated at 10 kV.

3. Results and discussion

Cathodes with four different carbon to Kynar ratios were evaluated to study the influence of the amount of Kynar binder on the discharge performance of the lithium–oxygen battery. Based on the composition, the electrodes displayed different capacities, as shown in Fig. 1. The discharge capacity of the Li–O_2 cell was founded to be increased by increasing the carbon to Kynar ratio. For example, the battery with a carbon content of 80% (20% Kynar) gave a discharge capacity (per gram of carbon) about four times higher than that with a carbon content of 20% or 40%.

The results encouraged us to further study the influence of the Kynar amount on the cathode porosity. Solid precipitates formed during the discharge need to be accommodated within the cathode structure, and it is presumed that a higher degree of porosity would increase the capacity of the battery. SEM micrographs of the cathode films with different ratios of carbon–Kynar showed that
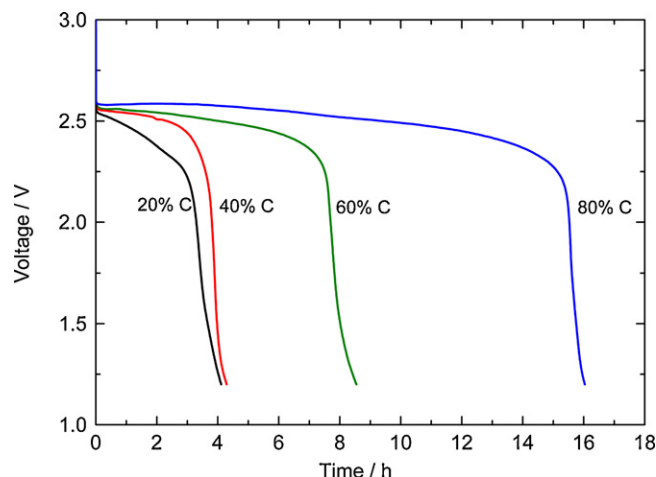

Fig. 1. Discharge profiles of the Li–O_2 cells with 1 M $LiPF_6$ in PC and different ratios of carbon–Kynar in the cathode. The current density was 80 mA g^{-1} of carbon.

for films with higher Kynar-content, the polymeric part of the film was dominating and the majority the carbon particles were more isolated from the ambient. The films with carbon to Kynar ratios of 80:20 and 60:40 were the most homogeneous as can be observed in the SEM micrographs with a lower magnification (Fig. 2a and b). They were also the most porous which can be seen at higher magnifications (Fig. 2a and b). Therefore, the electrodes with the lowest amount of binder represent the best available reaction sites to the lithium ions and to the oxygen since the polymeric coverage of the Kynar is low.

Gas adsorption was further used to find out how the different ratios between carbon and binder influenced the surface area, pore volume, and PSD of the cathode film. The gas adsorption experiments showed that the surface area and pore volume of the cathode films increased with increasing amount of carbon, which means that fewer pores were blocked by the binder (see Fig. 3). Comparing the gas adsorption results of the cast films with those of pure Super P carbon powder, it is obvious that even an addition of as low content as 20% of Kynar reduced the surface area and pore volume of Super P carbon by about 30% and 20%, respectively. Hence, both the morphology and the porosity investigations confirmed the hypothesis that more and more surface of the carbon was covered by the polymeric binder with increasing amounts of Kynar in the cast cathode films, and that this was significantly reducing the surface area and the pore volume.

The influence of the pore size of the carbon in the cathode film is important for the discharge capacity. The blockage of the pores is attributed to the discharge product deposition [9,10], the contact between carbon and catalyst [16], or the excess of electrolyte [17], but the role of the binder on the blockage of the pores when the cathode is cast, has not yet been considered. To investigate the Kynar effect on the blockage of the pores, also the pore size distribution of the Super P carbon powder and of the cathode films were evaluated (Fig. 4). The results indicated that the binder blocked the majority of the pores below 300 Å when the amount of Kynar exceeded 40%. It was also obvious that the addition of even 20% of Kynar to Super P carbon reduced the pore volume significantly. The unchanged peak positions in the PSD plot also suggested that the porosity is originated from the carbon only, while Kynar is non-porous.

Keeping the same cathode compositions, Li–O_2 batteries with two other electrolytes were assembled to investigate if these influence the discharge capacity as well. PC:DEC (1:1) and EC:DEC (2:1) based batteries with cathode films with 60% carbon obtained capacities which were significantly higher than the capacity achieved
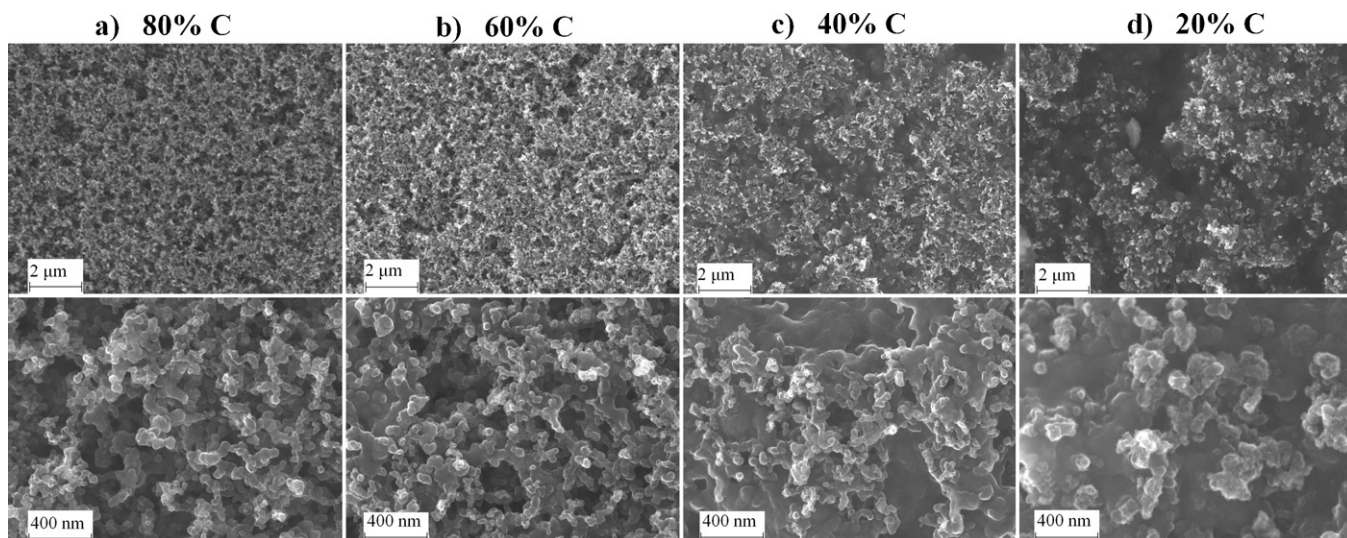
Fig. 2. SEM micrographs of the cathode films with four different carbon to Kynar ratios at two different magnifications: (a) 80:20, (b) 60:40, (c) 40:60, and (d) 20:80 carbon:Kynar, respectively.
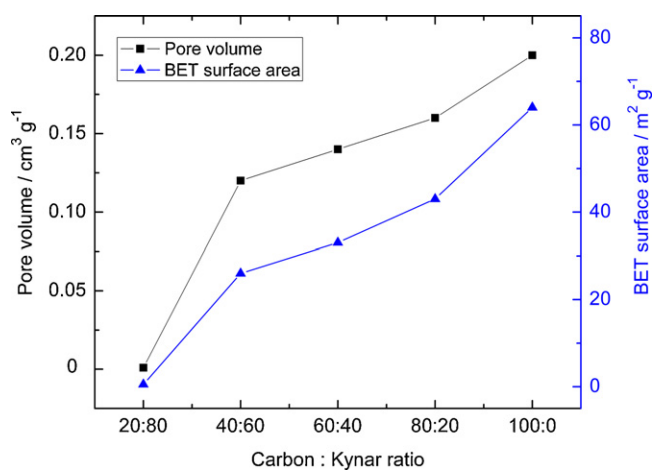

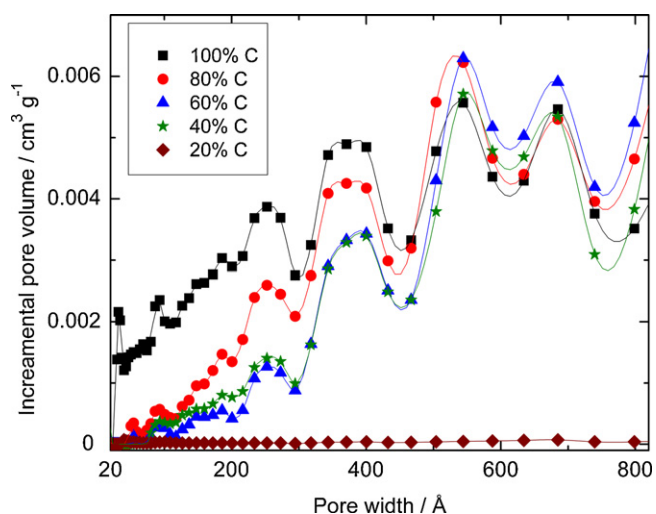**Fig. 3.** Pore volume and BET surface area of Super P carbon and cathode films with varying ratios of carbon–Kynar.

with PC as the solvent (Fig. 5). There were also small changes in the discharge voltage of the batteries with solvents variation. The discharge profiles for the other cathode compositions also showed similar small changes in the discharge voltage. Related to this, there are recent studies of the Li–O$_2$ battery concerned with the electrochemical stability of electrolytes during the discharge and charge reactions. Mizunio et al. [18] reported that carbonate-based solvents decomposed during the discharge reaction. Similar results were also published by Xu et al. [19] and Freunberger [20]. They showed that irreversible species were produced during the discharge due to decomposition of the carbonate-based electrolytes. Furthermore, it has also been reported that the PC:DEC solvent can react with the discharge products [7,21]. For Li–O$_2$ batteries, current density [22–24], type of catalyst [25–27], and electrolyte additives [28] are often mentioned as parameters influencing charge–discharge voltages, but since these are constant in our experiments, differences in the discharge voltages might be a result of electrolyte side reactions.

As the capacities of the cells with 60% carbon differed between the three electrolytes, the electrochemical performance of the cathode films with different carbon to Kynar ratios (specified in Fig. 1) was also evaluated with the PC:DEC and EC:DEC solvents. Elec-
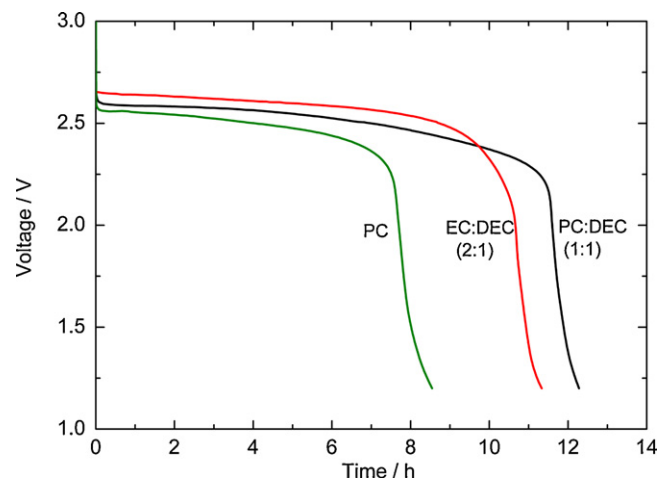

Fig. 4. PSD of Super P carbon and cathodes films with varying ratios of carbon–Kynar.

Fig. 5. Discharge profiles from Li–O$_2$ cells with 60% carbon in the cathode and 1 M LiPF$_6$ in PC, PC:DEC (1:1), and EC:DEC (2:1) solvents.
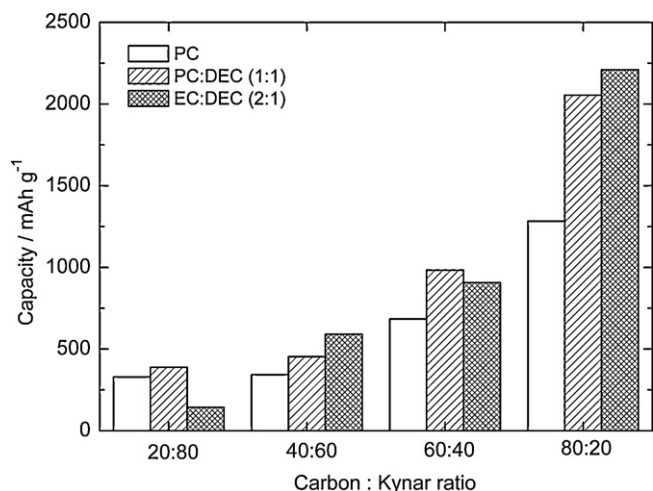
Fig. 6. Capacity as a function of the composition of the cathode and the electrolyte.

trolyte properties like oxygen solubility, diffusion coefficient of oxygen, viscosity, conductivity, types of ion conducting salt, and other parameters influencing the carbon–electrolyte interactions are very important for Li–air and Li–O_2 batteries as they can influence the capacity and discharge rate [7,21,29,30]. In this study, the electrolyte salt 1 M $LiPF_6$ was the same in all electrolytes and only the solvents were varied. Today, the PC and EC:DEC solvent are commonly used in Li–air and Li-ion batteries and that is why we chose these two solvents for the experiments.

As expected, the battery capacity increased with higher amounts of carbon in the cathode films also for the two new electrolytes, as can be seen in Fig. 6. In general, the highest capacities were obtained for the EC:DEC and PC:DEC based electrolytes. With lower amounts of carbon in the cathode films, these differences were less pronounced. However, the PC based electrolyte, often used for the Li–O_2 battery, showed the poorest performance irrespective of the electrode composition. The fact that the PC based electrolyte performs worse than PC:DEC (1:1) and EC:DEC (2:1) might be attributed to the lower conductivity [21,31]. It is also known that PC has a relatively high viscosity. It was shown by Read [21] that the viscosity of PC was decreased by mixing it with other carbonate base solvents like DEC, EC etc., and as a result the discharge capacity of the cell was increased. Thus, the electrochemical testing performed in this work showed the importance of the electrolyte properties and the air electrode porosity, and proved that a Li–O_2 battery performance is improved by employing cathode films with higher porosity.

4. Conclusions

Cathodes with varying carbon–Kynar ratios in combination with three different carbonate based electrolytes were studied to evaluate their influence on the Li–O_2 battery performance. Gas adsorption results confirmed that introduction of Kynar for the cathode films formation affects the carbon porosity by blocking smaller pores (below ~300 Å), and that by increasing the amount of

Kynar, the surface area and pore volume of the cathode were significantly decreased. Moreover, this was accompanied with a drastic drop of the battery capacity. Employment of a PC based electrolyte resulted in a lower capacity compared to the two other electrolytes based on EC:DEC (2:1) and PC:DEC (1:1), and this was especially pronounced for carbon rich cathode compositions. A similar study to this presented here can also be applied to electrodes containing catalyst for the rechargeable Li–O_2 battery to find out how Kynar will influence the porosity of the catalyst. Finally, mesoporous carbons with pore sizes larger than 300 Å can be considered as an approach to increase the discharge capacity.

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