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Using polyoxometalates to enhance the capacity of lithium-oxygen batteries

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The Keggin-type polyoxometalate α-$SiW_{12}O_{40}^{4-}$ increases the discharge capacity and potential of lithium-oxygen batteries, by facilitating the reduction of O_2 to Li_2O_2, as confirmed by in-situ electrochemical pressure measurements and XRD. Compared to organic redox mediators, polyoxometalates have higher chemical and structural stability, which could lead to longer cycling lithium-oxygen batteries.

Lithium-oxygen batteries have been studied intensively in recent years due to their very high theoretical specific energy, which makes them a promising contender for the post lithium-ion high energy rechargeable battery[1–10]. One of the most important improvements in the practical performance of lithium-oxygen batteries has been achieved via the incorporation of redox mediators. During discharge, redox mediators have been used to enhance the discharge capacity and increase the discharge voltage[11–23]. The discharge reaction of nonaqueous lithium-oxygen batteries involves the reduction of O_2 to form Li_2O_2, and redox mediators enhance the discharge capacity by facilitating the formation of Li_2O_2 away from the electrode surface, thus mitigating the problem of electrode passivation by deposition of Li_2O_2 which leads to an early end of discharge. A simplified reaction mechanism of the discharge reaction in the presence of redox mediators can be written as follows:

$$\mathrm{Ox} + e^- \rightarrow \mathrm{R} \quad (1)$$

$$2\mathrm{R} + O_2 + 2Li^+ \rightarrow Li_2O_2 + 2\mathrm{Ox} \quad (2)$$

where Ox, R are the oxidised and reduced forms of the redox mediator. The redox mediator is reduced at the electrode surface (reaction 1), after which, the reduced form of the redox mediator can diffuse away from the electrode surface and then react with O_2 producing Li_2O_2 as the discharge product and regenerating the oxidised form of the redox mediator (reaction 2). Similarly, on charge, redox mediators facilitate the oxidation of Li_2O_2 via the chemical reaction of the oxidised form of the redox mediator with Li_2O_2, thus increasing the charge capacity, the coulombic efficiency, voltage efficiency and capacity retention with cycling[24–36].

Redox mediators have also been applied successfully to suppress degradation reactions in lithium-oxygen batteries[13–15], which has been attributed to the alteration of the reaction pathway to bypass the formation or decrease the lifetime of problematic reaction intermediates such as superoxide. Other solution additives such as water or hydrogen donor species have also been used to achieve remarkable reduction in degradation reactions and enhanced capacities[17,37–45].

In this work, a new type of redox mediator is explored: polyoxometalates, which are inorganic polyanions with multiple redox states. Although polyoxometalates have been extensively used as redox mediators in a variety of systems[46–56], this is the first study in which polyoxometalates are used in lithium-oxygen batteries. We show here that the Keggin-type anion α-$SiW_{12}O_{40}^{4-}$ is an effective mediator of the discharge reaction of lithium-oxygen batteries. α-$SiW_{12}O_{40}^{4-}$ has been selected for this study for the following reasons:

- The reduction of α-$SiW_{12}O_{40}^{4-}$ to α-$SiW_{12}O_{40}^{5-}$ takes place at a potential close to 2.6 V vs. Li^+/Li, which is lower than the thermodynamic potential of O_2 reduction to Li_2O_2 of 2.96 V vs. Li^+/Li[57], and therefore, α-$SiW_{12}O_{40}^{5-}$ is reducing enough to chemically reduce O_2 to Li_2O_2 (reaction 2).
- Both α-$SiW_{12}O_{40}^{4-}$ and α-$SiW_{12}O_{40}^{5-}$ are highly stable, chemically and structurally, due to their high nuclearity and high strength of W-O bonds, and hence the extent of degradation during the highly oxidizing conditions of lithium-oxygen batteries is expected to be significantly lower than in the case of organic redox mediators[58,59].

Figure 1 shows the cyclic voltammogram of a glassy carbon electrode in the presence of α-$SiW_{12}O_{40}^{4-}$ (black curve). A reversible one-electron transfer process, corresponding to the formation of α-$SiW_{12}O_{40}^{5-}$, is observed in the chosen potential window, and additional processes are observed at lower potentials (see electronic supplementary information ESI, figure S1). The small peak to peak separation of the cathodic and anodic peaks (68 mV, figure S3) suggests fast electron transfer. In addition, electrolysis experiments in a thin layer cell (figure S4) confirm that, in the first reduction peak at ca. 2.6 V vs. Li^+/Li, one electron is consumed per α-$SiW_{12}O_{40}^{4-}$, thus forming α-$SiW_{12}O_{40}^{5-}$.

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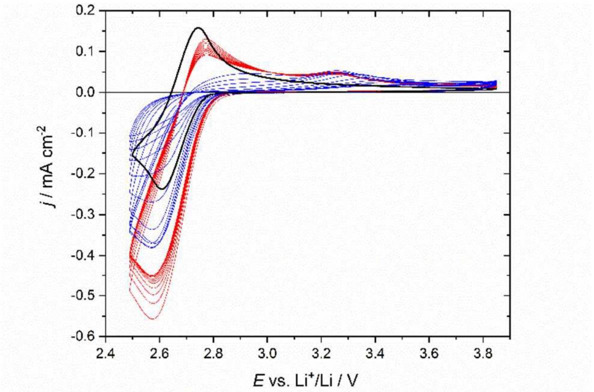

Figure 1: Cyclic voltammograms of a glassy carbon electrode in Ar saturated (black) and O_2 saturated (red) 10 mM $TBA_4SiW_{12}O_{40}$ with 1 M LiTFSI in DMSO and in O_2 saturated 1 M LiTFSI DMSO without $TBA_4SiW_{12}O_{40}$ (blue). Scan rate: 20 mV s^{-1}.

Figure 1 also shows that, in O_2 saturated solutions, in the absence of α-$SiW_{12}O_{40}^{4-}$ (blue curves), a reduction peak associated to the reduction of O_2 to Li_2O_2 is observed, in agreement with previous studies[60–62]. It has been shown that the process of O_2 reduction takes place via the formation of intermediate lithium superoxide species[63–65]:

$$O_2 + e^- + Li^+ \rightarrow LiO_2 \qquad (3)$$

$$LiO_2 + e^- + Li^+ \rightarrow Li_2O_2 \qquad (4)$$

$$2LiO_2 \rightarrow Li_2O_2 + O_2 \qquad (5)$$

Upon cycling, the magnitude of the current decreases markedly. This is because not all of the Li_2O_2 formed during reduction is oxidised back to O_2 during oxidation. Progressive accumulation of Li_2O_2 deposits at the electrode surface decreases the electrochemically active surface area, and after 10 cycles, the current has decreased by ca. 66%.

In O_2 saturated solutions containing α-$SiW_{12}O_{40}^{4-}$ (red curves in figure 1), a much higher reduction current is observed. This could be ascribed to the fact that two reduction processes take place at similar potentials: the reduction of α-$SiW_{12}O_{40}^{4-}$ and that of O_2. But more importantly, a much smaller decrease of peak current with cycling is observed during cycling. After 10 cycles, the current has only decreased by ca. 20%. This demonstrates that α-$SiW_{12}O_{40}^{5-}$ facilitates the reduction of O_2 in such a way that it effectively mitigates the problem of passivation of the electrode surface by deposition of Li_2O_2. The presence of O_2 also produces a decrease of the anodic peak at 2.7 V vs. Li^+/Li, associated to the re-oxidation of α-$SiW_{12}O_{40}^{5-}$ to α-$SiW_{12}O_{40}^{4-}$, thus confirming the reaction between α-$SiW_{12}O_{40}^{5-}$ and O_2. Further experimental proof is presented below, but in view of the results in figure 1, the following reaction mechanism can be proposed:

$$\alpha\text{-}SiW_{12}O_{40}^{4-} + e^- \rightarrow \alpha\text{-}SiW_{12}O_{40}^{5-} \qquad (6)$$

$$2\ \alpha\text{-}SiW_{12}O_{40}^{5-} + O_2 + 2Li^+ \rightarrow Li_2O_2 + 2\ \alpha\text{-}SiW_{12}O_{40}^{4-} \qquad (7)$$

where the diffusion of α-$SiW_{12}O_{40}^{5-}$ away from the electrode surface after the electron transfer process facilitates the formation of Li_2O_2 suspended in solution rather than on the electrode surface.

The effect of α-$SiW_{12}O_{40}^{4-}$ on the electrochemical performance of Li-O_2 cells is shown in figure 2. α-$SiW_{12}O_{40}^{4-}$ produces much higher discharge capacities and increases the discharge voltage, confirming the beneficial effect of α-$SiW_{12}O_{40}^{4-}$ on the kinetics and mechanism of the O_2 reduction reaction. The improved capacity in the presence of α-$SiW_{12}O_{40}^{4-}$ cannot be explained by the reduction of α-$SiW_{12}O_{40}^{4-}$ alone, since in the absence of O_2, the cells containing α-$SiW_{12}O_{40}^{4-}$ delivered a very small capacity (inset figure 2). Furthermore, the full reduction of all the α-$SiW_{12}O_{40}^{4-}$ in the cell to α-$SiW_{12}O_{40}^{5-}$ would only involve 0.021 mA h cm^{-2}. The beneficial effect of α-$SiW_{12}O_{40}^{4-}$ on the discharge performance of Li-O_2 cells is also observed at other discharge currents (see ESI, figure S8).

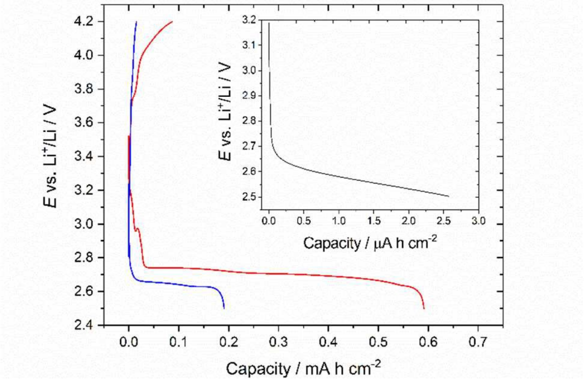

Figure 2. Galvanostatic cycling of Li-O_2 cells with (red) and without (blue) 50 mM $TBA_4SiW_{12}O_{40}$ with 1M LiTFSI in DMSO. Current density: 31.8 µA cm^{-2} (normalized by the geometric area of the electrode). The inset shows the results of the reference cell containing 50 mM $TBA_4SiW_{12}O_{40}$ in argon, which shows a much smaller capacity of 2.55 µA h cm^{-2}. The cells contain a carbon cloth positive electrode and a Li-conducting glass membrane to isolate the lithium electrode compartment which has no $TBA_4SiW_{12}O_{40}$.

To confirm the reaction mechanism proposed above, the change in the O_2 pressure inside the cells was monitored in situ during the galvanostatic discharge of Li-O_2 cells and used to quantify the oxygen consumption (figure 3). In both cases, with and without α-$SiW_{12}O_{40}^{4-}$, the change in pressure is consistent with a reaction consuming 2 electrons per O_2 molecule, in agreement with Li_2O_2 formation regardless of mediator.

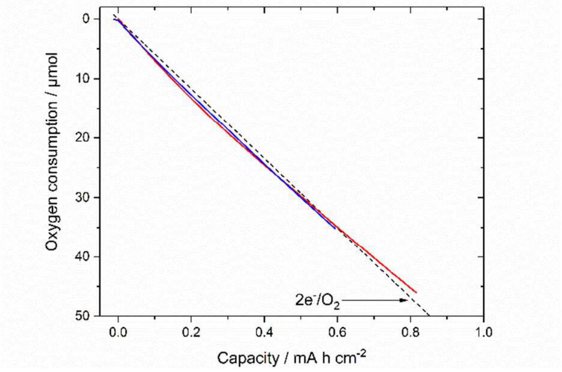

Figure 3. Consumption of oxygen as evaluated by in-situ pressure changes during the discharge of Li-O_2 cells with (red) and without (blue) 50 mM $TBA_4SiW_{12}O_{40}$ at 15.9 µA cm^{-2}. The dashed line shows the expected behaviour for a $2e^-$ per O_2 reaction.

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Finally, figure 4 shows the XRD pattern of an electrode discharged in a Li-O_2 cell containing α-$SiW_{12}O_{40}^{4-}$. The pattern shows two small peaks consistent with Li_2O_2 formation. The peaks are rather broad, indicating that Li_2O_2 is formed as small particles, and the small intensity of the peaks suggests that most Li_2O_2 formation takes place away from the electrode surface, consistent with the decrease in the extent of electrode passivation observed in figure 1.

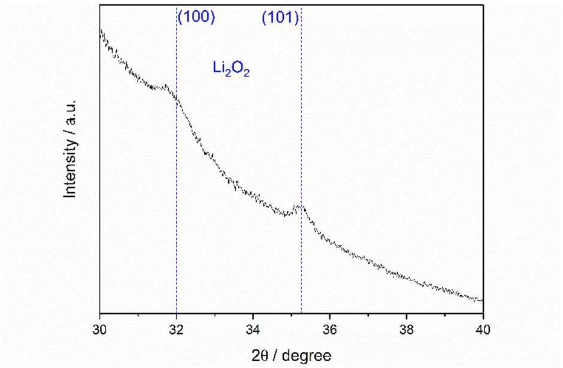

Figure 4. XRD pattern of an electrode discharged at 15 μA cm^{-2} up to 2.5 V vs. Li^+/Li (96 hours) in a Li-O_2 cell with 50 mM $TBA_4SiW_{12}O_{40}$.

In summary, we have demonstrated that the polyoxometalate α-$SiW_{12}O_{40}^{4-}$ is an effective mediator of the discharge reaction of Li-O_2 cells, which acts by facilitating the formation of Li_2O_2 away from the electrode surface and thus mitigating the problem of electrode passivation. Voltammetric measurements at a glassy carbon electrode show that the reduction of O_2 in the presence of α-$SiW_{12}O_{40}^{4-}$ involves significantly less electrode passivation than in the absence of α-$SiW_{12}O_{40}^{4-}$. Furthermore, introduction of α-$SiW_{12}O_{40}^{4-}$ into Li-O_2 cells leads to marked enhancement in the discharge capacity and discharge potential, thus confirming the beneficial effect of $SiW_{12}O_{40}^{4-}$ as a redox mediator for the O_2 reduction reaction. It is also demonstrated that $SiW_{12}O_{40}^{4-}$ acts as an efficient electrocatalyst, which is not consumed in the reaction, since in-situ monitoring of the O_2 pressure inside the Li-O_2 cells indicates that the overall reaction involves 2 electrons per O_2 molecule,and the formation of Li_2O_2 as the main discharge product. Finally, the XRD pattern of a discharged electrode shows the characteristic peaks associated to Li_2O_2 formation, and the peaks are broad and small, consistent with the formation of small particles of Li_2O_2 on the electrode surface, with most of the Li_2O_2 being formed in solution. Therefore, this work demonstrates a new type of redox mediator with promising performance in Li-O_2 cells.

Polyoxometalates are inorganic anions with multiple transition metal ions and multiple stable oxidation states, which are expected to be stable against degradation in aprotic solvents and hence they have the potential to produce longer cycling Li-O_2 cells. The stability of α-$SiW_{12}O_{40}^{4-}$ in the presence of superoxide has been demonstrated with UV-vis experiments (figures S13-15). In addition, the stability of the cyclic voltammograms with α-$SiW_{12}O_{40}^{4-}$ in solution (Figure 1,with no new peaks or peak splitting or disappearance during cycling) also suggests the absence of degradation reactions. This work has focused on the electrocatalysis of the discharge reaction, but further work is required to improve the charge reaction. Since the polyoxometalate α-$SiW_{12}O_{40}^{4-}$ facilitates the formation of Li_2O_2 suspended in solution (and hence disconnected from the current collector), a second redox mediator is required to improve the charge reaction[15,19,21,66], which could be achieved by using polyoxometalates with additional oxidation processes at potentials higher than 2.96 V vs. Li^+/Li.

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Improving Li-O_2 batteries with the highly stable Keggin type- polyoxometalate α-$SiW_{12}O_{40}^{4-}$.