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Using polyoxometalates to enhance the capacity of lithium-oxygen batteries

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The Keggin-type polyoxometalate $\alpha$-SiW$_{12}$O$_{40}^{4-}$ increases the discharge capacity and potential of lithium-oxygen batteries, by facilitating the reduction of $O_2$ to Li$_2$O, 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\textsuperscript{15-20}. 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\textsuperscript{11-13}. The discharge reaction of nonaqueous lithium-oxygen batteries involves the reduction of $O_2$ to form Li$_2$O$_2$, and redox mediators enhance the discharge capacity by facilitating the formation of Li$_2$O$_2$ away from the electrode surface, thus mitigating the problem of electrode passivation by deposition of Li$_2$O, 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:

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

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

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$_2$O$_2$ 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$_2$O$_2$ via the chemical reaction of the oxidised form of the redox mediator with Li$_2$O, thus increasing the charge capacity, the coulombic efficiency, voltage efficiency and capacity retention with cycling\textsuperscript{24-36}.

Redox mediators have also been applied successfully to suppress degradation reactions in lithium-oxygen batteries\textsuperscript{43-45}, 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\textsuperscript{13,37-45}.

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\textsuperscript{46-56}, this is the first study in which polyoxometalates are used in lithium-oxygen batteries. We show here that the Keggin-type anion $\alpha$-SiW$_{12}$O$_{40}^{4-}$ is an effective mediator of the discharge reaction of lithium-oxygen batteries. $\alpha$-SiW$_{12}$O$_{40}^{4-}$ has been selected for this study for the following reasons:

- The reduction of $\alpha$-SiW$_{12}$O$_{40}^{4-}$ to $\alpha$-SiW$_{12}$O$_{40}^{5-}$ takes place at a potential close to 2.6 V vs. Li$^+/\text{Li}$, which is lower than the thermodynamic potential of $O_2$ reduction to Li$_2$O$_2$ of 2.96 V vs. Li$^+/\text{Li}$\textsuperscript{57}, and therefore, $\alpha$-SiW$_{12}$O$_{40}^{5-}$ is reducing enough to chemically reduce $O_2$ to Li$_2$O$_2$ (reaction 2).
- Both $\alpha$-SiW$_{12}$O$_{40}^{4-}$ and $\alpha$-SiW$_{12}$O$_{40}^{5-}$ are highly stable, chemically and structurally, due to their high nucleity 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\textsuperscript{58,59}.

Figure 1 shows the cyclic voltammogram of a glassy carbon electrode in the presence of $\alpha$-SiW$_{12}$O$_{40}^{4-}$ (black curve). A reversible one-electron transfer process, corresponding to the formation of $\alpha$-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$^+/\text{Li}$, one electron is consumed per $\alpha$-SiW$_{12}$O$_{40}^{4-}$, thus forming $\alpha$-SiW$_{12}$O$_{40}^{5-}$.

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Figure 1: Cyclic voltammograms of a glassy carbon electrode in Ar saturated (black) and O₂ saturated (red) 10 mM TBAα-SiW₁₂O₄₀ with 1 M LiTFSI in DMSO and in O₂ saturated 1 M LiTFSI DMSO without TBAα-SiW₁₂O₄₀ (blue). Scan rate: 20 mV s⁻¹.

Figure 1 also shows that, in O₂ saturated solutions, in the absence of α-SiW₁₂O₄₀ (blue curves), a reduction peak associated to the reduction of O₂ to Li₂O₂ is observed, in agreement with previous studies. It has been shown that the process of O₂ reduction takes place via the formation of intermediate lithium superoxide species:

\[ \text{O}_2 + \text{e}^- \rightarrow \text{LiO}_2 \]  \hspace{1cm} (3)
\[ \text{LiO}_2 + \text{e}^- \rightarrow \text{Li}_2\text{O}_2 \]  \hspace{1cm} (4)
\[ 2\text{LiO}_2 \rightarrow \text{Li}_2\text{O}_2 + \text{O}_2 \]  \hspace{1cm} (5)

Upon cycling, the magnitude of the current decreases markedly. This is because not all of the Li₂O₂ formed during reduction is oxidised back to O₂ during oxidation. Progressive accumulation of Li₂O₂ deposits at the electrode surface decreases the electrochemically active surface area, and after 10 cycles, the current has decreased by ca. 66%.

In O₂ saturated solutions containing α-SiW₁₂O₄₀ (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-SiW₁₂O₄₀ and that of O₂. 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-SiW₁₂O₄₀ facilitates the reduction of O₂ in such a way that it effectively mitigates the problem of passivation of the electrode surface by deposition of Li₂O₂. The presence of O₂ also produces a decrease of the anodic peak at 2.7 V vs. Li/Li⁺ associated to the re-oxidation of α-SiW₁₂O₄₀ to α-SiW₁₂O₄₀⁺, thus confirming the reaction between α-SiW₁₂O₄₀⁻ and O₂. Further experimental proof is presented below, but in view of the results in figure 1, the following reaction mechanism can be proposed:

\[ \text{α-SiW}_{12}\text{O}_{40}^- + \text{e}^- \rightarrow \text{α-SiW}_{12}\text{O}_{40}^- \]  \hspace{1cm} (6)
\[ 2\text{α-SiW}_{12}\text{O}_{40}^- + \text{O}_2 + 2\text{Li}^+ \rightarrow \text{Li}_2\text{O}_2 + 2\text{α-SiW}_{12}\text{O}_{40}^- \]  \hspace{1cm} (7)

where the diffusion of α-SiW₁₂O₄₀⁻ away from the electrode surface after the electron transfer process facilitates the formation of Li₂O₂ suspended in solution rather than on the electrode surface.

The effect of α-SiW₁₂O₄₀⁺ on the electrochemical performance of Li-O₂ cells is shown in figure 2. α-SiW₁₂O₄₀⁺ produces much higher discharge capacities and increases the discharge voltage, confirming the beneficial effect of α-SiW₁₂O₄₀ on the kinetics and mechanism of the O₂ reduction reaction. The improved capacity in the presence of α-SiW₁₂O₄₀⁺ cannot be explained by the reduction of α-SiW₁₂O₄₀⁺ alone, since in the absence of O₂, the cells containing α-SiW₁₂O₄₀⁺ delivered a very small capacity (inset figure 2). Furthermore, the full reduction of all the α-SiW₁₂O₄₀⁺ in the cell to α-SiW₁₂O₄₀⁻ would only involve 0.021 mA h cm⁻². The beneficial effect of α-SiW₁₂O₄₀⁻ on the discharge performance of Li-O₂ cells is also observed at other discharge currents (see ESI, figure S8).

To confirm the reaction mechanism proposed above, the change in the O₂ pressure inside the cells was monitored in situ during the galvanostatic discharges of Li-O₂ cells and used to quantify the oxygen consumption (figure 3). In both cases, with and without α-SiW₁₂O₄₀⁺, the change in pressure is consistent with a reaction consuming 2 electrons per O₂ molecule, in agreement with Li₂O₂ formation regardless of mediator.

**Figure 2.** Galvanostatic cycling of Li-O₂ cells with (red) and without (blue) 50 mM TBAα-SiW₁₂O₄₀ 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 TBAα-SiW₁₂O₄₀ 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 TBAα-SiW₁₂O₄₀.

**Figure 3.** Consumption of oxygen as evaluated by in-situ pressure changes during the discharge of Li-O₂ cells with (red) and without (blue) 50 mM TBAα-SiW₁₂O₄₀ at 15.9 µA cm⁻². The dashed line shows the expected behaviour for a 2e⁻ per O₂ reaction.
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$_2$O$_2$ formation. The peaks are rather broad, indicating that Li$_2$O$_2$ is formed as small particles, and the small intensity of the peaks suggests that most Li$_2$O$_2$ formation takes place away from the electrode surface, consistent with the decrease in the extent of electrode passivation observed in figure 1.

![XRD pattern](image)

**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$_2$O$_2$ cell with 50 mM TBA$_2$SiW$_2$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$_2$O$_2$ cells, which acts by facilitating the formation of Li$_2$O$_2$ 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$_2$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$_2$O$_2$ cells indicates that the overall reaction involves 2 electrons per O$_2$ molecule, and the formation of Li$_2$O$_2$ as the main discharge product. Finally, the XRD pattern of a discharged electrode shows the characteristic peaks associated to Li$_2$O$_2$ formation, and the peaks are broad and small, consistent with the formation of small particles of Li$_2$O$_2$ on the electrode surface, with most of the Li$_2$O$_2$ being formed in solution. Therefore, this work demonstrates a new type of redox mediator with promising performance in Li$_2$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$_2$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$_2$O$_2$ 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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Notes and references


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Improving Li-O_{2} batteries with the highly stable Keggin type-polyoxometalate \( \alpha\text{-SiW}_{12}\text{O}_{40}^{4-} \).