

Design, Synthesis, and Applications of Reversible Oxygen Chemisorbents

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Abstract

Novel high-capacity oxygen selective adsorbents are described that bind oxygen reversibly at temperatures near ambient. The class of materials described employ a redox-active cobalt(II) site embedded within a coordination environment designed to ensure facile access to active sites. The specific compositions that will be presented are well-suited to trace oxygen removal from a variety of process streams. Oxygen capacities at saturation are in excess of 1.6 mmol/g and selectivity over nitrogen is very high. Regeneration is accomplished by pressure swing and this avoids the need for reducing atmospheres and elevated temperatures that are typically required for getter materials and deoxo processes. Extensive lifetime studies will be described that are parametric in temperature, oxygen partial pressure, and residual water content. Half-life for a typical example is over 4 years with 1% oxygen at 40F under cycling conditions.

Background

There are a number of commercial materials that chemisorb oxygen (oxygen getters), but the majority require chemical treatments for regeneration. Commercial systems that exhibit reversible oxygen chemisorption in the absence of chemical regeneration are largely unknown. We describe herein compositions that satisfy the majority of commercial requirements.

A well-known class of materials that exhibit reversible of chemisorption are the heme proteins, hemoglobin and myoglobin.¹ The development of synthetic analogs of the heme proteins has received considerable attention.²⁻⁶ These materials are described broadly in the literature as “oxygen carriers.” The first report of a reversible cobalt(II) oxygen carrier was made in 1939 when Tsumaki showed that the reversible color change for Co(salen) is attributable to oxygen binding.⁷ Structurally related compositions were considered to provide oxygen for aircraft.⁸

The majority of published data for oxygen carriers involve synthetic analogs of the heme proteins that function in dilute solution under transient conditions or where sophisticated molecular designs, such as ligand superstructure, are used to infer stability.²⁻⁶ These studies have proven valuable to identify key structural features that are essential for performance. Applications of oxygen carriers have been described as liquids, supported liquid membranes, and dispersed in polymeric membranes. In spite of considerable attention, we are not aware of any commercial manifestations of these systems.

While a large number of oxygen carrier compositions function in dilute solution, only a small fraction of materials function as solids.^{2,5,7,8} Perhaps the more promising examples are

the lithium pentacyanocobaltate solvates developed by Ramprasad and coworkers.⁹⁻¹¹ These compositions show a high degree of active site utilization and reversibility, and provided state of the art lifetimes. In spite of these and other extensive studies, to the best of our knowledge, there are no examples of solid state oxygen carriers where performance is adequate for anything other than niche applications.

Praxair Compositions and Properties

The current paper addresses a new class of oxygen selective materials developed by Praxair.¹² The compositions disclosed combine the following features:

- Active transition metal ion
- Primary donor set to the central ion
- Groups capable of assembly into porous frameworks

These characteristics provide high oxygen capacity, fast interaction rates, and structural versatility. Three examples are described (see **Figure 1**) that meet the structural criteria (see above), and exhibit reversible oxygen binding. Differences in behavior with composition are highlighted.

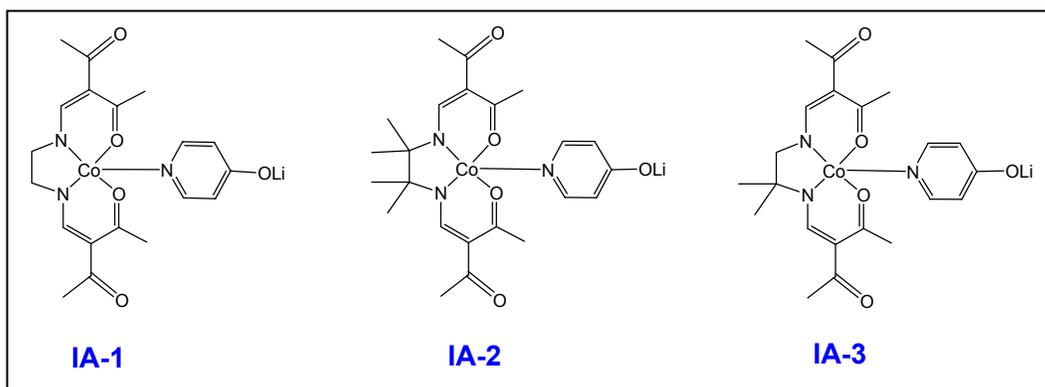


Figure 1. Praxair Oxygen Selective Adsorbent Compositions

The compositions described herein represent condensation products of diamines with two equivalents of carbonyl analogs. The structural versatility of the family is large and over 100 compositions have been prepared and evaluated including symmetrical, pseudo symmetrical and asymmetric versions. In all cases, we have focused on cobalt(II) as the active transition metal center based on an extensive literature and expectations concerning lifetime.²⁻⁶ The synthetic route (**Figure 2**) is typical of that used for the symmetric and pseudo symmetric examples. Synthetic details for specific examples are described elsewhere.¹²

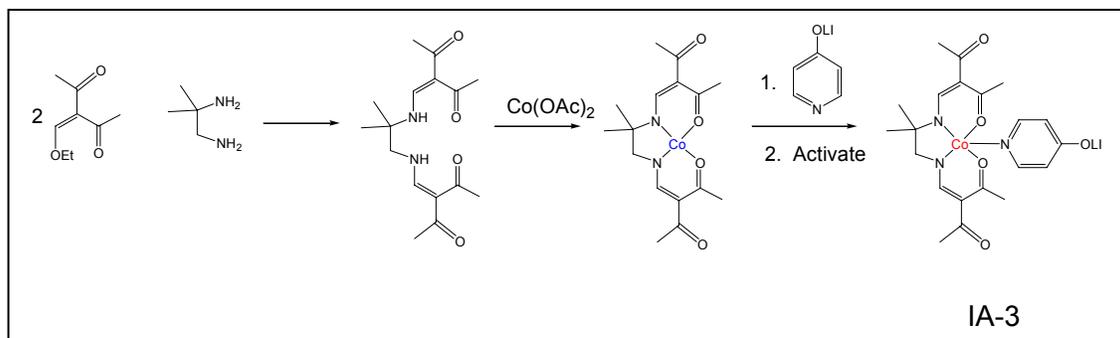


Figure 2. Synthetic Scheme for the Composition Designated IA-3

The crystal structure of the composition designated IA-1 was established as a methanol solvate (**Figure 3**) and confirms both the composition of the primary ligand and axial coordination by the lithium salt of hydroxypyridine. The lithium cations provide the pathway to self-assembly through interaction with acetyl groups of the primary ligand. The structure confirms the assembly process and also the provision of vacant coordination sites for oxygen interaction. Although the desolvated material did not provide crystals suitable for single crystal work, the crystalline order is evident from powder X-ray diffraction data. A change in powder diffraction pattern is observed upon oxygen exposure which is reversible under extended nitrogen purge or vacuum.

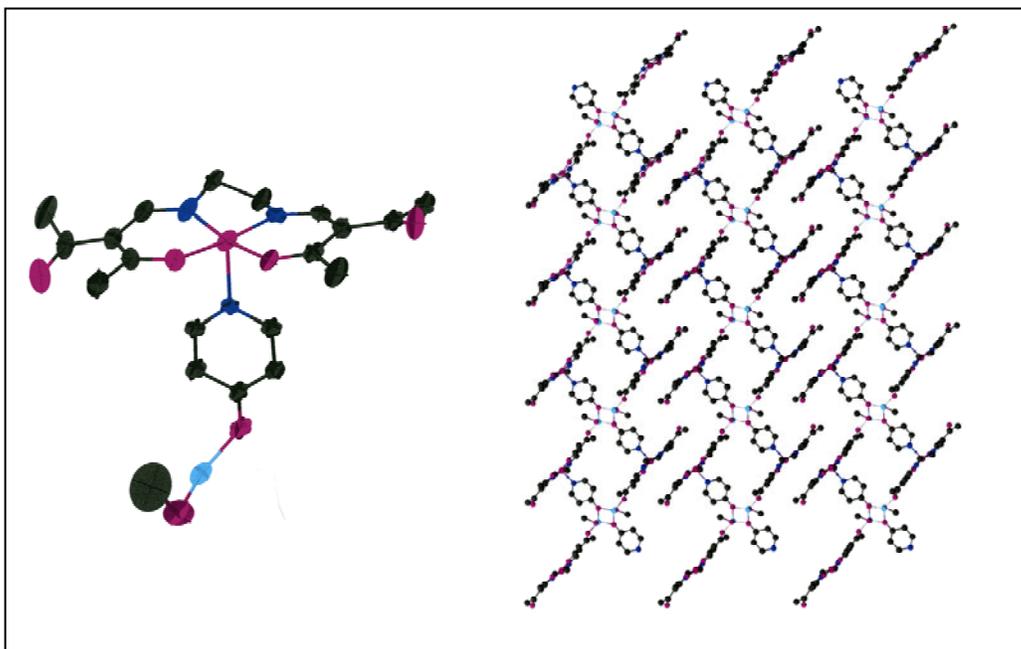


Figure 3. IA-1 molecular structure (left) and intermolecular assembly (right)

The oxygen binding for the composition designated IA-1 occurs at low oxygen partial pressures and the half-saturation pressure at 27 °C is ~1 torr. The material exhibits reversible

oxygen binding but complete regeneration requires deep vacuum and extended periods. The majority of the oxygen binding data were obtained for the composition designated IA-3 since early indications indicated that milder regeneration may be possible.

Isotherms for oxygen and nitrogen confirm high selectivity that we expect for chemisorption processes (**Figure 4**). The heat of oxygenation was determined by combining data from thermogravimetric studies and differential scanning calorimetry. The heat of oxygenation is -14.3 Kcal/mol.

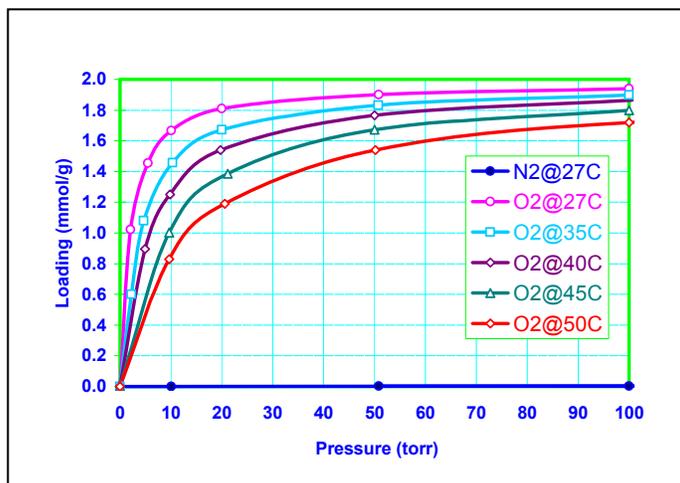


Figure 4. Isotherms for O₂ and N₂ with IA-3

Extended lifetime studies were performed under cycling conditions. The studies were parametric in oxygen concentration and temperature. A third parameter, moisture content, was found to have minimal impact on lifetime at concentrations below 5 ppm. Lifetime results are shown in **Table 1** expressed as adsorbent half lives. The results indicate that the materials are better suited to lower temperature operation. A disadvantage is that the increased binding constant tends to make regeneration more difficult at the lower temperatures.

Table 1. Projected Half-Lives for IA-3 under Cycling Conditions

Temp (°F)	Projected Half-Life (yrs)		
	1% O ₂	0.1% O ₂	0.01% O ₂
40	31.90	44.68	180.63
60	12.85	21.49	117.74
80	5.74	17.01	72.50
100	2.71	-	-

The composition designated IA-2 exhibits oxygen adsorption characteristics that are highly unusual. The oxygen isotherm is a strong function of material history. Samples that have not been exposed to oxygen provide modest capacities. Exposure to high pressure

oxygen at ambient temperature or to lower oxygen pressures at subambient temperatures changes the performance and increases the effective oxygen capacity. Two examples of oxygen isotherms are shown in **Figure 5**. We have found that the oxygen isotherm characteristics are continuously variable based on oxygen pretreatment. After the oxygen pretreatment, the performance is remarkably stable over a large number of conventional oxygenation-deoxygenation cycles. The reasons for this unique behavior are unknown, although structural rearrangement is likely to play a role.

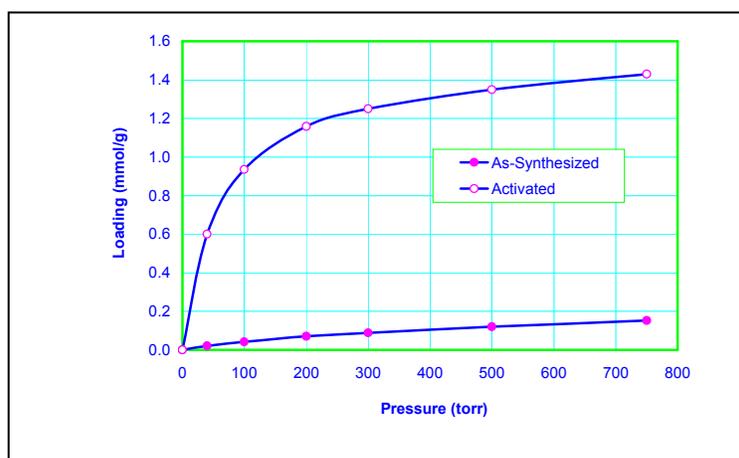


Figure 5. Oxygen Isotherms for IA-2 As-Synthesized and After Oxygen Activation

Conclusion

Praxair has developed a family of oxygen selective adsorbents that are highly selective for oxygen and offer long lifetimes. These compositions employ oxygen chemisorption and are suitable for oxygen removal from a variety of fluid streams. Compared to the oxygen getters, these materials can be regenerated without the need for reducing gases.

Acknowledgement

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