Studies on stability and oxygen and water absorption characteristics of $YBaCo_4O_{7+\delta}$ and $LiFePO_4$

Samuli Räsänen





DOCTORAL DISSERTATIONS

Studies on stability and oxygen and water absorption characteristics of $YBaCo_4O_{7+\delta}$ and $LiFePO_4$

Samuli Räsänen

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Abstract

Systematic engineering of functional oxide materials aims to either improve their functional properties or remove serious shortcomings. In this work various chemical and elevated-pressure techniques were employed as oxygen-engineering tools for first controlling the oxygen content of the perovskite cobalt oxide, SrCoO_{3-δ}, and then, more particularly, for evaluating the oxygen storage capability of the new oxygen storage material candidate, YBaCo₄O_{7+δ}. The oxygen nonstoichiometry range in YBaCo₄O_{7+δ} was found to be between $0 \le \delta \le 1.5$.

Effects of cation substitution on the oxygen storing capacity and thermal stability of $YBaCo_4O_{7+\delta}$ were also studied. The $YBaCo_4O_{7+\delta}$ phase has a problem of decomposition at around 600 °C in oxygen containing atmospheres, however, cobalt-site substitutions with Al and Ga were found to enhance the phase stability without any major effect on the oxygen storing capacity. For example a 20 % Ga-substituted material showed no phase decomposition in an oxygen containing atmosphere across a temperature range from 25 to 1000 °C.

High-sensitivity in-situ thermogravimetric measurements were carried out under controlled humidity conditions to investigate the water absorption/desorption characteristics of $LiFePO_4$ – a material used as a positive electrode material in Li-ion batteries. Plain $LiFePO_4$ powder and composite-electrode powders with polyvinylidene fluoride (PVDF), polyvinyl alcohol (PVA), acryle and carboxymethyl cellulose (CMC) binder were studied. It was found that the amount of absorbed water had a linear dependence on the humidity level of surrounding atmosphere. A major part of the absorbed water is uptaken in the first few minutes of exposure to humid air. It was also found that the binders (except CMC) or the conductive carbon in the composite electrode protect the material against water absorption to some extent. Partial substitution of Mn-to-Fe increases the amount of absorbed water but at the same time improves the reversibility of the water absorption/desorption process.

Keywords cobalt oxide, oxygen storage, thermogravimetry, chemical substitution, phase stability, Li-ion battery electrode, LiFePO₄, water absorption, water based binder

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Tiivistelmä

 $\label{eq:summation} Funktionaalisten oksidimateriaalien ominaisuuksia pyritään parantamaan systemaattisella suunnittelulla. Tässä työssä säädettiin koboltti pohjaisen perovskiitin SrCoO_{3-\delta} happipitoisuutta ja tutkittiin happivarastomateriaalin YBaCo_4O_{7+\delta} happiepästoikiometriaa soveltamalla happisuunnittelun työkaluja aina kemiallisista menetelmistä korkean paineen tekniikoihin saakka. Happivarastomateriaalin YBaCo_4O_{7+\delta} happiepästoikiometrian todettiin olevan välillä <math display="inline">0 \leq \delta \leq 1.5.$

Työssä tutkittiin myös osittaisen kationikorvauksen vaikutusta YBaCo₄O₇₊₆:n hapen varastointikykyyn ja faasin stabiilisuuteen. Korvaamalla osa koboltista alumiinilla tai galliumilla saatiin estettyä YBaCo₄O₇₊₆:n hajoaminen 600 °C:ssa happea sisältävässä kaasukehässä ilman merkittävää muutosta hapen varastointikyvyssä. Esimerkiksi kun 20% koboltista korvattiin galliumilla voitiin materiaalia lämmittää happea sisältävässä kaasukehässä 25 °C:sta aina 1000 °C:een ilman merkkejä faasin hajoamisesta.

Veden absorptiota ja desorptiota Li-ioniakkumateriaalissa LiFePO₄ tutkittiin korkean herkkyyden termovaa'alla kontrolloiduissa suhteellisissa kosteuksissa. Työssä tutkittiin sekä pelkkää aktiivista elektrodimateriaali LiFePO₄:a, että komposiittielektrodeja joissa käytettiin sidosaineena joko polyvinyylifluoridia (PVDF), akryyliä, polyvinyylialkoholia (PVA) tai hiilimetyyliselluloosaa (CMC). Tutkimuksissa huomattiin absorboituvan veden määrän olevan suoraan verrannollinen ympäröivään suhteelliseen kosteuteen. Suurin osa absorboidusta vedestä absorboituu muutaman minuutin sisällä näytteen altistuksesta kostealle ilmalle. Sidosaineiden (pois lukien CMC) tai komposiittielektrodeissa myös käytetyn johtavuushiilen huomattiin jossain määrin suojaavan elektrodia kosteusabsorptiolta. Osittainen raudan korvaus mangaanilla nostaa absorboituneen veden kokonaismäärää mutta samalla se parantaa faasin palautuvuuskykyä absorptio-/ desorptioprosessista. Tämä johtuu prosessin muuttumisesta fysi- ja kemisorption sekoituksesta puhtaaksi fysisorptioksi.

Avainsanat kobolttioksidi, happivarasto, termogravimetria, kemiallinen substituutio, faasin stabiilisuus, Li-ioniakun elektrodi, LiFePO₄, veden absorptio, vesipohjainen sidosaine

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PREFACE

The work presented in this thesis has been carried out in the Laboratory of Inorganic Chemistry at Aalto University School of Chemical Technology and in the Materials and Structures Laboratory at Tokyo Institute of Technology, between January 2008 and June 2012. Tekes (No. 3087/31/08), Finnish Foundation for Technology Promotion, The Emil Aaltonen foundation, European Union European Regional Development Fund (A31629) and Chydenius Institute Supporters' Association are gratefully acknowledged for the financial support of this work.

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LIST OF PUBLICATIONS

In addition to the present review, this thesis includes the following publications (I-VI), which are referred to in the text by their corresponding Roman numbers. The original publications are found in appendices I-VI.

- I L. Karvonen, S. Räsänen, H. Yamauchi and M. Karppinen, Chemical oxidation of SrCoO₃₋₆, *Chemistry Letters* 36 (2007) 1176-1177.
- II S. Räsänen, H. Yamauchi and M. Karppinen, Oxygen absorption capability of YBaCo₄O₇₊₈, *Chemistry Letters* 37 (2008) 638-639.
- III S. Räsänen, T. Motohashi, H. Yamauchi, M. Karppinen, Stability and oxygenstorage characteristics of Al-substituted YBaCo₄O_{7+δ}, *Journal of Solid State Chemistry* 183 (2010) 692-695.
- IV S. Räsänen, O. Parkkima, E.-L. Rautama, H. Yamauchi and M. Karppinen, Ga-for-Co substitution in YBaCo₄O₇₊₈: Effect on high-temperature stability and oxygenstorage capacity, *Solid State Ionics* 208 (2012) 31-35.
- V S. Räsänen, M. Lehtimäki, T. Aho, K. Vuorilehto and M. Karppinen, In-situ investigation of the water absorption/desorption behavior of LiFePO₄, *Solid State Ionics* 211 (2012) 65-68.
- VI S. Räsänen and M. Karppinen, Thermogravimetric study of water-based LiFePO₄ composite electrode powders, *Thermochimica Acta* 547 (2012) 126-129.

THE AUTHOR'S CONTRIBUTION

- Publication IThe author defined the research plan together with the co-authors,
carried out major part of the experimental work and data
collection. The results were interpreted together with the co-
authors. The author had a minor role in writing the manuscipt.
- **Publication II** The author defined the research plan together with the co-authors, carried out the experimental work and data collection. The results were interpreted together with the co-authors. The author had a major role in writing the manuscript.
- **Publication III** The author defined the research plan together with the co-authors, carried out the experimental work and data collection. The results were interpreted together with the co-authors. The author had a major role in writing the manuscript.
- Publication IVThe author defined the research plan together with the co-authors,
partially carried out the sample preparation and data collection.
The results were interpreted together with the co-authors. The
author had a major role in writing the manuscript.
- **Publication V** The author defined the research plan together with the co-authors, carried out the experimental work and data collection. The results were interpreted together with the co-authors. The author had a major role in writing the manuscript.
- **Publication VI** The author defined the research plan together with the co-author, carried out the experimental work and data collection. The results were interpreted together with the co-author. The author had a major role in writing the manuscript.

LIST OF ABBREVIATIONS AND SYMBOLS

- CMC Carboxymethyl cellulose
- ED Electron diffraction
- EDS Energy dispersive spectroscopy
- NMP N-methyl pyrrolidone
- OSC Oxygen storage capacity
- OSM Oxygen storage material
- PVA Polyvinyl alcohol
- PVDF Polyvinylidene fluoride
- T_c Critical temperature for superconductivity
- TG Thermogravimetry
- TPR Temperature programmed hydrogen reduction
- XRD X-ray diffraction
- δ Oxygen non-stoichiometry parameter per formula unit

1 INTRODUCTION

Transition metal oxides have revolutionized portable electronics since the discovery of the excellent energy storing properties of the lithium-ion intercalation material, $LiCoO_2$.¹ This innovation allowed Sony to launch the first safe Li-ion battery to the public at the beginning of the 1990's, offering an energy density of approximately five times higher than that of the conventional lead acid secondary battery.² Since then research on Li-ion batteries has been intense,^{3,4} however, improvements in energy densities of commercially successful electrode materials have been surprisingly small. At the moment $Li(Co_{1/3}Ni_{1/3}Mn_{1/3})O_2^{-5}$ and $LiFePO_4^{-6}$ are the most promising positive-electrode material candidates for large-scale batteries because of their structural stability at high charge states. Nevertheless these two materials have a common problem of water absorption from air and subsequent unwanted chemical reactions between the water and the electrode material deteriorating the parent phase which lowers the capability of reversible Li-ion intercalation and de-intercalation into and from the structure. This is seen as an abnormal decrease of the original capacity of the full battery cell.^{7,8}

Oxygen storage materials form another interesting and important group of functional transition metal oxide materials. Such materials are capable in accommodating and releasing large amounts of oxygen in a reversible manner, and are already in commercial use, e.g. CeO₂-based materials in automotive catalytic converters.⁹ Recently a highly promising new type of oxygen storage material was found, i.e. the complex cobalt oxide, YBaCo₄O_{7+δ}.^{10,11} It has already aroused considerable interest in e.g. solid oxide fuel cell,¹² oxyfuel combustion¹³ and oxygen separating membrane¹⁴ research although currently there is a major drawback as YBaCo₄O_{7+δ} undergoes phase decomposition when heated above 600 °C in oxygen containing atmospheres.¹⁰ This unfortunate flaw prevents the use of YBaCo₄O_{7+δ} in applications in which operation temperatures higher than 600 °C are required.

1.1 Material Humidity

Water vapor in humid air interacts readily with solid surface exposed to it. The surface will be more or less covered with physisorbed water molecules attracted by Van der Waals forces.¹⁵ A single molecule of H_2O is rare in free water but the bound water has different properties from those of free water.¹⁶ Hydrogen bonded clusters of water molecules are commonly found in connection with metal surfaces but not with the oxide powders. Molecular bonding of water to the surface happens through oxygen and the bonding is accompanied by net charge transfer to the surface. Formation of relatively strong bonds, so that molecular adsorbed H_2O can be stable up to room temperature, on some ionic surfaces is a distinctive feature of H_2O adsorption. Dissociation of H_2O on the powder.¹⁷

Table 1. Various types of water existing near solid surfaces.¹⁵

Type of Water	Formation process
Free bulk water	
volume water	Filling volumes
• interpacked water	Filling of macropores and interspaces between particles
Water bound physically at the solid surfacephysisorbed water layers	Adsorption (physisorption) at the outer surface and at pore walls and micropore filling
• capillary water in mesopores	Adsorption (physisorption) + condensation in mesopores (capillary condensation)
Water bound chemically at the solid surfacechemisorbed water	Adsorption + chemisorption at the outer surface and at pore walls
Water bound in the solid bulk material	Adsorption \pm diffusion $>$ absorption

Water is bound at solid materials in various different ways so that the water uptake can vary from low-temperature single-molecular layer physisorption to substantial room-temperature water absorption resulting in material to swelling. Table 1 lists the main types of water existing near solid surfaces and the corresponding formation processes. Free bulk water can simply fill large pores and spaces between grains. Water bound physically at the solid surface is reversibly bound physisorbed water as the electron orbital is not influenced, in other words there is no electron exchange between adsorbed water and the adsorbent i.e. there is no chemical reaction between these constituents allowing fully reversible adsorption/desorption process. Physically bound water can be partly vaporized by either decreasing vapor pressure or increasing the temperature to reach new equilibrium state with the surroundings. Water bound chemically is irreversibly bonded dissociative water. Enough energy can release chemisorbed water molecules through recombination of hydroxyl groups, however, formation of hydrate and binding as a water of crystallization are chemical reactions which can be fully reversible. Water bound in the solid bulk is water that has diffused into the interior of the material and in a practical sense water is always interacting with the impurities on particle surfaces where it may for example emulsify or dissolve such species.¹⁵

1.2 Oxygen Nonstoichiometry

Oxygen nonstoichiometry refers to an excess or lack of oxygen within an oxide material which is not in a molar ratio when compared to the parent material. There are four major ways for oxygen nonstoichiometry to be realized in oxide lattices: (i) interstitial oxygen atoms, (ii) cation vacancies, (iii) oxygen vacancies and (iv) interstitial cations. The first two options give an overall oxygen excess, whereas the latter two result in an oxygen deficiency.¹⁰ These structural sources for oxygen nonstoichiometry can occur randomly or in an ordered manner in the parent oxide lattice and Table 2 summarizes the manifestation of oxygen nonstoichiometry in transition metal oxides. Oxygen nonstoichiometry is characteristic for transition metal oxides and this can be explained by the characteristic nature of transition metals which have multiple oxidation states that can stabilize structural deformations.

Source of oxygen nonstoichiometry	Description	Result
Interstitial oxygen atoms	There exist enough empty space in the structure for extra oxygen ions to accommodate.	Oxygen
Cation vacancies	Oxygen is close packed in a way that leaves unfilled spaces into the structure.	excess
Oxygen vacancies	There are holes in the close packed oxygen structure.	Oxygen
Interstitial cations	There are extra cations located in the left over space of closed packed oxygen structure.	deficiency

Table 2. Structural manifestations of oxygen nonstoichiometry in transition metal oxides.

Metal oxides release oxygen when heated; this follows from the second law of thermodynamics and has been demonstrated experimentally.¹⁸ However, the energetically preferred oxygen release can be inhibited by a large activation energy causing the metal oxide structure to be stabilized by the kinetics of the reaction. Nonstoichiometric oxide ceramics are currently of tremendous research interest as they can reversibly store and release oxygen at moderate temperatures in a rapid manner. The reversible oxygen absorption/desorption phenomenon can be controlled by changing the temperature in an oxygen containing atmosphere or by changing between oxidizing and reducing gas atmospheres.

Figure 1 demonstrates the temperature control of the oxygen absorption/desorption which can be seen as a hump in the dynamic thermogravimetric (TG) heating curve for a YBaCo₄O_{7+ δ} sample recorded in O₂ gas flow. This hump is due to quick oxygen absorption starting around 100 °C and even faster desorption of equal amount of oxygen around 400 °C. Figure 1 also shows the corresponding TG curve for the superconducting cuprate YBa₂Cu₃O_{6+ δ} as a comparison. The gradual rather than step-wise oxygen desorption behavior of YBa₂Cu₃O_{6+ δ} is common among perovskite transition metal oxides but it is clearly different from that of YBaCo₄O_{7+ δ}. In other words, not all nonstoichiometric ceramic oxides are ideal candidates for oxygen storage material.



Figure 1. TG curves for YBaCo₄O_{7+δ}^{III} and YBa₂Cu₃O_{6+δ}¹⁹ recorded in O₂ gas flow with a heating rate of 1 °C/min.

1.3 Scope of the Present Thesis

In this work two highly prominent functional ceramic materials, i.e. the positive Liion battery electrode material LiFePO₄ and the promising new oxygen storage material candidate YBaCo₄O_{7+ δ}, have been investigated for their water and oxygen absorption characteristics and phase stabilities under humid or oxygen-containing atmospheres, respectively. Efforts were made to enhance the properties of these materials through various cation substitutions and thermogravimetric (TG) measurements played a central role in this research for both the materials.

In order to study the water absorption/desorption process of $LiFePO_4$ a humidity-TG apparatus was constructed and methods were developed to systematically investigate the effects of Mn-for-Fe substitution. In addition the effect of different electrode compositions with various binders on the extent and reversibility of the water absorption in LiFePO₄ was also investigated.

Oxygen storage properties of $YBaCo_4O_{7+\delta}$ were studied by applying the tools of oxygen engineering from soft chemistry to ultra-high-pressure O_2 annealing.

Moreover, Al and Ga substitutions were utilized as a method to enhance the intrinsically poor phase stability of $YBaCo_4O_{7+\delta}$ under oxygen-containing atmospheres.

2 THERMOGRAVIMETRIC EVALUATION OF H₂O AND O₂ ABSORPTION/DESORPTION CHARACTERISTICS

Thermogravimetry (TG) is an excellent tool for the quantitative evaluation of changes in water or oxygen content in solid samples and hence is a practical choice for the research of hygroscopic or nonstoichiometric oxide materials. There is large variety of different types of test which can be performed with thermogravimetric equipment to elucidate the material properties related to the surrounding atmosphere and the temperature.

2.1 Material Humidity study of hygroscopic materials by Using Thermogravimetry

Removal of water from a solid material is based on heating the sample in a dry gas flow or vacuum in an effort to reduce the partial pressure the water vapor in the surrounding gaseous phase. It also is possible that chemisorbed water leaves the material together with the physisorbed water when the sample is heated and the resulting mass decrease of the sample reflects the material humidity.²⁰ Figure 2 shows a typical TG curve for LiFePO₄ powder sample exposed to ambient air, measured using a dynamic heating program in an ordinary thermobalance.



Figure 2. Dynamical TG curve for carbon-coated LiFePO₄ powder exposed to ambient air, measured in air with a heating rate of 5 °C/min.

When a moist sample is measured using a dynamic heating program it is often hard to separate the different types of water present and discern the optimum temperature for drying; a characteristic that is especially critical for materials which decompose at low temperatures. A solution to this is illustrated in Figure 3 where samples of LiFePO₄ powders kept at a standard humidity have been measured isothermally by TG at various temperatures to determine the amounts of water desorbing at each temperature. The leveling of TG curve at each temperature means that the all water available for desorption has left the material.



Figure 3. Isothermal TG curves recorded for LiFePO₄ powder in an N_2 flow at 80, 100, 120, 140, 160, 180 and 200 °C.^V

As can be seen, the drying is a complex process of mass/heat transfer and TG can be used to construct isotherms for both water adsorption and desorption.²¹ In order to evaluate the adsorptive/desorptive properties of porous materials in-situ or to construct reliable isotherms a humidity generator can be combined with a thermobalance to construct a so-called humidity-TG apparatus.^{22,23,V} Figure 4 shows a schematic of a humidity-TG apparatus used for in-situ water absorption/desorption measurements.



Figure 4. TG setup for humidity exposure measurements.²²

Water absorption of hygroscopic material can be recorded as a function of time by using humidity-TG. An example for this kind of measurement result is displayed in Figure 5.



Figure 5. Level of moisture regain for Biodynetm B membranes as a function of pore size.²³

Humidity-TG is a practical instrument for constructing isotherms illustrating the behavior of material at different relative humidity levels. The sample under investigation can be kept under a selected relative humidity for as long as it takes the mass change to become saturated and after that the relative humidity can be changed to another value until mass saturation is once again achieved. This is continued until there are enough data points to construct an isotherm, a typical example of which is shown in Figure 6 which illustrates an isotherm plot for a silica sample from data measured using a traditional TG.



Figure 6. Moisture isotherms for silica gel, type 59.²¹

Humidity-TG offers numerous possibilities for studying humidity-sensitive materials. When constructed by incorporating modern highly sensitive TG apparatus it can be used for detailed in-situ study of both water absorption and desorption properties.^V It also is possible to use humidity-TG to accelerate slow reactions between absorbed water and the absorbent by gently heating the sample in a humid atmosphere. Figure 7 shows a TG curve with mass increase for a LiFePO₄ powder sample when heated in a water containing atmosphere. This type of measurement

can help to overcome slow reaction mechanisms for water sensitive materials absorbing water from air.



Figure 7. TG curve of an atmosphere preserved LiFePO₄–C sample during a 24 h $120 \text{ }^{\circ}\text{C}$ stage in dry O₂ followed by a stage in a wet atmosphere.²⁴

2.2 Oxygen Content study of Nonstoichiometric Oxide Materials by Using Thermogravimetry

The oxygen content of nonstoichiometric oxide materials is relatively straightforward to modify through control of the surrounding atmosphere and temperature. TG offers comparable or superior accuracy and speed when compared to other quantitative analytical techniques for solving the exact oxygen content in nonstoichiometric transition metal oxides.²⁵ TG is not only an extremely useful analytical tool; it can also be used as a method for oxygen engineering.

Figure 8 shows a collection of TG curves recorded for nonstoichiometric LaCuO_{3- δ} sample powders. The oxygen stoichiometry of this material can be adjusted by controlling the temperature of thermal treatment in an argon atmosphere. It was because of the standard practice of using TG to study the oxygen stoichiometry for nonstoichiometric functional oxides that an oxygen storage material YBaCo₄O_{7+ δ} was discovered.¹⁰ Since then this thermoanalytical method proved to be an essential tool for engineering the properties of the new oxygen storage material.^{III, IV} The functional parameters to compare for practical application between the oxygen

storage materials are: (i) phase stability, (ii) operation temperature, (iii) oxygen storage capacity, (iv) speed of oxygen absorption/desorption and (v) cyclic stability for oxygen storage/release. All these parameters can be determined experimentally by thermoanalytical methods.



Figure 8. TG curves for in-situ oxygen depletion of LaCuO₃ in Ar.²⁶

Figure 9 outlines the oxygen storage and release mechanism in different atmospheres for one particle of an oxygen storage material. Oxygen permeation properties have been modeled for ceramic membranes by assuming that if grain size is less than 50 μ m then the surface reactions are the rate-limiting step.²⁷ Similarly the TG method can be applied for evaluating oxygen storage properties as the mass change upon the switching of the gas atmosphere between oxygen containing and inert/reducing in an isothermal TG study gives the oxygen storage capacity for the studied material. Figure 10 (a) illustrates the oxygen storage and release phenomena of YBaCo₄O_{7+δ} as an oscillating TG curve when the atmosphere is changed between O₂ and N₂ gas. This method can also give information about the speed and reversibility of the oxygen storage / release phenomena as shown by Figure 10 (b)

which shows the high speed and good stability of $BaYMn_2O_{5+\delta}$ when the gas atmosphere is switched between O_2 and H_2/Ar for 100 cycles.



Figure 9. Schematic drawing of a particle of an oxygen storage material in isothermal switching gas TG experiment.²⁷



Figure 10. Isothermal TG curves recorded for (a) YBaCo₄O_{7+ δ} at 350 °C when switching the gas between O₂ and N₂¹⁰ and (b) BaYMn₂O_{5+ δ} at 500 °C when switching gas between O₂ and 5% H₂ / 95% Ar²⁸.

Phase stability of oxygen storage material can be checked by heating the sample in a selected atmosphere using TG. The optimum operation temperature for an oxygen storage material can be estimated by first heating the fully reduced form of material in an O_2 atmosphere and then by heating the fully oxygenated form in an

inert/reducing atmosphere. Figure 11 shows a combination of both of these TG curves from which the optimum operational temperature can be estimated from the overlap of the oxygen absorption and oxygen desorption curves.



Figure 11. TG curves for the fully-oxygenated and reduced forms of $Pb_2CuSr_2LaCu_2O_{8+\delta}$ recorded in N₂ and O₂ gas flows, respectively, with a heating rate of 1 °C/min. The temperature range in which both the oxygen absorption and desorption are possible is highlighted.¹⁹

Oxygen storage capacity and the speed of oxygen absorption can be evaluated by performing isothermal heating in an oxygen containing atmosphere using TG, an example of which is displayed in Figure 12 which shows the isothermal TG curves for $YBaCo_4O_{7+\delta}$. Maximum oxygen storage capacity for each temperature is reached after the weight change has leveled off. The speed of oxygen desorption can be determined by heating a fully oxygenated sample in an inert/reducing atmosphere isothermally at various temperatures.



 $\label{eq:Figure 12.} Figure 12. Isothermal TG curves recorded at different temperatures for oxygen-depleted $YBaCo_4O_{7+\delta}$ after switching the gas flow from N_2 to O_2.10}$

3 OXYGEN STORAGE MATERIAL YBaCo₄O_{7+δ}

3.1 Material Variety for Oxygen Storage

Oxygen storage materials (OSM) are solid materials that store and release oxygen reversibly. Oxygen storage and release properties of oxygen storage materials are based on elements within the crystal structure that are flexible with their oxidation state. Large, reversible oxidation state changes and oxygen mobility in these materials rely either on crystal defects and interstitial sites creating oxygen ion vacancies for e.g. CeO_2 based materials²⁹ or on reversible phase transitions as with YBaCo₄O₇₊₈³⁰.

Table 3 lists a representative collection of different oxygen storage materials and their oxygen storage capacity in an isothermal oxidation/reduction cycle (initiated by changing the gas atmosphere). The transition metal is the element within the structure which reversibly changes the oxidation state during the oxygen storage and release process in all the materials in Table 3 with one exception, that of $Pr_2O_2SO_4$ -type material³¹ where the sulphur is the element changing the oxidation state. The operational temperatures for these materials can vary from 300 to 700 °C and the oxygen storage capacity (OSC) is between 530 to 8000 µmol-O/g. The materials are listed according to decreasing oxygen storage capacity in Table 3 but it does not automatically mean that the top one is the best option for practical application. Neither are the values of the OSC fully comparable as many experiments have been done in different atmospheres and Table 3 merely provides a general picture of oxygen storage materials under current academic interest.

Material	Temperature (°C)	OSC (µmol-O/g)	Oxidizing Gas	Reducing Gas	Reference
Pd/Pr ₂ O ₂ SO ₄	700	8000	20 %-O2/He	5 %-H ₂ /N ₂	31
Pb2CuSr2LaCu2O8+8	450	3800	100 %-O2	100 %-N ₂	19
$Ce_{2/3}Cr_{1/3}O_{2+\delta}$	550	2500 [*]	-	-	32
BaYMn ₂ O _{5+δ}	500	2300	100 %-O2	5 %-H ₂ /Ar	28
$Dy_{0.7}Y_{0.3}MnO_{3+\delta}$	300	2300	100 %-O2	100 %-Ar	33
YBa(Co _{0.9} Al _{0.1}) ₄ O _{7+δ}	300	2200	100 %-O2	100 %-N ₂	Ш
YBaCo ₄ O _{7+δ}	350	1900	100 %-O2	100 %-N ₂	10
$(Ce_Zr)O_{2+\delta}$	500	1500	50 %-O2/N2	20 %-H ₂ /N ₂	34
CuMnO2	300	530	50 %-O2/He	3 %-H ₂ /He	35

 Table 3.
 Collection of representative oxygen storage materials and their oxygen storage capacities obtained thermoanalytically.

*Determined by using temperature programmed hydrogen reduction (TPR)

The YBaCo₄O_{7+ δ} compound³⁶ possesses unique low-temperature oxygen diffusion and absorption/desorption characteristics.¹⁰ In addition it also has high electrochemical activity^{37,38} and structure-dependent electric^{10,38-40} and magnetic^{38,40-⁴² properties. The unique properties of the YBaCo₄O_{7+ δ} system make this material a promising candidate material for applications requiring high oxygen mobility, high selectivity of oxygen absorption and/or large oxygen storage capacity.¹¹ The material has already been investigated for solid-oxide fuel cell (SOFC) components,⁴³⁻⁴⁶ oxygen separation membranes¹⁴ and ceramic sorbents to enhance the oxyfuel combustion process.^{13,47} In terms of its potential use in future applications, both the oxygen absorption/desorption properties and the phase stability of YBaCo₄O_{7+ δ} are considered to be of the upmost importance.}

3.2 Crystal Structures of Oxygen-Varied YBaCo₄O_{7+δ} Phases

In the YBaCo₄O_{7+ δ} system oxygen content can vary in the range of $0.0 \le \delta \le 1.5$.^{10,II} The structure of the oxygen-stoichiometric $\delta = 0$ phase was determined as hexagonal, space group *P*6₃*mc* (#186), having the cell parameters a = 6.298 Å and c = 10.247 Å, by Valldor *et al.*³⁶ using single crystal X-ray and powder neutron diffraction data. In contrast, Caignaert *et al.*⁴⁰ soon after suggested an orthorhombic symmetry in space group *Pbn*2₁ (#33), with the cell parameters a = 6.298 Å, b = 10.939 Å and c = 10.228 Å, based on powder X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS) data. In both crystal symmetries, $P6_3mc$ and $Pbn2_1$, the structure can be described as consisting two layers of corner-sharing CoO₄ tetrahedra (shown in Figure 13 (a)). The Co1 tetrahedra form a so called *Kagomè* lattice, displayed in Figure 13 (b) These layers are connected to each other by Co2 tetrahedra in a ratio 1:3.³⁶ When the oxygen content is 7 ($\delta = 0$) the mean oxidation state of cobalt is +2.25 which gives a ratio of 1:4 for Co³⁺:Co²⁺. Average bond length calculations show that CoO bonds are shorter in the Co2 (1.898(6) Å) than in the Co1 (1.921(7) Å) tetrahedra, suggesting that the *Co2* site contains relatively more Co³⁺ than the Co1 site does.^{36,42}



Figure 13. Schematic drawing of the (a) layered Y114 structure and (b) kagomè layer illustrated by showing CoO_4 tetrahedrons Co(1) and Co(2). Hexagonal unit cell is shown in (a).

The location of intercalated "excess" oxygen of $\delta > 0$ phase in YBaCo₄O_{7+ δ} has been under investigation since it was first discovered. It has been estimated, based on lattice parameters and ionic radii, that the YBaCo₄O₇ structure possesses enough space to allow extra-oxygen intercalation.¹⁰ In addition, experimental results from in situ XRD and XANES suggest that the oxygen absorption increases the number of different crystallographic sites for cobalt.⁴⁸

In the case where yttrium has been substituted with ytterbium, giving a phase similar to $YBaCo_4O_{7+\delta}$, it has been suggested that the oxygenated phase could comprise of two different phases separated by a miscibility gap.⁴⁹ The minor phase would essentially contain all the excess oxygen and the major phase of this biphasic sample would be really close to stoichiometric $\delta \approx 0$ YBaCo₄O_{7+ δ} phase. This would explain why the crystal structure does not appear to change upon oxygenation when

measured by XRD. Neutron and XRD data refinement comparisons between stoichiometric YBaCo₄O_{7.0} phase and oxygenated YBaCo₄O_{8.1} phase (having space group *Pbc*2₁ (#29) and the lattice parameters a = 12.790 Å, b = 10.845 Å and c = 10.149 Å) have given promising structural projections where the excess oxygen could be located in the YBaCo₄O₇-type structure.³⁰ It has been proposed that the parent structure - which originally has only CoO₄ tetrahedrons - can form a new superstructure of edge-sharing octahedra with the addition of two oxygen atoms. These octahedra form isolated zigzag chains parallel to the c-axis. Figure 14 illustrates the new structure with isolated octahedral columns for the YBaCo₄O_{7+δ} phase.



Figure 14. Kagomé layers for (a) $YBaCo_4O_7$ and (b) $YBaCo_4O_8$. Projection of the $YBaCo_4O_8$ structure along the [100] direction.³⁰

This structure was later verified by using electron diffraction, which showed that excess oxygen forms several types of ordering in the parent lattice depending on the oxygen content.⁵⁰ It was also observed that the extra oxygen has high mobility as it migrated back and forth in the lattice when heated with the ED beam.⁵⁰ An oxygen insertion mechanism with metal-oxygen octahedron formation has been proposed based on Mössbauer experiments performed for a sample phase with 1% ⁵⁷Fe-to-Co substitution.⁵¹ Figure 15 outlines how a single oxygen site can split into three separate sites changing the metal-oxygen tetrahedron to an octahedron.



Figure 15. Schematic of the extra oxygen insertion mechanism into the Kagomé layer of YBaCo₄O₇ structure.⁵¹

3.3 Oxygen-Content Control of YBaCo₄O_{7+δ}

Various synthesis and post-annealing techniques have been developed for precise oxygen-content tailoring of functional transition metal oxides. The most common techniques can be divided into six groups (i-vi). (i) Normal-pressure annealing techniques where either pure oxygen gas followed by an inert gas (N₂ or Ar) or a mixture of these two is used at rather low temperatures to obtain samples with accurately controlled oxygen contents.^{25,52-56} (ii) In the encapsulation technique the partial pressure of oxygen is controlled inside a closed ampoule by means of an oxygen getter^{57,58} or an oxygen generator⁵⁹. (iii) The gas-medium high-pressure technique utilizes special gas compressing systems where the oxygen pressure can be increased to between 300 ~ 500 MPa^{60,61}, (iv) whereas the ultra-high-pressure method uses a solid-medium pressure technique to raise the pressure as high as 8 GPa⁶¹. (v) In the electrochemical technique,⁶² electric potential and (vi) in the chemical technique,^I chemical potential are used as the driving force for the redox reactions at room temperature.

Applying different oxygen engineering techniques for the YBaCo₄O_{7+ δ} phase produces samples with various oxygen contents depending on the oxygenation power of each technique on the studied compound. Table 4 lists oxygenation results for YBaCo₄O_{7+ δ} phase oxygenated using various techniques and conditions. It seems that maximum amount of oxygen that the structure can hold is $\delta \approx 1.5$, which coincides with the cobalt reaching an average valence of 3+. After this point forcing more oxygen into the structure by increasing the partial pressure of oxygen results in the destruction of the parent YBaCo₄O_{7+ δ} structure.^{II} If the maximum density for the YBaCo₄O_{7+ δ} structure is reached at the point when $\delta \approx 1.5$, then the destruction of the structure by increased physical compression through ultra high pressure can be explained by Le Chaterlier's Principle which states that higher pressures promote structures with higher density.

Treatment	δ	Average Co Valence
N ₂ , 1 atm, 500 °C, 2h	0.03	2.27
as-synhesized	0.13	2.32
Br ₂ /H ₂ O, 25 °C, 20h	0.38	2.44
Air, 1 atm, 340 °C, 24h	1.01	2.76
O ₂ , 1 atm, 340 °C, 24h	1.19	2.85
O ₂ , 10 atm, 340 °C, 24h	1.32	2.91
O ₂ , 100 atm, 340 °C, 24h	1.46	2.98
KClO ₃ , $2 \cdot 10^4$ atm, 500 °C, 1h	1.56	3.03

Table 4.Oxygenation conditions with the resultant oxygen contents and average
valence of cobalt for $YBaCo_4O_{7+\delta}$ samples.^{II}

Chemical oxidation with Br_2 was found to be less effective than the techniques which involve the application of elevated pressures. It has been shown that there are two possible rate limiting steps for oxygen permeation in oxides having mixed ionic and electronic conductivity, i.e. bulk diffusion and surface exchange kinetics.⁶³ As YBaCo₄O₇-type phase has mixed ionic and electric conductivity,³⁷ careful electrochemical oxygenation studies of YBaCo₄O_{7+ δ} in alkaline solution were recently performed and the results suggest, that the rate determining step in chemical and electrochemical oxygenation is the bulk diffusion.⁶⁴ Using these oxygenation methods results in a compact crystal structure which prevents the complete oxidation of cobalt ions.⁶⁴ The poor bulk diffusion after a small level of successful oxygenation could explain the ineffectiveness of the chemical oxidation with Br₂.^{II}

3.4 Material-Property Engineering of YBaCo₄O_{7+δ}

The three most important properties for an oxygen storage material are its (i) oxygen absorption/desorption capability, (ii) oxygen mobility and (iii) structural stability.

The YBaCo₄O_{7+δ} phase exhibits these desired capabilities for the first two properties, (i) and (ii), but it is not thermally stable in the temperature range from 550 °C up to 1000 °C in oxygen-containing atmospheres which is needed for many practical applications.^{10,III} Figure 16 shows a typical TG curve for a YBaCo₄O_{7+δ} sample when heated in O₂ flow. The hump marked in part (a) illustrates the absorption/desorption process of oxygen. The amount of absorbed oxygen is relatively high as the oxygen storage capacity (OSC) in Figure 16 is equivalent to ~2100 µmol-O/g, *cf.* commercial oxygen storage material CeO₂-ZrO₂ which has an OSC ≈ 1500 µmol-O/g.³⁴ Unfortunately the hump seen in part (b) arises from full phase decomposition into BaCoO_{3-δ}, Y₂O₃, Co₃O₄ and some unidentified compounds instead of oxygen absorption.^{10,46}



Figure 16. Thermogravimetric curve for $YBaCo_4O_{7+\delta}$ sample heated in an O_2 flow, dotted boxes highlight the (a) oxygen absorption/desorption and (b) phase decomposition humps.

It is possible to systemically study and modify the properties of oxygen storage material.^{III,IV,65,66} The YBaCo₄O_{7+ δ} phase is rather flexible and can accept various

cation substitutions, e.g. Ca and the smaller rare earth elements for $Y^{39,65,67-70}$, and Fe, Ni, Zn Al and Ga for Co^{39,46,66,68,69,71-73III,IV}. Therefore it is possible to devise a number of different approaches using chemical substitution in order to tailor the YBaCo₄O_{7+ δ} phase in order to increase its phase-decomposition temperature for example. The elements which have been used for Co-site substitution are outlined in Table 5 along with their respective ionic valences and ionic radiuses for tetrahedral coordination. Table 5. also gives qualitative estimations, based on TG curves that show the effect of substitution on oxygen absorption property and phase stability. The elements substituted for cobalt (no data for Ni exist) seem to more or less impair the oxygen absorption. However, addition of Zn, Ga and Al improve the stability of the YBaCo₄O_{7+ δ}-type phase under oxygen-containing atmosphere, the exception is when Fe-for-Co substitution takes place as there is a further deterioration in the high phase stability.

 Table 5.
 Elements used for 4-coordinated Co-site substitution and qualitative estimations of their effect for oxygen absorption and phase stability.

Element	Valence	Radius (Å) ⁷⁴	Oxygen uptake	Phase stability	Reference
Fe	II/III	0.63/0.49	worsened	worsened	39,71
Zn	Π	0.60	worsened	improved	39,46,68,71,72
Со	II	0.58	-	-	-
Ni	II	0.55	-	-	73
Ga	III	0.47	worsened	improved	IV ,71
Al	III	0.39	worsened	improved	III,66,69

Systematic substitution studies show that the unit-cell volume of YBaCo₄O_{7+δ} decreases with the Al-for-Co^{III} substitution and increases with the Ga-for-Co^{IV} substitution. As the ionic radius of tetrahedrally-coordinated Co^{III} is just in between those of Al^{III} (0.39 Å⁷⁴) and Ga^{III} (0.47 Å⁷⁴) in tetrahedral coordination then the resultant cell-volume *versus* substitution-level plots for the Al and Ga substitutions are nearly mirror images of each other. In order to see possible cell-volume-change effects, a sample co-substituted by both Al and Ga, i.e. YBa(Co_{1-x}Al_{x/2}Ga_{x/2})₄O_{7+δ} with x = 0.10 was investigated.^{IV} Figure 17 shows that the cell volume of this sample is nearly equal to that of the unsubstituted YBaCo₄O_{7+δ} phase. As seen from the levelling of the cell volume change at $x \approx 0.125$ for Al and $x \approx 0.30$ for Ga in Figure

17 it can be concluded that the solubility limits for the elements are reached for the synthesis conditions used in these experiments.^{III, IV}



Figure 17. Unit-cell volume of YBa(Co_{1-x}(Ga/Al)_x)₄O_{7+ δ} samples plotted against the substitution level *x* of Ga (\blacksquare), Al (o) and their mixture (\blacktriangle).^{IV}

It is clear based on Figure 18 (a) that the phase decomposition is drastically affected by the Al-for-Co substitution. Firstly, the magnitude of the hump decreases rapidly as the Al content increases. At the same time, the onset temperature of the weight gain, i.e. the phase-decomposition temperature, is gradually shifted towards higher temperatures, hence, increasing the Al-for-Co substitution level stabilizes the YBaCo₄O_{7+δ}-type structure. Similarly, as shown in Figure 18 (b), with increasing Ga-substitution level *x* the temperature where the phase starts to decompose under oxygen-containing atmospheres gradually increases with the exception that for $x \ge$ 0.20 no indication of phase decomposition is seen upon heating in 1 atm O₂ up to 1000 °C. The Ga-for-Co substitution stabilizes the YBaCo₄O_{7+δ} structure such that for the x = 0.20 sample no high-temperature hump anymore observed. Since both the Al and Ga substitutions enhance the phase stability we may conclude that the changes in the unit-cell volume most probably do not play any significant role here. To further confirm this Figure 18 (c) shows a flat TG-curve at high temperatures for co-substituted YBa($Co_{1-x}Al_{x/2}Ga_{x/2}$)₄O_{7+ δ} with x = 0.10 sample, which has nearly equivalent unit cell size to that of pristine YBaCO₄O_{7+ δ}. The enhanced phase stability could be due to an entropic effect (i.e. the so-called entropy of mixing⁷⁵) - although this would not explain why Fe-for-Co substitution does not improve the phase stability as would be expected based on lowered free energy level with increased entropy of mixing. Experiments performed so far indicate that the enhanced stability has more to do with chemical properties, such as bonding strength and the oxidation state stability of the substituent rather than its physical size or general laws of thermodynamics. Interestingly, the instability of brownmillerite Sr₂Co₂O₅ was attributed to the instability of trivalent cobalt in tetrahedral oxygen coordination⁷⁶ and this could also be the case with the YBaCO₄O_{7+ δ} phase as phase stability improves when trivalent cobalt is substituted with trivalent aluminum^{III} or gallium^{IV}.



Figure 18. TG curves showing the weight change due to the decomposition at high temperature in an O₂ flow for samples in (a) $YBa(Co_{1-x}Al_x)_4O_{7+\delta}$, (b) $YBa(Co_{1-x}Al_x)_4O_{7+\delta}$, (b) $YBa(Co_{1-x}Al_x)_4O_{7+\delta}$, (c) $YBa(Co_{1-x}A$

Al-for-Co substitution has only a small effect on the oxygen absorption properties as can be seen from Figure 19 (a) as all the TG curves obtained from dynamic heating

in O₂ flow resemble each other. Ga-for-Co substitution on the other hand has a drastic effect on oxygen absorption as shown in Figure 19 (b). Clearly, using gallium as a substituent affects the rate limiting mechanism of the oxygenation process by slowing it down markedly. This effect does not have anything to do with the size of the unit cell as can be seen from Figure 19 (c) where sample YBa(Co₁. $_{x}Al_{x/2}Ga_{x/2})_{4}O_{7+\delta}$ with x = 0.10 behaves according to the Ga substitution shown in Figure 19 (b) and it is possible to force more oxygen in to the Ga-substituted structure by applying high pressure oxygenation than shown in Figure 19 (b).^{IV} The average particle size of Ga-substituted samples (~6 µm) determined by SEM observations to be somewhat larger than that of either the pristine or Al-substituted YBa(Co_{1-x}Al_x)₄O_{7+ δ} samples (~3 µm)^{IV} and this difference in particle size could in theory act as a threshold for the switching between the dominant oxygen absorption rate limiting mechanism. In larger particles the oxygen has to travel relatively longer distances in the crystal structure which would make bulk diffusion the dominant mechanism. This could lead to a more dense crystal structure, as suggested for chemical and electrochemical oxygenation,⁶⁴ bringing any further oxygenation to a halt.



Figure 19. TG curves showing the oxygen absorption/desorption behavior in an O₂ flow for representative samples (a) YBa(Co_{1-x}Al_x)₄O_{7+δ}, (b) YBa(Co_{1-x}Ga_x)₄O_{7+δ} and (c) YBa(Co_{1-x}(Al/Ga)_x)₄O_{7+δ} (x=0.10).

The factors affecting the phase stability in $YBaCo_4O_{7+\delta}$ have been further studied through isovalent cation substitutions at the yttrium site where the Y^{III} ion may be replaced by any of the intermediate- and small-sized lanthanoid ions ranging from Dy^{III} to Lu^{III.65} Replacement of Y^{III} by Dy^{III} or Ho^{III} was found to result in an undesirable increase in the excess-oxygen desorption temperature and a decrease in the phase-decomposition temperature.⁶⁵ On the other hand, the targeted enhancement in phase stability was achieved by replacing Y^{III} with Er^{III}, Tm^{III}, Yb^{III} or Lu^{III}. It was found that decreasing the size of the rare earth constituent (*i.e.* by going from Dy, Ho and Y to Er, Tm, Yb and finally to Lu) resulted in gradually decreased oxygen up take (based on dynamic heating study at O₂ flow) and increased phase decomposition temperature.⁶⁵ Aliovalent substitution is also possible at the yttrium site as trivalent yttrium may be partly substituted by divalent calcium.⁶⁸⁻⁷⁰ With such a substitution the unit-cell volume increases as the Ca^{II} ion is slightly larger than Y^{III,74} however, in this case the phase stability was found to decrease⁶⁹. This difference from the case of isovalent cation substitution was attributed to weakened Coulombic attractions in the cation-oxygen bonding.⁶⁹ In addition, Ca-for-Y substitution is also disadvantageous due to the fact that it depresses the oxygen-absorption capability of YBaCo₄O_{7+ δ}⁶⁹. The elements used for Y-site substitution and their effects for oxygen absorption and phase stability are outlined in Table 6.

Element	Valence	Radius (Å) ⁷⁴	Oxygen up take	Phase stability	Reference
Y	III	0.90	-	-	-
Dy	II/III	1.07/0.91	improved	worsened	39,65,67
Но	III	0.90	improved	worsened	39,39,39,65
Er	III	0.89	worsened	improved	39,65
Yb	II/III	1.02/0.87	worsened	improved	39,65,67
Lu	III	0.86	worsened	improved	39,65,67
In	III	0.80	worsened	worsened	39
Tm	II/III	1.03/0.88	worsened	improved	65
Ca*	Π	1.00	worsened	worsened	68-70

 Table 6.
 Elements used for 6-coordinated Y-site substitution and qualitative estimations of their effect for oxygen absorption and phase stability.

*Ca substitution (x=0.5) includes also Zn at Co site (y=1.5).

4 Li-ion battery electrode material LiFePO₄

An era of constant market growth for portable electronics was launched at the beginning of 90's by Sony's introduction of the Li-ion battery to the consumer markets. The key material for this breakthrough technology, use of LiCoO₂ for the positive electrode, was found by a research group at Oxford led by Professor Goodenough in 1980.¹ Almost two decades later Professor Goodenough introduced another commercially successful positive electrode material LiFePO₄ to the scientific world.⁶ Since then the inexpensive, environmentally friendly and safe LiFePO₄ allowed the use of Li-ion batteries, for example, in power tools and the material is becoming more widely used in large scale battery markets against other positive electrode materials.

One aim for the near future is the development of large scale Li-ion batteries which have more environmentally friendly manufacturing processes and produce easily recyclable batteries. Both of these issues could be improved by using water-based binders which would help to remove the need for the use of (i) toxic organic solvent during the manufacturing process and (ii) fluorine based plastic binder in the battery electrode. As a result an understanding of the processes occurring between LiFePO₄ and H_2O is of great importance for the development of better electrode and battery manufacturing processes.

4.1 Crystal Structure and Electrochemical Characteristics of LiFePO₄

At room temperature the lithium extraction/insertion for the Li_xFePO_4 ($0 \le x \le 1$) system proceeds at around 3.5 V vs. Li^+/Li , in a two-phase reaction between LiFePO₄ and FePO₄. Both of these phases have the same structure with orthorhombic space group Pnma (#62) having unit cell parameters a = 6.008 and 5.792 Å, b = 10.334 and 9.921 Å and c = 4.693 and 4.788 Å, respectively.⁶ Iron is located in the middle of slightly distorted FeO₆ octahedron, phosphorus is in the PO₄ tetrahedra (which are connecting the corner shared FeO₆ octahedron planes) and lithium is located in an edge-sharing LiO₆ octahedra that form one-dimensional Li

chains into the crystal. Schematic drawings for both LiFePO₄ and FePO₄ phases are shown in Figure 20. The equilibrium potential of a single-phase electrode is composition-dependant, whereas that of a two-phase electrode is constant over the entire composition range. Figure 21 illustrates the representative flat charge/discharge potential curves for the Li_x FePO₄ system for the whole range of lithium content and it is these properties that make it an attractive electrode material for Li-ion batteries.



Figure 20. Schematic structure of LiFePO₄ and FePO₄ where octahedra are made by FeO₆, tetrahedra by PO₄ and single rows of free elements illustrate lithium.⁶



Figure 21. Charge and discharge curves for carbon coated LiFePO₄ at 0.1C current.⁷⁷

The Li_xFePO₄ system has a relatively low electric conductivity of $10^{-9}-10^{-10}$ S/cm,^{78,79} however, carbon coating has been shown to improve the electrochemical performance of the material^{77,80,81} and conductivity values up to 10^{-2} to 10^{-4} have been reported⁸². After carbon coating the electrical conductivity is not the limiting step for Li-ion diffusion in the Li_xFePO₄ system.⁸³ A simple shrinking core model was proposed to describe the intercalation of lithium into FePO₄ where lithium proceeds from the surface of the particle towards the two-phase interface.⁶

Figure 22 (a) shows a schematic drawing of the shrinking core model for LiFePO₄/FePO₄ particle. If applied current is constantly increased, at some point a critical phase boundary surface area will be reached where the rate of lithium transported across the interface is not able to sustain the applied current and at this point the cell performance becomes diffusion limited. Figure 22 (b) illustrates this phenomenon by showing how discharge capacity deteriorates with increasing discharge current. The diffusion coefficient for Li in the Li_xFePO₄ ($0 \le x \le 1$) system is in the order of 10^{-14} to 10^{-16} cm²/s depending on the Li content *x*.^{84,85} Li ions have been shown to diffuse one-dimensionally in the tunnels along [010] direction of the crystal lattice.⁸⁶ For this reason defects in the Li site, such as Fe atoms,⁸⁷ damage the cell performance⁸³ as the presence of Fe in the Li site can decrease the Li diffusion coefficient by two to three orders of magnitude.^{88,89}



Figure 22. Schematic representation of the motion of (a) $LiFePO_4/FePO_4$ interface on lithium insertion to a particle of $FePO_4^6$ and (b) rate performance for $LiFePO_4$ electrode ⁹⁰.

4.2 Water Absorption and Stability of LiFePO₄

Recent studies have indicated the following stability issues of LiFePO₄ when the material is (i) heated up to temperatures as low as 200 °C in air^{91,92}, (ii) immersed into water^{8,93,94}, (iii) aged in humid air at room temperature^{8,95} or at elevated temperatures^{24,95,96}, (iv) aged in LiPF₆-containing electrolyte solutions⁹⁷⁻¹⁰⁰. All these studies report some level of degradation in the electrochemical properties of a LiFePO₄ electrode due to the instability of the compound under the conditions studied. Interactions between LiFePO₄ and H₂O are of the upmost interest as water apparently plays a major role in most of the aforementioned deterioration processes^{8,24,93-100} and LiFePO₄, itself, is extremely hydrophilic.⁸

A LiFePO₄ electrode experiences notable capacity losses when stored for extended periods at 25-60 °C in a humid atmosphere. This is attributed to delithiation from the surface due to the reaction between Li and H₂O, but it is also suspected that the deterioration process is somewhat more complicated.⁸ This was recently confirmed to be true as small amounts of a partially hydrated ferric phosphate phase, $\text{Li}_x\text{FePO}_4(\text{OH})_x$, were found in samples aged in humid air at 120 °C.²⁴ The water-driven deterioration mechanism differs from that occurring upon hot air annealing^{91,92} as the irreversible formation of Fe₂O₃ does not occur, which allows almost full regeneration of the LiFePO₄ phase and its electrochemical properties by thermal treatment at 600 °C in an inert atmosphere.⁹⁶ The degradation process is

faster when LiFePO₄ is in contact with liquid water and the formation of a Li_3PO_4 layer on the LiFePO₄ particles has been reported.⁹⁶ Apparently this impurity layer does not significantly affect the electro chemical properties of LiFePO₄-based cells; as estimated capacity losses are only 5 % for water-based electrode manufacturing processes.⁹⁴

The water absorption/desorption process of LiFePO₄ is believed to be reversible within a time scale of few hours.⁸ However, even a small amount of water may cause serious deterioration leading to lower capacities in the actual battery as water reacts with the electrolyte salt of the most common electrolyte solution, LiPF₆.⁹⁷⁻¹⁰⁰ Such problems need to be addressed by either using some additives that inhibit the reaction⁹⁹ or by drying and keeping the electrodes dry before assembling the battery.

Figure 23 displays TG curves recorded for two LiFePO₄ samples - carbon-coated powder and composite electrode powder - using a program where first the sample is annealed at 130 °C in dry air for 2 hours to remove the water absorbed in the sample prior to the experiment. The fact that the 2-hour annealing period was long enough is seen as a clear flattening of the mass curve. For the sake of clarity this level is defined as the zero H₂O-content level of the sample. The next step involved cooling of the sample down to 30 °C in dry air. Here the two LiFePO₄ samples apparently behave differently: the plain powder (with carbon-coating only) absorbs water up to ca. 500 ppm while the composite electrode powder does not show any water absorption at this point. The lack of water absorption by composite electrode powder under low humidity level is attributed to the surface protection of LiFePO₄ particles by the PVDF binder and/or conductive carbon. In the case of the plain LiFePO₄ powder the amount of water absorbed increases upon the lowering of the temperature until it reach saturation at ca. 50 °C. For the both samples the water content increases rapidly over the course of a few minutes when the relative humidity of the surrounding atmosphere is raised to 35% in Step iii. The maximum water content (~1800 ppm determined from the in-situ TG data) for the plain LiFePO₄ powder is in reasonable agreement with the water content values (1000~1500 ppm) reported earlier⁸ for an LiFePO₄ powder which was first kept in 55 % relative humidity but was then transferred for ex-situ water-content measurement (using a commercial water-content analyser).

Figure 23 illustrates how the composite electrode powder absorbs less water than the plain LiFePO₄ powder. The difference is larger than the mass ratio of the additives (10 mass-%) in the composite, suggesting there is some level of surface protection for the composite electrode system even under high humidity. Once the relative humidity level is reduced back to the 1.8 %, the amount of absorbed water clearly decreases (in both samples) but not down to the zero level and this part of the absorbed water that follows the surrounding humidity level is assigned to surface-adsorbed water. The final heating in dry air drops the water level in both samples close to the zero level, showing that the water absorption/desorption process is nearly reversible with the parameters used in the experiment. From the results discussed above, it may be concluded that the amount of absorbed water is – once the temperature is fixed – controlled by the relative humidity level of the surrounding atmosphere.



Figure 23. *In-situ* water absorption/desorption TG curves for LiFePO₄ powder (grey line, (i)) and LiFePO₄ composite electrode powder (black line, (ii)) recorded using Program I (see Experimental Section for details). Dashed line (a) stands for temperature and dotted line (b) stands for relative humidity.^V

In Figure 24, the amount of water absorbed by the sample upon 6-, 12- and 120-min exposure to humid air is plotted against the humidity level. Figure 24 shows how the absorbed water content grows linearly against relative humidity and that the most of the water is absorbed within the first few minutes of humidity exposure.



Figure 24. Amount of water absorbed by the LiFePO₄ composite electrode powder in 6 (■), 12 (□) and 120 (●) minutes upon exposed it to different levels of humidity.

Figure 25 illustrates the effect of partial Mn-for-Fe substitution on the waterabsorption/desorption characteristics of the lithium iron phosphate phase. The water absorption/desorption process is not completely reversible for LiFePO₄ once the process is repeated several times and this can be seen in Figure 25 as a gradual rising of the "zero" baseline for the non-substituted sample (black curve) with increasing number of cycles, indicating irreversible reaction between LiFePO4 and water. The Mn-for-Fe substituted sample (grey curve) behaves somewhat differently; compared to LiFePO₄ it absorbs more water but at the same time the water absorption/desorption process remains reversible over all 13 cycles, indicating that iron plays a major role in the irreversible reaction under the conditions used in the experiment. The irreversible reaction of LiFePO₄ with water lowers the amount of water absorbed in the next cycle meaning that the places for absorbed water to occupy are decreasing and suggests that both the reversible (physisorbtion) and irreversible (chemisorbtion) reactions are happening on the surface of the particles. Divalent iron oxidises easier than divalent manganese when it has octahedral oxygen coordination because of the intra-atomic exchange stabilisation of a highspin $3d^5$ state.¹⁰¹ This could explain at least partly why the Mn-for-Fe substituted powder remains stable against the irreversible reaction involving water. In addition there could also be impurities on the surface of LiFePO₄ grains which are missing from Mn substituted particle surfaces.



Figure 25. Repeated water absorption/desorption cycling TG-curves for LiFePO₄ (black line) and Li(Fe_{0.4}Mn_{0.6})PO₄ (grey line) powder samples.^V

A number of reaction mechanisms have been suggested between water and LiFePO₄,^{8,24,94} including the formation of Li₂CO₃,⁸ Li₃PO₄^{8,94} and ferric Li_xFePO₄(OH)_x which is reversibly decomposed back to LiFePO₄ upon heat-treating the material in an Ar gas flow at 600 °C ²⁴.

4.3 Water-Based Binders for LiFePO₄

The main function of the binder is to bind particles of active material to the current collector. This improves electrical contact and mechanical strength in the electrode which are both vital for the battery operation. Requirements for a good binder are high; it should have properties such as (i) good adhesion to the current collector, (ii) electrochemical stability, (iii) be resistant to the electrolyte, (iv) low required amount, (v) flexible for dimension changes, (vi) give optimal porosity and (vii)

cheap price. The first property (i) is the most important and the last (vii) is the strongest driving force for the research. The conventional binder polyvinylidene fluoride (PVDF) has high adhesion strength and excellent electrochemical stability¹⁰² which have made it the most popular binder for Li-ion battery electrodes. However, it has some drawbacks such as low flexibility and at elevated temperatures it can become swollen or be dissolved by organic electrolytes.¹⁰² Additionally, PVDF needs to be dissolved in an expensive, toxic and volatile solvent N-methyl pyrrolidone (NMP). The industrial price of PVDF (15-18 €/kg) is quite high when compared to the water based binder carboxy methyl cellulose (CMC) which is about one order of magnitude cheaper (1-2 €/kg).¹⁰³

Water soluble binders are in industrial use for manufacturing graphite anodes. The scientific interest towards using water based binders for making cathodes and especially LiFePO₄ electrodes seems to be on the increase as various water soluble binder materials have recently been tested for LiFePO₄ electrodes.^{90,103-111} Table 7 lists these water based binders and their improvements against PVDF binder if found any. The reactivity of LiFePO₄ with water raises some reservations but the capacity losses due to this have been estimated to be at the relatively low level of 5% in the water based electrode manufacturing process.⁹³ It has been demonstrated that the conventional PVDF binder lessens the humidity absorption of the composite electrode^V and recently this type of study was expanded to three different water based binder chemistries: (i) acryle, (ii) polyvinyl alcohol (PVA) and (iii) carboxymethyl cellulose (CMC) based.^{VI}

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Binder	Price vs.	Mechanical properties	Electrochemical	Reference
	PVDF	vs. PVDF	performance vs. PVDF	
CMC	cheaper	higher electrode density	higher capacity retention	90,103,104
				,108
PAA	cheaper	higher electrode density	higher capacity retention	105, 106
WSE	-	higher electrode flexibility	higher capacity retention	107
CMC/PAA	cheaper	-	-	109
SBR/CMC	cheaper	-	-	110
PVA/PEG	-	-	-	111

Table 7.Water based binders tested for LiFePO4 electrodes and their mechanical and
electrochemical improvements against conventional polyvinylidene fluoride
(PVDF) binder.

CMC = carboxymethyl cellulose, PAA = polyacrylic acid, WSE = water soluble elastomer from ZEON Corp., SBR = styrene butadiene, PVA = polyvinyl alcohol, PGE = polyethyl glycol

Figure 26 shows how in the ratio of 90:7:3 (LFP:C:binder) mixed composite electrode powders (black line) behave in humid conditions compared to plain LiFePO₄ powder (gray line). The acryle composite imitates closely the behaviour of the PVDF composite^V. The water absorption capability of PVA composite is somewhere between acryle composite and pure LiFePO₄ powder, however, in contrast the PVA composite desorbs a larger amount of H₂O ending up with approximately the same water content as the acryle composite at a low humidity level. The CMC composite almost doubles the amount of absorbed water compared to plain LiFePO₄ powder resulting from the water absorption capability of CMC.¹⁰³ The absorbed water content in the CMC composite drops to the same level as that observed with the plain LiFePO₄ powder when the relative humidity is lowered to ~1.8% level. This suggests that the absorbed water is only loosely bound in CMC.



Figure 26. In-situ water absorption/desorption TG curves for LiFePO₄ powder (grey line), a) LiFePO₄-acryle composite electrode powder (black line), b) LiFePO₄-PVA composite electrode powder (black line recorded) and c) LiFePO₄-CMC composite electrode powder (black line) Dashed line stands for temperature and dotted line stands for relative humidity.^{VI}

TG and DSC curves were recorded for all the composite electrode powders and for the plain LiFePO₄ powder to determine the stability of the samples when heated in an air flow. The results displayed in Figure 27 show that all the samples have a small and identical mass decrease until \sim 230 °C after which the mass of all

composite electrode powders starts to drop faster than that of LiFePO₄ powder. This highlights the fact that either the binder or the conductive carbon starts to react at this temperature. In contrast plain LiFePO₄ powder reacts strongly at \sim 380 °C and is seen as a rapid rise on the TG curve. The same behaviour is also seen in Figure 28 as a sharp exothermic peak on DSC-curve for all samples.

Interestingly the binder of the composite electrode seems to slightly to affect the exact temperature of the exothermic peak, with a sift of the peak to higher temperature especially visible for PVDF composite sample. At around 600 °C there is large drop in the masses of all the composite samples as shown in Figure 27. The DSC curves also show large exothermic peak suggesting some type of spontaneous reaction as illustrated in Figure 28. As this peak is missing from the curve in Figure 28 (a), it must be connected to the oxidation of either binder, conductive carbon or both. When the TG-curve for plain LiFePO₄ powder was subtracted from the TGcurves of the composite electrodes it left the curves just for binder and conductive carbon mixture. These curves are plotted in Figure 29 and it is clear based on twostep mass drop that; 1) the binders are decomposing first (at 200-400 °C) as the mass drop equals the percentage of binder in original composite (3%) and 2) then the conductive carbon decomposes (400-600 °C) as the mass drop equals the original amount of conductive carbon (7%) in the composite powder. This proves that the all binders studied in this work decompose and evaporate totally when the composite electrode is heated in air, a result that correlates with an earlier study performed on PVDF-based composite.²⁴



Figure 27. TG curves for LiFePO₄ and LiFePO₄-carbon-binder composite electrode powders (binder = PVDF, acryle, PVA or CMC) heated in an air flow.^{VI}



Figure 28. DSC curves recorded in air flow for a) LiFePO₄ and b) LiFePO₄-carbon-PVDF composite electrode, c) LiFePO₄-carbon-acryle composite electrode, d) LiFePO₄-carbon-PVA composite electrode and e) LiFePO₄-carbon-CMC composite electrode powders.^{VI}



Figure 29. Modified TG curves for LiFePO₄-carbon-binder composite electrode powders heated in air flow (binder = PVDF, acryle, PVA or CMC) obtained by subtracting TG curve of plain LiFePO₄ powder sample from the original result.^{VI}

5 CONCLUSIONS

Engineering functional materials requires a rich knowledge of the properties under development. In this work, two functional ceramic materials $LiFePO_4$ and $YBaCo_4O_{7+\delta}$, have been investigated and efforts were made to enhance the material properties through various cation substitutions. Thermogravimetric (TG) measurements provided new and critical knowledge of both materials as a part of this research.

Various oxygenation approaches were employed in order to find the limits of the oxygen-storage capability of YBaCo₄O_{7+ δ}. It was possible to regulate the oxygen content between $0 \le \delta \le 1.5$ in YBaCo₄O_{7+ δ}. The YBaCo₄O_{7+ δ} structure has been shown to be very flexible for elemental substitution and the presence of the Co^{III} at the tetrahedral coordination within the parent lattice is suggested to be the cause of the observed thermal instability in an oxygen containing atmosphere. This thermal stability was improved by replacing part of the Co within the lattice with either trivalent Al or Ga. The systematic study and engineering of YBaCo₄O_{7+ δ} done in this work revealed and improved the limitations of the promising oxygen storage material and demonstrated the power of elemental material engineering for tailoring physical properties of functional materials.

Li-ion battery positive electrode material LiFePO₄ captures significant amounts of H_2O within minutes of exposure to humid air. In the irreversible water-driven deterioration reaction(s) between LiFePO₄ and humid air iron apparently plays a major role. It was found that the reversibility of the water absorption/desorption process could be improved through partial Mn-for-Fe substitution in LiFePO₄. The water absorption process is surface driven for LiFePO₄ and thus can be lessened by making a composite electrode where the binder and conductive carbon cover part of the surface area. The methods developed to study interactions between LiFePO₄-type electrode materials and humid air and the results obtained in this work are highly applicable for both academia and industry working with various Li-ion battery electrode materials.

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