Interfacial phenomena/capacities beyond conversion reaction occurring in nano-sized transition-metal-oxide-based negative electrodes in lithium-ion batteries : a review

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Review on interfacial phenomena/capacities beyond conversion reaction occurring in nanosized transition metal oxide based negative electrodes in lithium ion batteries

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Abbreviations

AEI	Anode electrolyte interphase
AFM	Atomic force microscopy
ALD	Atomic layer deposition
AM	Active material
BET	Brunauer Emmett Teller
CB	Carbon black
CC	Conductive carbon
CMC	Carboxymethyl cellulose
CNT	Carbon nanotubes
CV	Cyclic voltammetry
DEC	Diethyl carbonate
DEI	Desorption electron impact
DMC	Dimethyl carbonate
EC	Ethylene carbonate
EELS	Electron energy loss spectroscopy
EIS	Electrochemical impedance spectroscopy
emf	Electromotive force
ESCA	Electron spectroscopy for chemical analysis
ESI	Electrospray ionization

FFT	Fast Fourier transform
GIC	Graphite-intercalation compounds
GITT	Galvanostatic intermittent titration technique
GNS	Graphene nanosheets
GO	Graphene oxide
HOMO	Highest occupied molecular orbital
HRTEM	High resolution transmission electron microscopy
IR	Infrared
KIT-x	Karlsruhe Institute of Technology (ordered mesoporous material)
LHCA	Layered hydroxide cobalt acetate
LIB	Lithium ion battery
LUMO	Lowest unoccupied molecular orbital
MAS NMR	Magic-angle spinning nuclear magnetic resonance
MICN	Mesoporous interconnected carbon networks
MIONC	Mesoporous iron oxide nanoparticle cluster
MWCNT	Multi walled carbon nano tubes
NAB	Non-aqueous battery
NaFSI	Sodiumbis(fluorosulfonyl)imide
NIB	Sodium ion battery
NMP	N-Methylpyrrolidone
PAA	Poly(acrylic acid)
PC	Propylene carbonate
PEG	Polyethylene glycol
PEO	Poly(ethylene oxide)
PPy	Polypyrrole
QDs	Quantum dots
RAION	Random aggregates of iron oxide nanoparticles
rGO	Reduced graphene oxide
SAED	Selected-area electron diffraction
SEI	Solid electrolyte interphase
SIMS	Secondary ion mass spectrometry
SOC	State of charge
SPI	Solid permeable interface
STEM	Scanning transmission electron microscopy
SWNT	Single-walled carbon nanotubes
TEM	Transmission electron microscopy
TG-MS	Thermogravimetry and mass spectrometry
THF	Tetrahydrofuran
TM	Transition metal
TMO	Transition metal oxide
t ₋	Anionic defect number
t ₊	Cationic defect number
t _e	Electron transference number
VC	Vinylene carbonate
VGCF	Vapor-grown carbon nanofiber
XAS	X-ray absorption spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray powder diffraction
γ-BL	γ-Butyrolactone

Abstract: Nanosized transition metal oxides are of topical interest in current research towards high capacity negative electrodes for rechargeable lithium ion batteries. Schematically, an interaction with Li⁺ via conversion reaction is commonly accepted. However, experimentally observed capacities often exceed significantly the correlating theoretical quantity of

transferred charge carriers based on conversion reaction. The origin of the additional capacity is under intense debate, although the indispensability of interfacial phenomena and material dimensions in the nanometer regime for concrete explanations are widely noticed. Scenarios associated with additional capacities are electrode/electrolyte interphases (SEI,

polymer/gel-like film), additional Li^+ accommodation through reaction with grain boundary phases in nanostructures, interfacial Li^+ accommodation along with charge separation at phase boundaries, or additional Li^+ uptake in unique structural architectures with high specific surface areas that often exhibit an extensive hierarchical meso- and/or nanopore system. In addition, interfacial phenomena are strongly related with battery safety, and hence a topic of highest relevance. Since the number of related articles became intense, this review article provides an up-to-date summary, and a first attempt is made to systematically classify capacity profiles of nanosized transition metal oxides that exhibit additional capacities beyond the theoretical value based on the concept of conversion reaction.

1. Introduction

Confronted with scarcity of fossil fuels and global warming, modern societies conduct intense research on advanced energy storage devices that are able to manage the energy supply from renewable resources, such as solar and wind power. Owing to high energy densities in the range of 650 Wh l^{-1} (210 Wh kg^{-1}), the rechargeable lithium ion battery (LIB) is now the preferred energy storage technology, and subject of intense research and development.^{[1], [2]} Among other factors, phenomena occurring at electrode/electrolyte interfaces significantly affect performance, safety and lifespan of LIBs. Presently, graphite and its modified derivatives are widely employed as LIB negative electrodes. To a smaller extent, amorphous carbons, lithium titanate, or lithium metal alloys based on silicon and tin are also being utilized.^[3]

In addition, nanosized transition metal oxides (TMOs) are identified as a new class of materials that show high potential as negative electrodes. The interaction of Li^+ with nanosized TMOs in the solid state attracted high attention since it was presented by Tarascon's research team in 2000. The observed capacity values were in the range of twice compared to the commonly applied graphite that exhibits a calculated lithium storage capacity of 372 mAh g^{-1} based on a stoichiometry of LiC_6 .^{[4], [5]} Several nanosized TMOs even exceed theoretical capacities of 1000 mAh g^{-1} , such as $\alpha\text{-Fe}_2\text{O}_3$ (1007 mAh g^{-1}), or Cr_2O_3 (1058 mAh g^{-1}).^{[6], [7]} Already earlier literature describes the research on compounds based on transition metals or post transition metals for lithium storage that led to new concepts of lithium uptake and removal,^[8] e.g. Idota et al. (1997, tin based amorphous composite oxide),^[9] or Leroux et al. (1998, $\text{Na}_{0.25}\text{MoO}_3$).^[10]

With particular emphasis on interfacial phenomena, the formation of a solid electrolyte interphase (SEI) is considered as one of the most important processes.

Negative electrodes require low operating potentials down to $\sim 0 \text{ V vs. Li/Li}^+$ for lithium ion storage, hence commonly utilized carbonate based electrolytes are outside of their thermodynamic stability region, leading to electrolyte decomposition, whose products can precipitate on the negative electrode and form a film denoted as SEI.^{[11], [12]} Nowadays, this film is recognized widely as a 3D independent interphase that is essential for proper battery operation.

At the ideal case, the SEI exhibits characteristics such as $t_+ = 1$, and $t_e = 0$ (t_+ : cationic defect number, t_e : electron transference number), thus it is a cationic conductor and electronic insulator with a protective function to prevent further electrolyte decomposition.^{[13], [14], [15]} Safety, Coulombic efficiency, irreversible capacity loss, and cycle life of a battery are strongly determined by SEI factors such as composition, mechanical flexibility, homogeneity, and adhesion to the electrode material.^{[16], [17]} Voltage of SEI formation, its composition, and thickness depend on the ingredients of the electrolyte, current densities, temperature, and the type of electrode material including its possible pretreatment (e.g. surface modifications of carbonaceous materials).^{[18], [19]}

Although interfacial phenomena for negative electrodes based on carbonaceous materials, lithium and alloying materials are intensively investigated, the full picture is still not yet completely clear, and results partially might appear to be contradictory. This is even more true for nanosized TMOs that are supposed to interact with Li^+ through a conversion reaction, schematically illustrated as $\text{TM}_x\text{N}_y + z\text{Li}^+ + ze^- \rightarrow \text{Li}_z\text{N}_y + x\text{TM}$ (TM: transition metal, N: anion).

Several nanosized TMOs (including TMOs in nanocomposites and -hybrid structures) show initial and/or reversible capacities that significantly exceed the correlating theoretical quantity of transferred charge carriers based on conversion reaction. Literature screening revealed a lithium storage capacity excess by 10 - 100 %, also at higher current densities of 34 - 2000 mA g^{-1} during 4 - 100 cycles.^[20] An example for remarkable high additional capacities was reported by our own group for mesoporous FeC_2O_4 that delivered stable reversible capacities of 117 - 221 % higher than the theoretical value (for 100 cycles at various C rates).^[21] The capacity excess is often stated as *over capacity*, *extra capacity*, or even as *super stoichiometric*. However, these terminologies can be misleading, since besides conversion reaction, additional potential lithium storage and capacity providing processes for nanosized TMO/Li systems that contribute to the overall delivered capacity have been identified (as listed below). Therefore, in this article we use to the term *additional capacity*. Furthermore, the schematic character of the conversion reaction needs to be discerned. The exact interaction of nanosized TMOs and further battery compounds with Li^+ (and between them) is still under debate. Also the reversibility of conversion reaction is a point of discussion and determined by several thermodynamic and kinetic factors.^[22] For instance, the classical conversion reaction for Co_3O_4 is stated as $\text{Co}_3\text{O}_4 + 8\text{Li}^+ + 8e^- \rightarrow 4\text{Li}_2\text{O} + 3\text{Co}$, but also subsequent reactions according to $\text{Co} + \text{Li}_2\text{O} \rightarrow \text{CoO} + 2\text{Li}$, or a coexistence of Co_3O_4 and CoO for the following cycles were reported.^[23] A further example is provided by mesoporous Cr_2O_3 electrodes for that a preferred formation of chromium monoxide (CrO_{1-x}) instead of Cr_2O_3 could be evidenced during recharge.^[24] In general, the formation of TM

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particles in the nanometer range after complete conversion of TM_xN_y seems to be an essential aspect for the reversibility of the conversion reaction, since a huge amount of interfacial surface is provided that shows high activity towards decomposition of the surrounding lithium binary matrix (Li_2N_y).^[25]

Although the origin of the additional capacity could not be clarified in detail yet, the indispensability of interfacial phenomena and material dimensions in the nanometer regime for concrete explanations is widely noticed.

Additional capacities have been partially attributed to:

- 1) Formation of electrode/electrolyte interphases (SEI, polymer/gel-like film) based on electrolyte degradation and subsequent processes.^{[20], [26], [27]}
- 2) Capacity providing reactions originating from SEI compounds, e.g. electrochemically catalytic conversion reactions of CO_3^{2-} (the observed additional capacity is attributed to the reduction of C^{4+} in CO_3^{2-} to C^0 and/or other low valence C species).^{[28], [29]} or the reversible reaction of LiOH with lithium leading to Li_2O and LiH (identified for RuO_2 electrodes).^[30]
- 3) Additional Li^+ accommodation through reactions with grain boundary phases in structures with nano-dimensions.^[31]
- 4) Interfacial Li^+ accommodation along with charge separation at phase boundaries.^[32]
- 5) Unique structural architectures that provide additional Li^+ accommodation through high specific surface areas, nanocavities, and interconnected meso- and/or nanopore systems.^{[33], [34], [35]}

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Further sources for additional capacities are stated in literature, such as the intrinsic lithium storage capacity of conductive additives,^{[36], [37]} which are often applied in comparatively large amounts during cell preparation, especially for TMOs with low electronic conductivity e.g. Fe_2O_3 , (generally 15 - 50 % conductive additives, see Table 2). Further aspects regarding the cell preparation protocol need to be considered in the discussion of the overall capacity output. For instance, most laboratory-made cells contain electrolyte in excess, and since processes based on electrolyte degradation have an impact on observed higher capacities/cycle life, the amount of excess electrolyte is also a factor that determines the cycling behavior. Furthermore, electrodes based on nanostructured materials have often very low areal loadings (mg cm^{-2}) that might increase the error when determining the electrode's weight and hence might lead to deviations from the true capacity value.

For the discussion of the overall capacity output of TMO/carbon nanocomposite and -hybrid structures the excellent lithium storage capacity of some carbonaceous materials needs to be considered. For instance, graphene that has attracted more and more attention in the synthesis of TMO/carbon composites and hybrids, exhibits a substantial lithium storage capacity. Concrete values are affected by layer number, spacing between the GNS, defects within the material and functional groups,^[38] and reported to be in the range of 600 - 2042 mAh g^{-1} for the initial discharge capacity and between 540 - 1264 mAh g^{-1} for reversible capacities,^[39] which is higher than the theoretical capacity for several TMOs. Also processes that involve remaining oxygen-containing groups on surfaces of carbon derivatives,^{[40], [41]} as well as synergistic effects between the carbon and the TMO part needs to be regarded. In this context please see section 3.4.6. *Nickel oxide based negative electrodes* where the strong C-O-Ni linkage formed by NiO and oxygenated graphene that supports fast electron hopping from the graphene part to NiO associated with enhanced electrochemical performance against Li/Li^+ as an example for *synergistic effect* is presented.^[42]

As listed above, nanostructural features are often stated in connection with additional capacities. In this context it was pointed out by Su et al. that nanostructures exhibit beneficial characteristics such as large active surface and grain boundary areas, which are supportive for enhancement of Li^+ and e^- diffusion coefficients and improvement of reaction activities, but cannot provide additional active sites for Li^+ storage. Hence, the synthesis of TMOs with nanostructural characteristics is seen as a beneficial tool to get close to theoretical capacity values, but not necessarily to exceed them.^[20] For other additional capacity providing processes, size effects take over an essential role, e.g. for the interfacial Li^+ accommodation along with charge separation at phase boundaries, for which the correlating capacity depends on the grain size in the first place. In this model, the Li_2O surface serves as host for additional Li^+ , and atoms on the TM surface are considered as electron sinks (depending on TM's electronegativity). Since the involved TM and Li_2O phases do not exhibit lithium storage properties in their bulk, it is a *synergistic two phase effect* that allows the additional accommodation of charge carriers (please see section 3.3 *Heterogeneous interfacial accommodation of lithium involving charge separation at phase boundaries*).^{[32], [43], [44]}

The additional capacity is usually ascribed to the sloping voltage curve at low potentials (normally below 0.8 vs. Li/Li^+),^[45] but considering the complex and not yet fully understood reasons for the additional capacity, a partial contribution of higher potential processes cannot be fully excluded. Especially for explanations that are based on film formation (e.g. SEI and subsequent processes of SEI species) some reports state higher voltages. For instance, Kim et al. investigated crystalline RuO_2 powder with TEM at potentials of 2.0, 0.8, and 0.05 V and revealed SEI films at all discharged states (different from graphite samples, where SEI formation takes place at low voltages), suggesting lithium consumption by SEI already starting from 2.0 V for RuO_2 .^[46]

In general, interfacial phenomena and additional capacities for nanosized TMOs as negative electrodes in LIBs have been identified as subjects of intense debates, and precise knowledge about interfacial phenomena is indispensable to design optimized active materials for batteries that meet maximum safety standards.

Hence, this review article is a first attempt to systematically classify and summarize capacity profiles of nanosized TMOs that exhibit additional capacities beyond the theoretical value based on the concept of conversion reaction. For this, literature is analyzed mainly starting from 2000 for oxides of cobalt, iron, manganese, ruthenium, chromium, nickel and copper, including reports about these TMOs in nanocomposite and -hybrid structures. For reasons of comparability, selected milestones in SEI investigations for commonly applied and well investigated negative electrodes (graphite, lithium, lithiated carbons) are briefly and chronologically summarized.

2. SEI for negative electrodes in LIBs - development and state of the art

SEI formation involves electrolyte decomposition whose driving force is the difference of the Fermi energy levels of the positive or negative electrode (their electrochemical potentials μ_c and μ_A), and the position of the HOMO or LUMO of the electrolyte. The energy gap between LUMO and HOMO of the electrolyte is referred as the electrolyte window E_g (Figure 1). If μ_c is located below the HOMO of the electrolyte, and μ_A is located above the electrolyte LUMO, oxidation and reduction processes of the electrolyte will occur until suppressed by SEI formation.^{[2], [12]}

SEI characteristics are different for various negative electrodes (lithium metal, graphite, alloys). For lithium metal, SEIs with inhomogeneous compositions and variations in thickness are reported that lead to locally different lithium depositions through the SEI. As a consequence, dendritic metal deposition occurs and serves as substrate for more inhomogeneous SEI formation. The dendrites can grow into fibers and possibly lead to cell damage by short circuit.^[47]

For layered graphite negative electrodes, basically two types of SEIs that differ in their morphological aspects, chemical composition and function are considered. Graphite is composed of basal plane surfaces and edge (prismatic) surfaces. Ideally, basal planes are homogenous and consist of only carbon, whereas edge surfaces are heterogeneous and show additional oxygen-containing functional groups. Main difference to above

mentioned lithium metal is the accommodation of lithium in the graphite structure, hence the surface in contact with the electrolyte remains stable, and in consequence a stable and protective SEI layer is formed. As a further difference to metallic lithium, the SEI formation on graphite materials occurs in a defined time period (mainly at 1st cycle) and therefore also provides the possibility to be controlled at the 1st cycle.

Figure 1. Relative energies of the electrolyte window E_g and the electrode electrochemical potentials μ_A and μ_c with no electrode/electrolyte reaction for a liquid electrolyte with solid electrodes, V_{oc} : open-circuit voltage ($V_{oc} = (\mu_A - \mu_c)/e$). "Reprinted with permission from J.B. Goodenough, K.-S. Park, The Li-ion rechargeable battery: a perspective, Journal of the American Chemical Society 135(4) (2013) 1167-1176, Copyright © 2017 American Chemical Society".

In contrast, SEIs for alloy negative electrodes need to be more flexible due to the intrinsic strong volume changes of the active material during lithiation and delithiation.^[47]

Several SEI models have been proposed and evolved during the last four decades. For reasons of comparability, selected milestones in SEI investigations for commonly applied negative electrodes are briefly and chronologically summarized:

The term *solid electrolyte interphase* was introduced by Peled in 1979 within studies about the electrochemical behavior of alkali and alkaline earth metals in non-aqueous battery (NAB) systems. By contact of metals with solutions, a layer is instantly formed and consists of insoluble products resulting from reactions of the metal with its surrounding solution. This early work describes the requirement of controlling SEI properties such as cationic defects (t_+), anionic defects (t_-) and the transference number of electrons (t_e) for proper operation of NABs.^[13] Since the described layer exhibited properties of a solid electrolyte, Peled denoted it as *solid electrolyte interphase*,^[13] although over time in some publications the term *solid electrolyte interface* is used, which became also a generally accepted expression nowadays. In more earlier literature the phenomenon of layer formation was also described, but denoted as *passivating layer* (studied on magnesium electrodes in thionyl chloride solutions),^[48] or *insulating film* (studied on lithium electrodes in LiClO_4/PC).^[49]

In Peled's first descriptions, a subdivision of the passivating layer into a thin and compact layer (the SEI) and a more porous

second layer (if exists) on top of the SEI was suggested. Ordered or disordered crystals that are thermodynamically stable with respect to lithium were described to be integral parts of the SEI.^{[13], [50], [51]}

Nazri et al. (1985) investigated the composition of surface films formed on lithium electrodes in LiClO₄/PC with low angle XRD, IR, SIMS, ESCA, and SEM. Chlorine containing polymers and Li₂CO₃ were primarily detected, additionally Li₂O was observed in systems with traces of water. Depth profiling revealed a non-homogeneous structure and concentration gradients across the film for the different components.^{[52], [53]}

Aurbach et al. (1987) studied surface films formed on lithium in PC solutions of LiAsF₆, LiClO₄, and LiSO₃CF₃ with FTIR, XPS, and IR. Lithium alkyl carbonates (RCO₂Li) were mainly detected in the initial films. Systems containing EC showed the formation of lithium ethyl carbonate (CH₃CH₂CO₂Li). In addition, the results indicated that LiAsF₆, LiClO₄ and LiSO₃CF₃ are subjected to reduction processes by lithium, leading to halide ions on the lithium surface. Two possible mechanisms for the formation of alkyl carbonates were described: 1. *Partial reduction involving a single-electron transfer followed by radical termination reactions*, and 2. *the nucleophilic attack on propylene carbonate by OH⁻ generated by the reaction with lithium by trace water*.^[54]

Aurbach et al. (1994) investigated the behavior of lithium electrodes in various salt solutions including LiBr, LiI, LiBF₄, LiPF₆, LiSO₃CF₃, and LiN(SO₂CF₃)₂ in THF and PC. Precipitations of insoluble species resulting from reduction processes, and salt ions trapped in the interphase were observed that strongly affected the surface characteristics, interfacial properties, morphology, and cycling efficiency of lithium in THF and PC. Based on impedance spectroscopy data, Aurbach et al. suggested a multilayer structure (consisting of a compact and a porous part) for the interphase formed on lithium.^[55]

Kanamura et al. (1995) discussed the impact of physicochemical properties of the electrolyte on surface processes for immersed lithium metal. Surface films on lithium in LiBF₄/PC, LiBF₄/γ-BL, and LiBF₄/THF electrolytes were investigated, and LiF and small amounts of organic species were detected for LiBF₄/PC and LiBF₄/γ-BL systems, whereas LiF and large amounts of organic species were found in surface films of lithium immersed in LiBF₄/THF. LiF and organic species are supposed to be formed through reactions of LiOH, Li₂CO₃, and Li₂O with HF, and the interaction between solvent and lithium, respectively. For the latter case, the permeation of the LiF layer by the solvent is necessary, and the authors suggested a dependence of the formation of organic compounds in surface films on the solvent permeability (estimated by surface tension and viscosity). In the discussed study, the LiBF₄/THF has the lowest viscosity and surface tension, leading to a higher permeation rate associated with more pronounced lithium solvent interactions and accumulation of organic species in the surface film.^[56]

Besenhart et al. (1995) studied graphite based LiC_n electrodes in LiClO₄/EC/DMC and pointed out that electrolyte decomposition in systems with lithium/carbon electrodes is a complex three-dimensional incident, and not only confined to surface processes. At potentials in the range of 1.0 - 0.5 V vs. Li/Li⁺, graphite materials form ternary solvated graphite-intercalation compounds (GICs), and as a result massive

expansion of the graphite (>150 %) was observed. Decomposition of the solvated GICs led to the formation of a protective layer on the graphite.^[57]

Aurbach et al. (1999) focused on the structural elucidation of surface films formed on lithium and lithiated carbonaceous electrodes. The observed surface films are complex formations with a multilayer and mosaic-type microstructure, since these electrodes are subjected to various possible surface reactions, including several reduction processes of solution species, secondary reactions between surface compounds and solution compounds, dissolution of surface compounds followed by re-deposition once the saturation point is reached in solution, and also reactions/interactions with water (such as hydration of surface species, diffusion of water through the surface film and water reduction).^[58]

Edström et al. (2006) suggested a strong impact of investigation method, cell design (quality of hermetic sealing), and sample handling on the compounds detected in the SEI (studies were conducted on graphite, LiPF₆/EC/DEC). For instance, the controversially discussed SEI component Li₂CO₃ that have been reported to be the main SEI component, is found to play a minor role or is not detected in graphite SEIs in some cases. Besides explanations based on chemical reactions, (e.g. initially formed Li₂CO₃ reacts with traces of HF, or PF₅ leading to LiF, H₂O and CO₂, or P-O species, CO₂, and LiF, respectively), Edström et al. assumed a dependence of the Li₂CO₃ amount on the moisture level, and for hermetically sealed samples that were never exposed to air, Li₂CO₃ could not be detected. Furthermore, the possibility that Li₂O as SEI compound could be an artifact of Ar⁺ sputtering was discussed. For instance, Li₂O can be generated through Ar⁺ sputtering of Li₂CO₃ (Li₂CO₃ → Li₂O + CO₂).^[59] Also, earlier literature gave a hint on the impact of Ar⁺ sputtering. Kanamura et al. (1995) investigated surface films on lithium immersed in various electrolytes, and observed an intensity decrease of XPS peaks assigned to carbonates after Ar⁺ sputtering for several investigated lithium/electrolyte systems.^[56]

Chattopadhyay et al. (2012) studied the crystal structure of compounds in the SEI of graphene (epitaxial graphene on SiC was utilized as a model system, LiPF₆/EC/DMC). The preferred orientation of crystallites in the SEI is supposed to have an impact on the battery performance, since it might modify the lithium ion diffusion rate to the surface of the electrode through these crystallized components. Chattopadhyay et al. reported LiF as crystallized component in the graphene SEI, whose quantity and vertical domain size increased the higher the lithiation dose. A pronounced texture was found for LiF crystals, and LiF (002) planes are approximately parallel arranged to the graphene sheets of the investigated carbonaceous material. Further results indicated an amorphous character of all other species in the SEI (organic compounds).^[60]

Malmgren et al. (2013) investigated the SEI on lithiated graphite in a balanced full cell configuration using delithiated LiFePO₄ (LiPF₆/EC/DEC). The thickness of the SEI formed on the negative electrode was in the range of two tens of nanometers. Innermost parts included Li₂O and alkoxide compounds, while C-H and C-O containing species were preferentially detected in the outermost part of the SEI. For both, the SEI and the cathode/electrolyte interface (solid permeable interface, SPI),

evidence of an intermixture of SEI/SPI compounds and porous binder could be observed.^[61]

3. Interfacial phenomena and additional capacities for nanosized transition metal oxides as negative electrodes in LIBs

This section starts with a brief general description of the scenarios 1 - 5 (as stated in the introduction part) that are suggested to have a significant contribution to additional capacities observed in nanosized TMO/Li systems. Since the type of TM is found to have a strong impact on interfacial phenomena and additional capacities, and also historically some types of TMOs have been preferentially utilized to investigate a particular phenomenon, detailed presentation of the respective scenarios can be found in the following separate sections for different TMOs. For instance, cobalt oxide, which was one of the first investigated nanosized TMO as negative electrode in LIBs, has been extensively applied to evaluate the formation of the polymer/gel-like film.^[4] Therefore, detailed information regarding polymer/gel-like films can be found in the section 3.4.1 *Cobalt oxide based negative electrodes*. Whereas the heterogeneous interfacial Li^+ storage mechanism along with charge separation was mainly evaluated with ruthenium oxides, hence details regarding this process can be found in the section 3.4.4 *Ruthenium oxide based negative electrodes*.

3.1. Film formation processes on surfaces of negative electrodes based on electrolyte degradation

Chemical and physical phenomena of materials are strongly affected by their particle sizes. The smaller the particle size, the higher is the total number of atoms near the surface, and impact of surface catalyzed processes becomes more and more significant. Due to the intrinsic high surface area of nanosized TMOs, the classical electrolyte degradation is enhanced, leading to a huge amount of inorganic and organic species that form excessive SEI. Consequently, Li^+ can be trapped with substantial 1st cycle capacity loss.^{[62], [63], [64]} Material fractures are potentially caused by expansion and contraction during repetitive lithium uptake and removal, providing new active surfaces for SEI growth. This is associated with consistent consumption of electrolyte compounds and Li^+ , retardation of Li^+ diffusion based on longer distances through thicker SEIs, weakening of electrical contacts between the current collector and the active material due to the electrically insulating nature of the SEI, and destruction of the SEI.^{[65], [66], [67]} Even the possible disappearance of the SEI during electrochemical cycling was reported for several nanosized TMOs. For instance, Balaya et al. observed vanishing of a previously formed SEI for RuO_2 at complete reoxidation (at a potential of 4.3 V),^[68] and Débart et al. reported an organic type layer for CuO of about 3000 Å that vanished for partially reoxidized samples (stopped at 1.6 V).^[69] Hence, conditions leading to more dynamic and flexible SEI layers are preferred, and geometric configuration control of the active material towards stable interphases between electrolyte species and the active material is important for nanosized TMOs.

As initially stated, SEI is often associated with additional capacities observed for TMOs. Common explanations include:

- 1) Excessive Li^+ , which was consumed by the initially formed inhomogeneous SEI, is gradually released after the SEI had sequentially developed and reached a relatively steady state (or after the SEI had decomposed during recharge), reflected in an apparent increase in the reversible capacity.^{[70], [71]}
- 2) Formation of a polymer/gel-like film that exhibits pseudocapacitive character.^[26]
- 3) A direct capacity contribution of SEI species, e.g. CO_3^{2-} that undergoes redox reactions and is reduced to low valence C species,^{[28], [29]} or the reversible reaction of LiOH with lithium leading to Li_2O and LiH (identified for RuO_2 electrodes).^[30]

Already in earlier publications about nanosized TMOs, Tarascon's group described the accompaniment of the interaction between lithium and metal oxides (resulting in metallic nanoparticles finely dispersed in a Li_2O matrix), by the formation of an inorganic solid electrolyte interphase, e.g. SEI (at higher potentials around 0.7 V for CoO/Li cells), similar to processes observed for carbonaceous electrode materials. In addition, the formation and dissolution of a polymer/gel-like film was reported (at lower potentials down to 0.02 V for CoO/Li cells). An additional capacity corresponding to 0.5 - 0.7 lithium was suggested to be associated with the growth of the polymer/gel-like film.^[26]

Nowadays, the terms *SEI* and *polymer/gel-like film* seem to become indistinct, and expressions such as *polymeric-like SEI/polymer-like SEI* are also found in literature.^{[72], [73]} Other reports state that the polymer/gel-like film is confirmed as a SEI film, which is composed of various organic and inorganic species with a protective function. In contrast to other stable SEI compounds, the unstable gel-like one is assumed to reversibly form and decompose open discharge and charge processes along with electron transfer and energy storage at potentials below 0.8 V.^[20] In newer literature, authors have started to clarify the notation of surface films (e.g. SEI or gel-like polymeric film) for their articles.^[22] In general, latest research results regarding film formation processes in nanosized TMO/Li systems revealed a layered structure with an inorganic-rich inner part, and an organic-rich outer part, as for instance investigated for CuO and Fe_2O_3 (and solely true for measurements against Li/Li^+ , since a different situation is found when these materials are applied in Na batteries).^{[22], [74]} For this review article, we use the notations given by the respective authors for detailed presentations of research results about film formation processes.

3.2. Additional lithium accommodation through reactions with grain boundary phases in structures with nano-dimensions

Nanostructured SnMn_3C as one of the most prominent examples for this lithium storage mechanism was presented by Dahn's group. SnMn_3C , considered as inert against lithium, delivered a reversible capacity of 150 mAh g^{-1} ($\text{LiPF}_6/\text{EC/DEC}$) without fading when nanostructured. The applied SnMn_3C particles were composed of grains (~12 nm). The areas between these grains are denoted as *grain boundary*. Atoms in the grain boundary

region are not in regular crystallographic sites, and hence a reactivity towards lithium was suggested. As revealed through XRD, no changes are detected for the grains within the SnMn_3C particles during interaction with lithium (tested after 162 cycles). It was suggested that grain boundaries take over a channel function to let lithium enter the particles of the active material, followed by a reversible interaction with tin atoms located at and within the grain boundaries. This process is believed to deliver the observed (additional) capacity. An analogy to the intercalation process of alkali metals in crystalline fullerenes was suggested, for that the C_n molecules remain unchanged in size or shape, but only reversibly shift apart when an intercalant is added.^[31]

3.3. Heterogeneous interfacial accommodation of lithium involving charge separation at phase boundaries

This lithium storage mechanism was proposed by Jamnik and Maier. The precise mechanism of interfacial storage depends on

Figure 2. Sequence of three different stages of a Li storage, a) Insertion in the bulk of MX, b) if the solubility limit is exceeded a heterogeneous solid state reaction characterised by phase separation occurs, c) finally, the interfacial charging takes place. "Reprinted with permission from J. Jamnik, J. Maier, Nanocrystallinity effects in lithium battery materials, Aspects of nano-ionics. Part IV, Physical Chemistry Chemical Physics 5(23) (2003) 5215-5220, Copyright © 2017 Royal Society of Chemistry."

3.4. Impact of transition metal oxide type on interfacial film formation and additional capacities

Different capacity curve shapes are often observed for various nanosized TMOs vs. Li/Li^+ that show additional capacity occurrences. For further discussion and systematic classification, we have defined 4 types of shapes (Figure 3), representative over a monitored area starting from the 2nd cycle to approximately 50 - 200 cycles. In this review article, *type I (mound-shape)* is used to describe capacity profiles that show an initial increase followed by a decrease with a clear defined capacity maximum. A dependence of the maximum position on

the material characteristics (e.g. particle size, electronegativity, ability for alloy formation with lithium).^[32] In case of TMs finely dispersed in Li_2O , the accommodation of Li^+ occurs at the Li_2O side in the boundary regions, whereas e^- are confined to the TM side. One up to three monolayers of inserted lithium are assumed be stored at an interface of $\text{TM/Li}_2\text{O}$ that is saturated with extra lithium along with transfer of e^- to the TM surface. In this model, the Li_2O surface serves as host for additional Li^+ , and atoms on the TM surface are considered as electron sinks (depending on TM's electronegativity).^[43] This scenario could be compared with an ordinary double-layer capacitor, but exhibit the space charge layer in the inward part rather than on the outer electrode surface (Figure 2).^[32] Since the involved TM and Li_2O phases do not exhibit lithium storage properties in their bulk, it is a *synergistic two phase effect* that allows the additional accommodation of charge carriers.^[44]

the applied C rates (please also see Figure 4) are shown for some nanosized TMO/Li cells with this type of capacity profile.^{[34]. [75]} *Type II (upward-shape)* is used to describe capacity profiles with a continuous capacity raise over the monitored area. *Type III (U-shape)* is used to describe capacity profiles that show an initial decrease followed by an increase in capacity with a clear defined minimum. This shape was previously denoted as *U-shape* by some authors to describe their investigated TMO systems.^[76] *Type IV (horizontal-shape)* is used to describe capacity profiles that show capacities over the theoretical value based on conversion reaction, but a stable

cycling behavior without any significant maximum or minimum over the monitored area.

Figure 3. a) Schematic capacity shape profiles often observed for nanosized TMO/Li systems with additional capacities (representative over a monitored area starting from the 2nd cycle to approximately 50 - 200 cycles), and respective literature examples: b) *Type I*, reversible lithium storage capacity vs. cycle number for KIT-6 mesoporous Co₃O₄ electrode at different C rates. "Reprinted with permission from G. Wang, H. Liu, J. Horvat, B. Wang, S. Qiao, J. Park, H. Ahn, Highly ordered mesoporous cobalt oxide nanostructures: synthesis, characterisation, magnetic properties, and applications for electrochemical energy devices, Chemistry–A European Journal 16(36) (2010) 11020-11027, Copyright © 2017 John Wiley and Sons". c) *Type II*, cycling performance of MnO/graphene hybrid electrode cycled at 200 mA g⁻¹, "Reprinted with permission from Y. Sun, X. Hu, W. Luo, F. Xia, Y. Huang, Reconstruction of conformal nanoscale MnO on graphene as a high-capacity and long-life anode material for lithium ion batteries, Advanced Functional Materials 23(19) (2013) 2436-2444, Copyright © 2017 John Wiley and Sons". d) *Type III*, capacity–cycle number curves and rate performances of MnO MICN and free MnO nanoparticles. "Reprinted with permission from W. Luo, X. Hu, Y. Sun, Y. Huang, Controlled synthesis of mesoporous MnO/C networks by microwave irradiation and their enhanced lithium-storage properties, ACS applied materials & interfaces 5(6) (2013) 1997-2003, Copyright © 2017 American Chemical Society". e) *Type IV*, charge-discharge performance of the electrode made from mesoporous α-Fe₂O₃. "Reprinted with permission from B. Sun, J. Horvat, H.S. Kim, W.-S. Kim, J. Ahn, G. Wang, Synthesis of mesoporous α-Fe₂O₃ nanostructures for highly sensitive gas sensors and high capacity anode materials in lithium ion batteries, The Journal of Physical Chemistry C 114(44) (2010) 18753-18761, Copyright © 2017 American Chemical Society".

3.4.1. Cobalt oxide based negative electrodes

The conversion reactions for cobalt(II) oxide and cobalt(II,III) oxide nanoparticles with Li⁺ are stated as $\text{CoO} + 2\text{Li}^+ + 2\text{e}^- \rightarrow \text{Co} + \text{Li}_2\text{O}$, and $\text{Co}_3\text{O}_4 + 8\text{Li}^+ + 8\text{e}^- \rightarrow 3\text{Co} + 4\text{Li}_2\text{O}$ with correlating theoretical capacities of 715 and 890 mAh g⁻¹, respectively. [77], [78] In practice, capacity values that significantly exceed the theoretical value based on the transfer of two or eight charge carriers are widely reported for the initial cycle and in the long-term. Some cobalt oxide based electrodes that exhibit high first cycle capacities over the theoretical value are for instance Co₃O₄-graphene sheet-on-sheet nanocomposites that showed 1235 mAh g⁻¹ (0.1 C), suggested to be attributed to abundant

nanocavities or defects in graphene nanosheets and Co₃O₄ porous sheets, [33] Co₃O₄ nanocages with an initial discharge capacity of 1150 mAh g⁻¹ (50 mA g⁻¹), attributed to SEI film and possibly interfacial lithium storage, [35] or graphene anchored with Co₃O₄ nanoparticles that delivered an initial discharge capacity of 1097 mAh g⁻¹ (50 mA g⁻¹), possibly ascribed to the high electrochemically active surface areas and/or grain boundary areas. [39]

Additional capacities during long-term cycling for various cobalt oxides, their cycling performance and stated hypotheses for the additional capacities are listed in Table 1.

Table 1. Electrochemical performance against Li/Li⁺ of various cobalt oxide based electrodes with additional capacities beyond the theoretical value based on conversion reaction reported in literature.

Sample	Electrolyte, AM/CC/binder, C	1 st cycle capacity	Long-term cycling	Hypothesis for additional capacity	Ref.
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	rate	[mAh g ⁻¹]	behavior	during long-term cycling	
Mesoporous Co₃O₄ , prepared using KIT-6 silica as hard template, BET: 126.2 m ² g ⁻¹	LiPF ₆ /EC/DMC, 60/30/10, 50 mA g ⁻¹	1760 (lithiation)	<i>type I</i> with maximum at ~1550 mAh g ⁻¹ /20 cycles, (100 cycles presented)	extra active sites for Li storage via high surface area and interconnected porous structures	[34]
Mesoporous Co₃O₄ , BET: 130 m ² g ⁻¹	LiPF ₆ /EC/DMC, 70/15/15, 100 mA g ⁻¹	>1300 (lithiation)	<i>type I</i> with maximum at ~1100 mAh g ⁻¹ /20 cycles, (60 cycles presented)	polymeric surface layer	[79]
Co₃O₄ nanowires , BET: 90 m ² g ⁻¹	LiPF ₆ /EC/DMC, 70/15/15, 100 mA g ⁻¹	~1300 (lithiation)	<i>type I</i> with maximum at ~1100 mAh g ⁻¹ /15 cycles, (60 cycles presented)	polymeric surface layer	[79]
Hierarchical pompon-like Co₃O₄ microspheres , particle size: 20 - 50 μm, consisting of contorted petal-like lamellas with several nanometers in thickness	LiPF ₆ /EC/PC/DEC, 80/10/10, C/10	1286.8 (discharge)	1000 mAh g ⁻¹ /50 cycles, relative stable with slight decrease until 8 th cycle, followed by slight increase up to 20 cycles, followed by slight decrease (52 cycles presented)	gradual release of excessive Li that was consumed by SEI in the initial cycle	[70]
Co₃O₄ microcubes , ~2.37 μm in side length, consist of nanoparticles with 20 - 200 nm in diameter, and 30 - 40 nm in thickness	LiPF ₆ /EC/PC/DEC, 7:2:1, 0.1 C	1298 (discharge)	<i>type I</i> with maximum at 1173 mAh g ⁻¹ /30 cycles, (60 cycles presented), mound-shape vanishes the higher the C rate	Li ⁺ diffusion is activated and stabilized gradually during cycling	[80]
Co₃O₄ porous nanocages , BET: 66.5 m ² g ⁻¹	LiPF ₆ /EC/DEC, 5/3/2, 300 mA g ⁻¹	1557 (discharge)	<i>type I</i> with maximum at 1545 mAh g ⁻¹ /22 cycles, (50 cycles presented)	polymeric gel-like film and mesoporous structure	[81]
Rhombus-shaped Co₃O₄ nanorod arrays , length: ~15 μm	LiPF ₆ /EC/DMC, CC and binder free, 1 C	1192 (discharge)	~1000 mAh g ⁻¹ /20 cycles, relative stable, (20 cycles presented)	more interfacial bonding for extra active sites of Li ⁺ insertion in porous structure	[82]
1D mesoporous single-crystalline Co₃O₄ nanobelts , BET: 36.5 m ² g ⁻¹	LiPF ₆ /EC/DME, 75/15/10, 0.1 A g ⁻¹	1204 (discharge)	980 mAh g ⁻¹ /60 cycles, flat mound-shape that vanishes at higher C-rate (60 cycles presented)	additional accommodation of Li in mesopores and more grain boundaries of nanocrystals for lithium insertion	[83]
Anisotropic Co₃O₄ porous nanocapsules , diameter: ~400 nm, length: ~1 μm	LiPF ₆ /EC/DEC, 80/15/5, 110 mA g ⁻¹	1572 (discharge)	~1000 mAh g ⁻¹ /22 cycles, slight increase until 16 cycles (22 cycles presented)	Unique nanostructure	[84]
Co₃O₄ nano-octahedra , particle size: ~387 nm	LiPF ₆ /EC/DMC/DEC + 2 wt-% VC, 70/20/10, 0.1 A g ⁻¹	1118.5 (discharge)	955.5 mAh g ⁻¹ /200 cycles, <i>type IV</i> (200 cycles presented)	decomposition of irreversible Li ₂ O, polymer/gel-like layer, nano-size and (111) facets that enclose the octahedra	[85]
Triple-shelled Co₃O₄ hollow microspheres	LiPF ₆ /EC/DEC, 5/3/2, 50 mA g ⁻¹	2063.7 (lithiation)	1615.8 mAh g ⁻¹ /30 cycles, <i>type IV</i> (30 cycles presented)	SEI film, or interfacial lithium storage mechanism	[86]
Mesoporous Co₃O₄ , BET: 20.2 m ² g ⁻¹	LiPF ₆ /EC/DEC, 70/20/10, 50 mA g ⁻¹	1732 (discharge)	<i>type I</i> with maximum at 1240 mAh g ⁻¹ /30 cycles (70 cycles presented, 100 mA g ⁻¹)		[87]
Graphene anchored with Co₃O₄ nanoparticles , particle size: 10 - 30 nm for Co ₃ O ₄ , graphene content: ~24.6 wt-%	LiPF ₆ /EC/DMC, 80/12/8, 50 mA g ⁻¹	1097 (discharge)	935 mAh g ⁻¹ /30 cycles, <i>type II</i> with continuous increase (30 cycles presented)	synergistic effect between Co ₃ O ₄ and graphene sheets	[39]
Co₃O₄-graphene sheet-on-sheet nanocomposites , particle size: ~60 nm for Co ₃ O ₄ , Co ₃ O ₄ content: 53.8 %	LiPF ₆ /EC/DEC, 80/10/10, 0.1 C	1235 (discharge)	1065 mAh g ⁻¹ /30 cycles, relative stable, tend towards <i>type IV</i> (30 cycles presented)	structural characteristics	[33]
Graphene-encapsulated mesoporous Co₃O₄ , pore diameter of mesoporous Co ₃ O ₄ : ~3.8 nm	LiPF ₆ /EC/DEC/DMC, 70/15/15, 111 mA g ⁻¹	1298.2 (discharge)	1150 mAh g ⁻¹ /30 cycles, slight increase up to ~15 cycles followed by slight decrease (30 cycles presented)	SEI formation	[88]
3D Co₃O₄/graphene composite films , Co ₃ O ₄ content: 75.3 wt-%	LiPF ₆ /EC/DMC/DEC, CC and binder free, 50 mA g ⁻¹	1285 (discharge)	~1000 mAh g ⁻¹ /50 cycles, <i>type IV</i> (50 cycles presented)	3D porous heterostructure	[89]

Please note: theoretical capacity of nanocomposite and -hybrid structures not clearly defined due to intrinsic lithium storage capacity of carbonaceous materials.

Especially CoO based negative electrodes have been used to investigate the polymer/gel-like layer formation. This interfacial phenomenon is attributed to kinetically activated electrolyte degradation.^{[26], [75]} First investigations were presented by Laruelle et al. using CoO/Li cells (LiPF₆/DMC/EC) cycled at RT. The initial discharge voltage-composition curve of these cells exhibited a voltage plateau of about 2 Li at 0.7 V followed by a voltage drop down to 0.02 V that corresponds to additional 0.5 - 0.7 Li (additional capacity of approximately 150 mAh g⁻¹), (Figure 4). The process at 0.7 V was attributed to the conversion reaction associated with the formation of an inorganic solid electrolyte interphase (e.g. SEI), similarly observed for carbon electrodes. The low voltage process was ascribed to the growth of the polymer/gel-like film that disappears with subsequent charging up to 3 V. Functional groups similar to the SEI layer (investigated via IR) have been detected.^[26] Further investigation of the composition with CoO/Li or SSH/Li cells, (hydrogen-treated Co-free stainless steel substrate) that were pre-treated at 55 °C to generate high quantities of the organic layer, revealed PEG (polyethylene glycol) chains (CH₂-CH₂-O)_n, phosphate-ending PEG-type chains, or polypropylene glycol chains (CH(CH₃)-CH₂-O)_n (n = 1 - 9), and also trimethyl phosphate depending on the applied lithium salts (LiPF₆, LiCF₃SO₃) or solvents (DMC, PC, EC and mixtures of these).^[90] A pseudocapacitive character of the polymer/gel-like layer was suggested based on *I* vs. *V* profile shapes at different discharge and charge cutoff voltage values, and by measuring of *I* as a

function of the scanning voltage rate (*dV/dt*), (for detailed information please see ^[26]).

Grugéon et al. demonstrated a strong temperature-sensitivity regarding the growth of the polymer/gel-like layer. Cycling at 55 °C compared to 20 °C led to capacity enhancement, and to an appearance of a capacity maximum that shifts towards increased cycle numbers the higher the C rate (Figure 4). In detail, multiplication of the cycling rate by two/four leads to a doubling/fourfold increase in the maximum cycle number retention, indicating that the duration of high temperature is critical and that the growth of the polymer/gel-like layer is kinetically governed. The temperature-sensitivity was further confirmed through experiments at 75 °C that showed a progressive capacity increase (1700 mAh g⁻¹/400 cycles) with high reversibility, since a full recovery was possible after a temperature decrease to 20 °C associated with a capacity loss of 33 %. Mass spectroscopy data indicated ring-opening reactions of electrolyte molecules as part of the formation mechanism for the polymer/gel-like layer. The detailed mechanism remained speculative, but the following scenario was assumed: charge transfer of one electron to alkyl carbonates that lead to radical anions. Adsorbed Li⁺ on metallic particles stabilizes the radical anions whose amount increases during reduction and that are supposed to give back solvent or by product species through oxidation at higher potentials, leading to the observed additional reversible capacity.^[75]

Figure 4. (l) Voltage-composition profile for a CoO/Li cell cycled at a C/5 rate between 3 and 0.02 V. A 1 cm² plastic laminate disk containing 6 mg of CoO (15 % of carbon) was used as the positive electrode. Numbers 1 and 2 refer to the two different electrochemical domains. "Reprinted with permission from S. Laruelle, S. Grugéon, P. Poizot, M. Dolle, L. Dupont, J. Tarascon, On the origin of the extra electrochemical capacity displayed by MO/Li cells at low potential, *Journal of the Electrochemical Society* 149(5) (2002) A627-A634, Copyright © 2017 The Electrochemical Society. (r) 55 °C capacity retention of CoO/Li cells as a function of the cycling rate when cycled between 0.02 and 3 V, "Reproduced from S. Grugéon, S. Laruelle, L. Dupont, J.-M. Tarascon, An update on the reactivity of nanoparticles Co-based compounds towards Li, *Solid State Sciences* 5(6) (2003) 895-904, Copyright © 2017, published by Elsevier Masson SAS. All rights reserved".

Yuan et al. demonstrated a sensitivity of SEI formation towards the particle size of Co₃O₄ and further impact on the electrochemical performance (test series with Co₃O₄ of 15 nm to 51 nm). In detail, 15 nm particles showed a first charge capacity of 988 mAh g⁻¹, but a 3.3 % fading per cycle, whereas 37 nm

particles showed 931 mAh g⁻¹, but lesser fading of 0.1 % per cycle (LiClO₄/EC/DEC, tested between 3.0 and 0.01 V vs. Li/Li⁺ at a rate of C/5 up to 20 cycles). These results were attributed to differences in SEI formation. The smaller the particles, the faster the SEI is formed, and the subsequent decomposition is possibly

accelerated for small-ranged particles. A more pronounced SEI formation leads to thicker layers around the particles, which blocks the interaction with lithium followed by more pronounced capacity fading. In this work, the optimized particles size for the best electrochemical performance was found to be 37 nm.^[91]

Sun et al. presented the electrochemical performance of 3D hierarchically mesoporous Co_3O_4 hollow spheres (LiPF₆/EC/DMC), and demonstrated the stabilization of SEI and restructuring of structural features by high-rate lithiation-induced reactivation. This process is understood as a refinement of porous active materials in combination with SEI optimization. For the presented mesoporous Co_3O_4 , a pronounced capacity fading from 827 to 246 mAh g^{-1} ($1.0 \text{ A g}^{-1}/90$ cycles) was observed, attributed to mechanical degradation and formation of excessive unstable SEI (~50 nm thickness, with cracks) that consumed Li^+ and enlarged diffusion ways (Figure 5). Hereinafter a continuous capacity recovery (>300 % at 500 cycles) was observed, attributed to high-rate lithiation-induced reactivation that involved a refinement of the material structure towards 3D hierarchically

amorphous nanospheres with a more open mesoporous system. The refined structure exhibited larger pore sizes and consisted of flower-like nanosheets. As driving force for this process, the nanoscale Kirkendall effect based on different diffusion rates of the involved elements (relatively slow-moving oxygen in Li_2O , and faster-diffusing cobalt in cobalt nanograins) is stated. Particularly, the conversion reaction of Co_3O_4 and Li^+ leads to a nanocomposite structure of Co finely dispersed in Li_2O associated with strong volume expansion. The subsequent delithiation process induces a contraction of the active material, but resulted in spheres that exhibited a larger volume compared to the starting material, and more free volume was generated. Associated increase and/or accumulation of the mesopores resulted in interconnected nanosheets with flower-like shape. The new lithiation-tailored structure exhibited high volume expansion buffer capabilities and an optimized SEI could be formed (~15 nm in thickness) with high stability against volume changes, resulting in the observed enhanced rate performances without capacity fading over 7000 cycles.^[92]

Figure 5. Lithiation-induced reactivation, a) schematic evolution of mesoporous hollow spheres and SEI formation on long-term cycling, b) lithiation-induced reactivation process and cycling performance, c) and d) SEM images of synthesized Co_3O_4 electrodes before cycling, e) and f) SEM images after 90 cycles and removal of the inorganic SEI, g) and h) SEM images after 850 cycles and removal of the inorganic SEI, (SEI removal was done with acetonitrile, ethanol, methanol and water), Scale bars: 200 nm for c, e, and g; 100 nm for d, f, and h. "Reprinted with permission from H. Sun, G. Xin, T. Hu, M. Yu, D. Shao, X. Sun, J. Lian, High-rate lithiation-induced reactivation of mesoporous hollow spheres for long-lived lithium-ion batteries, Nature communications 5 (2014), Copyright © 2017 Nature publishing Group".

3.4.2. Iron oxide based negative electrodes

The conversion reactions for iron(III) oxide and iron(II,III) oxide nanoparticles with Li^+ are stated as $\text{Fe}_2\text{O}_3 + 6\text{Li}^+ + 6\text{e}^- \rightarrow 2\text{Fe} + 3\text{Li}_2\text{O}$, and $\text{Fe}_3\text{O}_4 + 8\text{Li}^+ + 8\text{e}^- \rightarrow 3\text{Fe} + 4\text{Li}_2\text{O}$ with correlating theoretical capacities of 1007 and 928 mAh g^{-1} , respectively.^[93] Iron oxide based electrodes are well known for additional capacity occurrences at the initial cycle and in the long-term. Some iron oxide based electrodes that show high first cycle capacities over the theoretical value and corresponding hypotheses are for instance $\alpha\text{-Fe}_2\text{O}_3$ nanotubes that delivered an initial discharge capacity of 1415 mAh g^{-1} (100 mA g^{-1}), which

was attributed to the higher proportion of atoms on the surface of the nanostructure (higher electrochemical activity compared to the bulk material).^[6] 3D rGO/MWCNTs/ Fe_2O_3 ternary composites that exhibited an initial discharge capacity of 1692 mAh g^{-1} (1000 mA g^{-1}) were presented by Liu et al. The high capacity value was attributed to SEI formation, a synergistic effect among the composite parts, and partially due to reduction of residual oxygen-containing groups.^[95] Additional capacities during long-term cycling for various iron oxides, their cycling performance and stated hypotheses for the additional capacities are listed in Table 2.

Table 2: Electrochemical performance against Li/Li⁺ of various iron oxide based electrodes with additional capacities beyond the theoretical value based on conversion reaction reported in literature.

Sample	Electrolyte, AM/CC/binder, C rate	1 st cycle capacity [mAh g ⁻¹]	Long-term cycling behavior	Hypothesis for additional capacity during long-term cycling	Ref.
Macroporous α-Fe₂O₃ submicron spheres , BET: 501 m ² g ⁻¹	LiPF ₆ /EC/DEC, 70/15/ 5 wt-% CMC/ 1 wt-% PAA, 1 C	<1400 (discharge)	1600 mAh g ⁻¹ /80 cycles, <i>type II</i> with maximum at 80 cycles followed by decreasing trend (100 cycles presented)	pseudocapacitive polymeric gel-like film within the hollow and porous nanostructures	[96]
Hollow type α-Fe₂O₃ submicron spheres , BET: 468 m ² g ⁻¹	LiPF ₆ /EC/DEC, 70/15/ 5 wt-% CMC/ 1 wt-% PAA, 1 C	<1250 (discharge)	1080 mAh g ⁻¹ /100 cycles, <i>type II</i> (100 cycles presented)	pseudocapacitive polymeric gel-like film within the hollow and porous nanostructures	[96]
Mesoporous α-Fe₂O₃ nanostructures , BET: 128 m ² g ⁻¹	LiPF ₆ /EC/DMC, 50/40/10, 200 mA g ⁻¹	1730 (discharge)	1293 mAh g ⁻¹ /50 cycles, relative stable, <i>type IV</i> (50 cycles presented)	mesoporous structure	[93]
α-Fe₂O₃ multi-shelled hollow microspheres , BET: 43.2 m ² g ⁻¹	LiPF ₆ /EC/DMC, 60/30/10, 50 mA g ⁻¹	2345 (discharge)	1702 mAh g ⁻¹ /50 cycles, <i>type IV</i> (50 cycles presented)	polymeric electrolyte interphase (SEI), and additional interfacial Li storage mechanism	[97]
Porous α-Fe₂O₃ nanorods , particle size: 30 - 60 nm, BET: 11.76 m ² g ⁻¹	LiPF ₆ /EC/DMC, 40/40/20, 0.1 C	1647 (discharge)	1275 mAh g ⁻¹ /30 cycles, <i>type IV</i> (30 cycles presented)	porous structure provides more sites for lithium ion insertion/extraction	[98]
Porous α-Fe₂O₃ , length: ~1.2 μ m, diameter: ~400 nm, BET: 137.58 m ² g ⁻¹	LiPF ₆ /EC/DMC, 50/40/10, 50 mA g ⁻¹	2234 (discharge)	1094 mAh g ⁻¹ /50 cycles, tend towards <i>type IV</i> with slight capacity fading (50 cycles presented)		[27]
1D hollow α-Fe₂O₃ electrospun nanofibers , BET: 25 m ² g ⁻¹	LiPF ₆ /EC/DEC, 30/50/20, 0.06 C	1795 (discharge)	1293 mAh g ⁻¹ /40 cycles, <i>type IV</i> (40 cycles presented)	extra Li storage via a nonfaradaic mechanism (pseudo-capacitance), interfacial reaction due to charge separation at the metal-Li ₂ O phase boundary, and polymeric layer	[99]
Electrospun α-Fe₂O₃ nanorods , (sample contains 8 % γ -Fe ₂ O ₃), particle size: 150 nm, BET: 27.6 ($\pm$ 0.2) m ² g ⁻¹	LiPF ₆ /EC/DMC, 70/15/15, 50 mA g ⁻¹	1515 ($\pm$ 20) (discharge)	1095 mAh g ⁻¹ /50 cycles, <i>type IV</i> (50 cycles presented)	morphological characteristics	[100]
Mesoporous Mn doped α-Fe₂O₃ nanorods , length: 1 - 2 μ m, diameter: 20 - 80 nm	LiPF ₆ /EC/DMC/DEC, 60/25/15, 500 mA g ⁻¹		1100 mAh g ⁻¹ /400 cycles, <i>type III</i> with minimum at ~100 cycles (400 cycles presented) <i>U-shape</i> often found for Mn containing electrodes (please see Table 3)	SEI layer, lithium insertion reaction in acetylene black, and interfacial storage	[36]
α-Fe₂O₃@rGO, core/shell composite , BET for α -Fe ₂ O ₃ : 47.84 m ² g ⁻¹ , graphene content: 30 wt-%	LiPF ₆ /EC/DMC/DEC, 80/10/10, 100 mA g ⁻¹	1089 (discharge)	1787.27 mAh g ⁻¹ /90 cycles, <i>type II</i> (90 cycles presented)	faradaic contribution from side reactions with electrolyte, SEI formation	[101]
Fe₂O₃ particles enwrapped by graphene , graphene content: 30 %	LiPF ₆ /EC/EMC/DMC, 80/10/10, 50 mA g ⁻¹	1561 (discharge)	1069 mAh g ⁻¹ /50 cycles, <i>type IV</i> (50 cycles presented)	remaining oxygen-containing groups on rGO surface, accessible sites on graphene for Li insertion/extraction, and interfacial lithium storage	[40]
Fe₂O₃/graphene composites , particle size for Fe ₂ O ₃ : ~1 μ m, graphene content: 27.3 wt-%	LiPF ₆ /EC/EMC/DMC, 80/10/10, 50 mA g ⁻¹	1538 (discharge)	1092 mAh g ⁻¹ /50 cycles, <i>type IV</i> (50 cycles presented)	decomposition of electrolyte and SEI formation, electrochemical reduction of remaining oxygen-containing groups on GO surface	[41]
α-Fe₂O₃@graphene core@shell nanostructures , thickness of GNS shells: ~2 - 10 nm, Fe ₂ O ₃ content: 80 %	LiPF ₆ /EC/DMC, 80/10/10, 200 mA g ⁻¹	1433.6 (discharge)	1040 mAh g ⁻¹ /180 cycles, <i>type IV</i> (100 cycles presented, 200 mA g ⁻¹)	polymeric layer (SEI), and Li insertion/desertion of GNSs.	[102]
α-Fe₂O₃/C nanocomposites , crystallite size: 20 - 40 nm, carbon content: 10.5 wt-%	LiPF ₆ /EC/DEC, 30/50/20, C/2	1858 (discharge)	2112 mAh g ⁻¹ /100 cycles, tend towards <i>type II</i> with capacity raise starting from ~40 cycles (100 cycles)	gel-like layer	[103]

Graphene-wrapped Fe₃O₄, BET: 53 m ² g ⁻¹ , graphene content: 13.3 wt-%	LiPF ₆ /EC/DMC/EMC, 80/10/10, 35 mA g ⁻¹	900 (charge)	presented) 1026 mAh g ⁻¹ /30 cycles, <i>type II</i> (with slight capacity increase, 30 cycles presented)	polymeric gel-like film	[104]
Hollow porous Fe₃O₄ beads– reduced graphene oxide composites, BET: 53.7 m ² g ⁻¹ , rGO content: ~19.0 wt-%	LiPF ₆ /EC/DEC/DMC, 80/10/10, 100 mA g ⁻¹	1233 (discharge)	1039 mAh g ⁻¹ /170 cycles, <i>type II</i> with slight capacity increase (170 cycles presented)	polymeric gel-like film	[105]
Hierarchically structured Fe₃O₄/carbon micro-flowers, BET: 61 m ² g ⁻¹ , carbon content: 12.2 wt-%	LiPF ₆ /EC/DMC/DEC, 75/15/10, 0.2 C	1502 (discharge)	1030 mAh g ⁻¹ /80 cycles, <i>type IV</i> (150 cycles presented)	polymeric gel-like film	[106]

Please note: theoretical capacity of nanocomposite and -hybrid structures not clearly defined due to intrinsic lithium storage capacity of carbonaceous materials.

A stable and homogenous SEI is a key factor towards beneficial electrochemical performances of nanosized TMOs. Carbon coatings, or specific controlling of electrode material's geometry are effective and well-investigated options to induce SEI formation with enhanced stability and homogeneity. In general, SEI layers on hard carbons are known to be stable, and can retard the formation of extensive SEI.^{[7], [107], [108]} Zhang et al. presented Fe₃O₄ nanospindles with carbon coating (~428 nm in length, and ~100 nm in diameter for the coated Fe₃O₄) that exhibited enhanced stability of SEI and superior electrochemical performance over pure iron oxides (LiPF₆/EC/DMC/DEC). Whereas the total thickness of outer carbon layer and SEI film was ~10 nm in the fully lithiated and delithiated states, without any significant alterations during charge/discharge processes, the pure α-Fe₂O₃, (here used as starting material to synthesize carbon coated Fe₃O₄) showed more pronounced SEI formation with variation in thickness, viz. 20 - 50 nm for the fully lithiated, and 0 - 20 nm for the delithiated samples.^[64]

An example for successful geometry control towards stable SEIs was presented by Lee et al. A bottom-up self-assembly method, involving the thermal decomposition of iron-oleate-complex, and

the stabilization of Fe₃O₄ nanoparticles with oleic acid was applied to obtain mesoporous iron oxide nanoparticle clusters (MIONCs) with carbon coating (7.7 % carbon). These MIONCs showed a specific surface area of 55.4 m² g⁻¹ and a uniform pore size distribution with an average size of 3.5 nm, and mesopores of ~40 nm among the clusters. Each composite particle is tightly surrounded by other particles, confining the SEI formation to the outer surface, and a thin SEI layer is exclusively formed on the individual surfaces on the clusters, leading to superior electrochemical performance, as demonstrated by high cycling stability up to 100 cycles and Coulombic efficiencies of 99.7 % after several cycles. The thin SEI layer and morphology could be preserved during repetitive lithiation/delithiation as revealed by TEM and SEM. In comparison, random aggregates of iron oxide nanoparticles (RAIONs) exhibited a higher surface area in contact with the electrolyte, leading to an intensive SEI that was subjected to shrinkage and breakage during lithiation/delithiation. Hence, additional surface was exposed to the electrolyte, which triggered further SEI formation (Figure 6).^[66]

Figure 6. Schematic illustration of SEI formation on a) MIONCs and b) RAIONs, Various states of MIONCs and RAIONs after 1 and 20 cycles. SEM images of MIONCs c) and RAIONs f) after 1 cycle. In MIONCs electrode, SEI was formed on outer surface of active materials, high magnification SEM images of MIONCs d) after 20 cycles. Certainly, the SEI was formed on the outer surface regions and SEI layer retained their initial morphology. On the contrary, the SEM images of RAIONs g) showed that they were buried in SEI and carbon additive and hard to distinguish since excessive SEI formation had been occurred. Low magnification SEM images of MIONCs e) and RAIONs h) after 20 cycles with selective SEI etching. "Reprinted with permission from S.H. Lee, S.-H. Yu, J.E. Lee, A. Jin, D.J. Lee, N. Lee, H. Jo, K. Shin, T.-Y. Ahn, Y.-W. Kim, Self-assembled Fe_3O_4 nanoparticle clusters as high-performance anodes for lithium ion batteries via geometric confinement, *Nano letters* 13(9) (2013) 4249-4256, Copyright © 2017 American Chemical Society".

Tian et al. investigated the composition and evolution of SEI films formed on $\alpha\text{-Fe}_2\text{O}_3$ (sample contained also small amounts of Fe_3O_4) thin-film model electrodes during the first cycle of

lithiation/delithiation (LiClO_4/PC). Mainly Li_2CO_3 , and minor ROCO_2Li were detected. This composition was found to be stable, but the SEI thickness drastically increased/decreased

during lithiation/delithiation. EIS and XPS surface analyses indicated the formation-start of SEI already at ~ 1.2 V after intercalation of Li^+ into Fe_2O_3 and formation of $\text{Li}_{1.03}\text{Fe}_2\text{O}_3$ (evidenced by XRD). This observation was rather unexpected, since SEI formation is commonly assumed to occur around the potential of conversion reaction (here ~ 0.75 V). At the end of lithiation (0.01 V) the SEI was increased to at least 15 nm.^[109] Further investigations by the same group over multi-cycling revealed a SEI composition of principally Li_2CO_3 , ROCO_2Li and/or RCH_2OLi . Also, penetration of the SEI layer into the bulk electrode material upon repetitive charge/discharge associated with cumulative trapping of Li^+ was reported. These processes led to irreversible swelling of the material, which caused morphological changes that are non-uniformly distributed over the electrode surface in the nanoscopic scale, and supported at defect sites of the metal surface substrate, which contributed to decreased electrochemical performance.^[110]

Philippe et al. studied and compared SEI characteristics for nanostructured Fe_2O_3 in lithium and sodium half-cell configuration ($\text{XCIO}_4/\text{EC}/\text{DEC}$, $\text{X} = \text{Li}$, or Na). The SEI was formed gradually during the first lithiation or sodiation, respectively. Whereas sodium electrodes established a pre-deposited layer (<5 nm) simply by electrolyte-contact, this behavior was absent for lithium electrodes. In general, sodium cells showed a more pronounced SEI formation with a thickness of $\sim 7 - 8$ nm at the end of sodiation. In contrast, $\sim 4 - 5$ nm SEI thickness was found for lithium cells. Composition investigations revealed alkoxides, alkyl carbonates, ROCO_2X , RCOOX , carbonates (X_2CO_3), and PEO chains for both, lithium and sodium cells, but different amounts for some SEI species, e.g. a higher proportion of hydrocarbons ($-(\text{CH}_2)_n-$) for lithium cells, and higher amounts of carbonates, alkyl carbonates and CO-rich compounds such as PEO chains and/or ROX for sodium cells (as analogue for lithium and sodium batteries with hard carbon electrodes). In addition, the authors pointed out that the layered SEI structure formed for lithium cells (inner inorganic and outer organic part) is deviating for sodium cells. Although both systems showed an inner part that is rich in X_2CO_3 , a more homogeneous distribution of species instead of a layered structure was detected for sodium systems as demonstrated in Figure 7.^[74]

Figure 7. Schematic drawing of the SEI formed on composite $\text{Fe}_2\text{O}_3/\text{CB}/\text{CB}$ electrodes when cycled in Li- or Na-half-cells with similar electrolytes (i.e.,

XCIO_4 with $\text{X} = \text{Li}$, or Na) and analogous voltage ranges (i.e., 0.05 - 2.80 V vs. Li/Li^+ and vs. Na/Na^+). "Reprinted with permission from B. Philippe, M. Valvo, F. Lindgren, H.K. Rensmo, K. Edström, Investigation of the Electrode/Electrolyte Interface of Fe_2O_3 Composite Electrodes: Li vs Na Batteries, Chemistry of Materials 26(17) (2014) 5028-5041,^[74] Copyright © 2017 American Chemical Society".

3.4.3. Manganese oxide based negative electrodes

The various oxidation states of manganese oxide species, such as manganese(II) oxide (MnO), manganese(III) oxide (Mn_2O_3), manganese(IV) oxide (MnO_2), and manganese(II, III) oxide (Mn_3O_4), contribute to the fact that manganese oxides for lithium storage are under intense discussion.^[111] Assuming an interaction with Li^+ according to the classical conversion reaction, the corresponding theoretical capacities are calculated to 755 mAh g^{-1} for MnO , 1019 mAh g^{-1} for Mn_2O_3 , 1233 mAh g^{-1} for MnO_2 , and 937 mAh g^{-1} for Mn_3O_4 .^[111] Experimentally, these values are hardly matched due to several drawbacks such as very low conductivities (e.g. $\sim 10^{-7} - 10^{-8} \text{ S cm}^{-1}$ for Mn_3O_4),^[78] and huge volume changes during lithium uptake/release associated with pulverization of active materials and weakening of electric contacts.^[113] Fang et al. investigated electrode reactions of MnO , Mn_2O_3 , MnO_2 , and Mn_3O_4 between 0.0 and 3.0 V vs. Li/Li^+ ($\text{LiPF}_6/\text{EC}/\text{DMC}$) through XRD and HRTEM, and concluded that Mn and Li_2O are the final products of the initial discharge, whereas MnO is identified as the resulting product of recharge for all the investigated manganese oxide types in this test series.^[111] This might contribute to the fact that theoretical capacities based on conversion reaction or even additional capacity phenomena are hardly observed for pure manganese oxides in experiments. However, modification with carbon derivatives towards manganese oxide/carbon nanocomposite and -hybrid structures, especial compounds with N-doped carbon derivatives can immensely enhance the electrochemical performance against Li/Li^+ . Besides the well-known positive impact of carbonaceous species on the electrochemical performance of nanosized TMOs (for detailed discussion please see ^[38]), the reoxidation of Mn^{2+} to higher oxidation states was reported in the presence of carbon for amorphous MnO_x -carbon nanocomposites, whereas absent for crystalline MnO_x .^[76] Similar effects were also reported by Zhong et al. who investigated MnCO_3 /large-area graphene composites ($\text{LiPF}_6/\text{DMC}/\text{EMC}/\text{EC}$) with super-long cycle life. The presented samples showed an initial capacity of 880 mAh g^{-1} and a stable capacity of $\sim 1450 \text{ mAh g}^{-1}$ at 200 mA g^{-1} for 200 cycles. The capacity was continually rising during galvanostatic measurements and analogically observed when tested at higher rates of 500 mA g^{-1} . The increase in capacity was ascribed to re-oxidation processes of Mn^{2+} in MnCO_3 to higher oxidation states.^[114]

Especially the synergy effect of N-doping and C-hybridization was reported to lead to ultrahigh capacities, possibly attributed to defect formations by N-doping and formation of Mn-N bonds that are supposed to play a crucial role in enhancing the electrochemical performance.^[115] For instance, Chen et al. reported superior lithium storage performance for nanoscaled MnO promoted by N-doped carbon webs of 1268 mAh g^{-1} at 700 cycles (1.0 A g^{-1} , $\text{LiPF}_6/\text{EC}/\text{DEC}$). The pyridinic N (polypyrrole webs were applied as template and precursor) is essential for

the enhanced lithium storage capacity of the final product, and reversible binding of Li⁺ with pyridinic N with nearly full extraction during delithiation was found.^[116] In contrast to pure manganese

oxides, their nanocomposites or -hybrids with carbon or N-doped carbon, show additional capacity phenomena during cycling as listed in Table 3.

Table 3. Electrochemical performance against Li/Li⁺ of various manganese oxide based electrodes reported in literature.

Sample	Electrolyte, AM/CC/binder, C rate	1 st cycle capacity [mAh g ⁻¹]	Long-term cycling behavior	Hypothesis for additional capacity during long-term cycling	Ref.
Interconnected porous MnO nanoflakes , layer thickness: ~300 nm	LiPF ₆ /EC/DEC/EMC, 246 mA g ⁻¹	810.9 (discharge)	645.8 mAh g ⁻¹ /100 cycles, slight increase up to 70 cycles (100 cycles presented)		[117]
Spongelike nanosized Mn₃O₄ , average size: ~80 nm	LiPF ₆ /EC/DEC, 70/20/10, 0.25 C	1327 (discharge)	800 mAh g ⁻¹ /40 cycles, quite stable (40 cycles presented)		[118]
Crystalline MnO_x	LiPF ₆ /EC/DEC, 80/10/10, 200 mA g ⁻¹		capacity fading to ~50 mAh g ⁻¹ /40 cycles (40 cycles presented)		[76]
MnO , as prepared from Mn(OAc) ₂ ·4H ₂ O	LiPF ₆ /EC/DMC/DEC, 80/10/10, 0.5 A g ⁻¹		572.6 mAh g ⁻¹ /170 cycles, slight decrease followed by slight increase (170 cycles presented)		[115]
Amorphous MnO_x-C , BET: 40.4 m ² g ⁻¹ , carbon content: 61 wt-%	LiPF ₆ /EC/DEC, 80/10/10, 200 mA g ⁻¹	~950 (lithiation)	~600 mAh g ⁻¹ /50 cycles, type III with minimum at ~400 mAh g ⁻¹ /10 cycles (130 cycles presented)		[76]
MnO/C-N hybrid , particle size: 20 - 50 nm, carbon content: 23.9 %, nitrogen content: 6.5 %	LiPF ₆ /EC/DMC/DEC, 80/10/10, 0.5 A g ⁻¹	1717.5 (discharge)	1699 mAh g ⁻¹ /170 cycles, type III with elongated "U part" at 5 A g ⁻¹ for 400 cycles	polymeric gel-like film, oxidation of Mn ²⁺ to a higher oxidation state, and defects formed by N-doping	[115]
Carbon-encapsulated nano-MnO composite loaded on N-doped carbon webs , particle size: ~10 nm for MnO, wrapped with thin carbon layer of ~1 nm, carbon content: 23.7 wt-%	LiPF ₆ /EC/DEC, 70/20/10, 1.0 A g ⁻¹		1268 mAh g ⁻¹ /700 cycles, type III with minimum at ~660 mAh g ⁻¹ /100 cycles (700 cycles presented)	MnO gradually becomes amorphous over cycling resulting in weakening of Mn-O bonds and/or enhancement of Li-ion diffusion kinetics	[116]
Mesoporous MnO/C networks , particles size: ~200 nm, composed of ultrafine nanocrystals with ~16 nm in size, BET: 82.7 m ² g ⁻¹ , carbon content: ~12.7 wt-%	LiPF ₆ /EC/DMC, 70/20/10, 200 mA g ⁻¹	1456 (discharge)	1224 mAh g ⁻¹ /200 cycles, type III with minimum at ~620 mAh g ⁻¹ /30 cycles (200 cycles presented)	formation of defects during cycling, leading to oxidation of Mn ²⁺ to a higher oxidation state	[119]
MnO/graphene hybrids , BET: 50.3 m ² g ⁻¹ , graphene content: ~17.4 wt-%	LiPF ₆ /EC/DMC, 80/10/10, 200 mA g ⁻¹		2014.1 mAh g ⁻¹ /150 cycles, type II with maximum at 120 cycles (150 cycles presented)	interfacial Li storage, and oxidation of Mn ²⁺ to Mn ⁴⁺	[120]
Mn₃O₄/VGCF , particle size: ~40 nm for Mn ₃ O ₄ , different diameters of ~50 to ~200 nm for VGCF, carbon content: 13.52 wt-%	LiPF ₆ /EC/DMC/EMC, 75/15/10, 0.1 A g ⁻¹	1223.6 (discharge)	1391 mAh g ⁻¹ /200 cycles, type III with minimum at ~700 mA g ⁻¹ /20 cycles (at 0.5 A g ⁻¹ , 200 cycles presented)	polymer-like network	[113]
MnO QD/graphene dot fabrics , particle size: 5 - 10 nm for MnO QDs well distributed on few-layered GNS, carbon content: ~19.8 wt-%	LiPF ₆ /EC/EMC/DMC, 80/10/10, 200 mA g ⁻¹	825.8 (charge)	766.8 mAh g ⁻¹ /80 cycles, type IV (80 cycles presented)	formation/dissolution of polymeric gel-like films, Mn nanoparticles can promote/activate reversible transformation of SEI components	[121]

Please note: theoretical capacity of nanocomposite and -hybrid structures not clearly defined due to intrinsic lithium storage capacity of carbonaceous materials.

Zhang et al. investigated MnO thin film electrodes (LiPF₆/EC/PC) through AFM during the initial cycle after cut-off voltages of 0.8, 0.3, 0.1, and 0.01 V. A fifth cell was lithiated to 0.01 V, and subsequently delithiated to 3.0 V. The MnO electrode evolution during the initial lithiation process involved a drastic increase in the MnO grain size from ~20 to ~200 nm, and variations in surface roughness of ~12 to ~280 nm, mainly attributed to formation/decomposition processes of a SEI film. The distribution of the SEI film showed high inhomogeneity. Electrodes stopped at 0.8 and 0.3 V, and the electrode that was subsequently delithiated up to 3.0 V, exhibited hard and thin SEIs with Young's modulus greater than 1 GPa (which is higher than for usual organic materials), whereas the SEI for the electrodes stopped at 0.1 and 0.01 V, exhibited a thicker and softer SEI. Deriving explanations from graphite/carbonate-based electrolyte cells, (for that SEI formation occurs via electron transfer processes from the electrode surface to solvent molecules, and two-electrons process tends to form Li₂CO₃ at higher voltages of >0.8 V, and single-electron processes tends to form lithium alkyl carbonate, lithium oligomers, and lithium polymers at lower voltages of <0.8 V), the absence of a soft organic SEI layer, and thus single-electron transfer processes in SEI films of MnO electrodes stopped at 0.8 and 0.3 V are indicated. The absence of such a SEI layer type for the fifth electrode that was delithiated to 3.0 V might be due to the low conductivity of MnO, or differences in surface reactions of graphite and MnO. In addition, the coexistence of a single-layered and doubled-layered structure, leading to thick and inhomogeneous SEI on MnO electrode surfaces, was found below 0.1 V. Further lithiation from 0.1 to 0.01 V was associated with an increase in thickness of both, the single-layered structure, and each layer of the double-layered structure, indicating that single-electron and two-electrons reactions occur at 0.1 V, and the SEI film with a thickness of tens of nanometers (measured for the electrode stopped at 0.1 V) does not provide enough resistance to suppress further electrolyte degradation. Delithiation back to 3.0 V led to a reduced SEI of ~9 nm with most Young's modulus >1 GPa, indicating a decomposition of the organic SEI, whereas the inorganic SEI film was partially preserved. This suggested a sufficient high instability of the soft organic SEI layer, which could contribute to reduced electrochemical performance of the electrode materials.^[122]

3.4.4. Ruthenium oxide based electrodes

The conversion reaction for ruthenium(IV) oxide nanoparticles with Li⁺ is stated as $\text{RuO}_2 + 4\text{Li}^+ + 4\text{e}^- \rightarrow \text{Ru} + 2\text{Li}_2\text{O}$ with a correlating theoretical capacity 806 mAh g⁻¹.^{[68], [46]} This material has attracted attention in the field of LIBs due to extremely high Coulombic efficiencies (nearly 100 %), metallic conductivity, and good mass transport properties.^{[30], [43], [68]} However, RuO₂ based electrodes show a rapid capacity fading, and are often reported to fail during long-term cycling,^{[68], [78], [123]} mainly attributed to huge volume changes (~100 %) during lithiation/delithiation.^[43] Therefore, RuO₂ is rather considered as a model material to investigate lithium storage, preferentially at the initial cycle.^{[43], [46], [68], [124]} Capacity values beyond the theoretical value based on conversion reaction are often observed for the initial cycles, whereas due to the above mentioned aspects, additional capacity phenomena or capacity raise behavior for subsequent cycles take over a very subordinate role (

Table 4). For instance, Gregorczyk et al. investigated RuO₂ ALD films (LiPF₆/EC/DEC) that showed a slight capacity increase for the first 10 cycles from ~500 to ~550 mAh g⁻¹ (and therefore still below the theoretical capacity), when operated at 2.5 C, but followed by a pronounced fading reaching ~150 mAh g⁻¹ at 100 cycles.^[123]

Balaya et al. studied RuO₂ (LiPF₆/EC/DMC) over a voltage range of 0.05 - 4.3 V, and provided insight into SEI layer evolution through HRTEM and SAED at different lithium insertion/extraction levels. The SEI film mainly formed below 0.8 V during discharge, decomposed in the range of 1.2 - 4.3 V during charging (occurs at the first and following cycles). The investigated RuO₂ showed an initial particle size of 30 - 200 nm that disintegrates into nanograins of 2 - 5 nm during insertion of 4 lithium. At this state, the sample was described as metallic ruthenium nanoparticles that are dispersed uniformly in a Li₂O matrix on a nanoscale level, and covered by a thin SEI layer of 1 - 2 nm. For the fully lithiated RuO₂ (here 5.6 lithium, and therefore beyond the theoretical value based on conversion reaction), a Ru/Li₂O nanocomposite covered with a thicker SEI layer of about 5 nm was observed, indicating that the SEI layer grows mainly during the sloped region of discharging (0.9 - 0.05 V). During charging up to 1.2 V, the nanostructure and the SEI film of about 5 nm was preserved. Samples charged to 3.7 V showed a reduced SEI layer of 2 - 5 nm, and an almost completely reformed RuO₂ nanophase. At 4.3 V (complete re-oxidation) the SEI layer had disappeared and nanocrystalline RuO₂ reformed.^[68]

Table 4. Electrochemical performance against Li/Li⁺ of various ruthenium oxide based electrodes reported in literature.

Sample	Electrolyte, AM/CC/binder, C rate	1 st cycle capacity [mAh g ⁻¹]	Hypothesis for additional capacity at initial cycle	Long-term cycling behavior	Ref.
Nanosized RuO₂ , particle size: 30 - 200 nm	LiPF ₆ /EC/DMC, 10/1/1/1 = (RuO ₂ /CB/GP/PVdF, GP: graphite), 0.27 mA cm ⁻²	1130 (discharge)	accommodation of additional Li via surface transfer mechanisms	capacity fades abruptly after 3 cycles and material peels off from Ti current collector	[68]
RuO₂ ALD film , 2000 cycles are deposited on substrate, ~80 nm films	LiPF ₆ /EC/DEC, C/200	1450 (discharge)	formation of heterogeneous Li phases on electrode interface	operating at 2.5 C shows slight capacity increase for the first 10 cycles from ~500 to ~550 mAh g ⁻¹ , followed by pronounced fading to ~150 mAh g ⁻¹ at	[123]

100 cycles				
Crystalline RuO₂ powder, particle size: ~10 nm	LiPF ₆ /EC/DEC, 10/1 (RuO ₂ /binder), 100 mA g ⁻¹	1027 (discharge)	additional capacity through fast Li storage in grain boundaries of newly formed nanosized Ru metal and Li ₂ O phases	only initial cycle investigated [46]
RuO₂ crystalline nanoplates, ~50 nm nanoplate stacks of ~450 nm thickness	LiPF ₆ /EC/DMC/DEC, CC and binder free, 100 μ A	875 (discharge)		647 mAh g ⁻¹ /20 cycles [125]

Hassan et al. did first-principles computational studies supported by practical experiments to investigate the molecular mechanism of lithium interaction for crystalline bulk RuO₂ (LiPF₆/EC/DMC/DEC) and found that lithium absorption in electrodes consisting of ruthenium island in Li₂O matrix can explain additional capacity phenomena (up to 1600 mAh g⁻¹), without contribution from processes based on an SEI.^[125]

Kim et al. investigated additional capacity phenomena and reaction mechanisms of crystalline RuO₂ powder during the first discharge (LiPF₆/EC/DEC, at 100 mA g⁻¹ between 0.05 - 4.30 V) with *in situ* methods (XRD and XAS), and TEM, XPS and GITT (Figure 8). The discharge profile showed two major plateaus at approximately 2.0 and 0.8 V, and a sloping part from ~0.5 V down to 0.05 V with a total initial capacity of 1027 mAh g⁻¹ (5.1 mol lithium per mol RuO₂). In total, 274 XRD and 30 XAS spectra were recorded during discharging to 0.05 V, revealing pristine RuO₂ at the start of discharge, the appearance of orthorhombic LiRuO₂ on insertion of ~0.65 mol lithium, and metallic ruthenium in Li₂O upon further overall lithium uptake of ~4 mol. Below 0.5 V, a storage of ~1.1 mol lithium occurred without further detectable changes in ruthenium oxidation state or structure, indicating the exclusion of ruthenium species in redox reactions below 0.5 V. Further investigations with TEM at potentials of 2.0, 0.8, and 0.05 V revealed SEI films at all discharged states (different from graphite samples, where SEI

formation takes place at low voltages), suggesting lithium consumption by SEI already starting from 2.0 V for RuO₂ (Figure 8a-d). However, the increase in SEI thickness observed below 0.5 V is not proportional to a ~1.1 mol lithium uptake. XPS spectra revealed Li₂O, LiOH and Li₂CO₃ as SEI species. Li₂O is intrinsically the result of conversion reaction, but on the surface, Li₂O formation could be based on interactions with the electrolyte. Li₂CO₃ is attributed to electrolyte decomposition, and LiOH is formed by lithiation of OH⁻ containing surface groups^[46] (also reported as a source of additional capacity).^[30] However, further measurements with GITT to investigate the diffusion coefficient of lithium with changing lithium content or voltage, revealed a steady increase of the lithium diffusion coefficient at the end of discharge with a steady-state maximum below 0.5 V. Therefore, it was suggested to attribute the additional capacity to an interfacial reaction mechanism with accommodation of additional lithium in the grain boundary between nanosized ruthenium and Li₂O (Figure 8f). The high diffusion coefficients in the sloping discharge region supported the assumption that reaction kinetics in this part are rather controlled by interfacial lithium storage processes, and not by conversion reaction, since the diffusion of lithium into grain boundaries of Ru and Li₂O exhibit naturally faster kinetics than the interaction of Li with electrode material based on conversion reaction.^[46]

Figure 8. TEM images of a) pristine RuO₂ powder where inset shows the electron diffraction pattern, and of RuO₂ electrodes b) discharged to 2.0 V, c) discharged to 0.8 V, and d) fully discharged to 0.05 V, e) discharge profile of the RuO₂ anode material during *in situ* XRD measurements at a current density of 100 mA g⁻¹, f) GITT curve of RuO₂ acquired using a current flux of 100 mA g⁻¹ for 30 min and relaxation time of 3 h; the calculated diffusion coefficient is also shown. "Reprinted with permission from Y. Kim, S. Muhammad, H. Kim, Y.H. Cho, H. Kim, J.M. Kim, W.S. Yoon, Probing the Additional Capacity and Reaction Mechanism of the RuO₂ Anode in Lithium Rechargeable Batteries, *ChemSusChem* 8(14) (2015) 2378-2384, Copyright © 2017 John Wiley and Sons".

Bekaert et al. used *ex situ* ⁶Li magic-angle spinning nuclear magnetic resonance (⁶Li MAS NMR) to investigate RuO₂ (nanocrystalline) that was electrochemically lithiated through a ⁶Li-enriched anode, and confirmed the presence of interfacial lithium. NMR spectra were recorded at different states of lithiation (for subsequent explanations: x = amount of Li per mole RuO₂). At x = 0.5 (~2.2 V) a signal at ~9 ppm was observed and ascribed to the lithiated phase LiRuO₂. A second broad signal at ~0 ppm was attributed to the beginning of SEI formation, containing diamagnetic lithium species. At x = 4 (~1.8 V, end of conversion reaction plateau) a well-defined signal at 2.82 ppm for Li₂O was observed. The signal for SEI at ~0 ppm is considerably narrower at this state of lithiation, possibly explained by changes in the SEI material. For lower lithiation states, the SEI is formed on LiRuO₂ that exhibit paramagnetism and therefore supposed to induce strong dipolar interactions on lithium nuclei in the SEI, associated with the observed NMR signal broadening. For x = 4, ruthenium metal had formed that is supposed to generate much lesser paramagnetic dipolar interactions with lithium, leading to a well-defined signal. In addition, a significant signal at 4 ppm was observed, which cannot be attributed to any diamagnetic phase that contains lithium, but could correspond to lithium located at Li₂O surfaces that also had chemical bonds with ruthenium including e⁻ transfer from lithium to ruthenium. Hence, this signal was

attributed to interfacial lithium (Figure 9). The authors assumed that the SEI growth occurs through contact of electrolyte with the (initial) RuO₂ grains, and interfacial lithium evolves in nanostructures that had formed in these grains. Therefore, an interference of SEI formation and development of interfacial lithium is excluded.^[43]

Using the interfacial mechanism to explain additional capacities at low potentials for conversion materials the work from Ponrouch et al. should be mentioned. By simple geometric calculations (assuming that the relative quantity of charge that can be stored by interfacial mechanism would be proportional to the lithium binary compound/metal interface) it was indicated that additional capacities based on interfacial storage play a very minor role. The calculations were done for most of the reported conversion materials including oxides, fluorides, sulfides, nitrides and phosphides. The results were supported by experiments with Co₃O₄ electrodes showing that the slope of the potential decay in the potential-discharge/charge curve and the influence of the current in the extent of stored capacity is not in agreement with the hypothetical mechanism of charge storage in the lithium binary compound/metal interface, and hence is suggested to be negligible compared to the additional capacity at low potentials provided by processes based on electrolyte decomposition.^[45]

Figure 9. (l): Decomposition of the ^6Li MAS NMR spectrum for $x = 4$ (x = amount of Li per mole RuO_2), (r) amount of Li observed by NMR per mass of sample in each signal for the various samples. "Reprinted with permission from E. Bekaert, P. Balaya, S. Murugavel, J. Maier, M. Ménétrier, ^6Li MAS NMR Investigation of Electrochemical Lithiation of RuO_2 : Evidence for an Interfacial Storage Mechanism, *Chemistry of materials* 21(5) (2009) 856-861, Copyright © 2017 American Chemical Society".

Hu et al. applied HR multinuclear/multidimensional solid-state NMR, with *in situ* synchrotron-based techniques and did theoretical calculations to investigate the behavior of RuO_2/Li cells. Changes in the electronic structure were investigated, and the evolution of RuO_2 was monitored in real time. As a major source for the additional capacity, reversible reactions of LiOH that lead to LiH and SEI formation were identified. As schematically illustrated in Figure 10, tetragonal RuO_2 particles with OH groups on the external and internal surfaces (here stated as $\text{RuO}_2 \cdot y\text{H}_2\text{O}$) interact with lithium ions to form orthorhombic LiRuO_2 through an intermediate tetragonal Li_xRuO_2 phase. At the beginning of the conversion reaction, LiOH was

detected that contained ^{17}O , therefore an involvement of surface OH groups rather than oxygen from the electrolyte for the formation process was suggested (for this study, RuO_2 was enriched with $^{17}\text{O}_2$ gas). Below 0.8 V the conversion of LiOH occurred, leading to Li_2O and LiH , which was suggested to contribute to the additional capacity (here $\sim 400 \text{ mAh g}^{-1}$ observed between 0.25 and 0 V). It was pointed out that other mechanisms, e.g. reversible SEI formation and adsorption of lithium on surfaces of nanosized Ru particles can also have a minor contribution to the additional capacity. The formation of SEI was also observed during the discharge process by NMR, and SEI species such as LiF and CH_3OLi were identified.^[30]

a

b

Figure 10. Summary of the reaction pathway, evolution of phase distribution and relevant experimental evidence of the RuO_2/Li battery system, a) summarized reaction pathway, b) the profile of the electrochemistry with schematics representing the phase distribution at each stage of discharge, with relevant supporting evidence given below. "Reprinted with permission from Y.-Y. Hu, Z. Liu, K.-W. Nam, O.J. Borkiewicz, J. Cheng, X. Hua, M.T. Dunstan, X. Yu, K.M. Wiaderek, L.-S. Du, Origin of additional capacities in metal oxide lithium-ion battery electrodes, *Nature materials* 12(12) (2013) 1130-1136, Copyright © 2017 Nature Publishing Group".

3.4.5. Chromium oxide based electrodes

The conversion reaction for chromium(III) oxide nanoparticles with Li^+ is stated as $\text{Cr}_2\text{O}_3 + 6\text{Li}^+ + 6\text{e}^- \rightarrow 2\text{Cr} + 3\text{Li}_2\text{O}$ with a correlating theoretical capacity of 1058 mAh g^{-1} .^[78] Besides the high theoretical capacity, Cr_2O_3 is considered as promising negative electrode material due to a relative low *emf* value and inexpensive procurement. However, poor electrochemical performances have been reported for pristine Cr_2O_3 , and among other factors attributed to large volume changes upon repetitive

lithiation/delithiation, and unstable SEI formation.^{[7], [107]} Hu et al. investigated pristine Cr_2O_3 based electrodes ($\text{LiPF}_6/\text{EC}/\text{DMC}$) and demonstrated the decomposition of a previously formed SEI layer during lithium extraction. Evaluated by HRTEM, fully lithiated Cr_2O_3 showed a SEI film with inhomogeneity in thickness (30 - 90 nm) that decreased below 10 nm at complete delithiation (Figure 11). In addition, SEM investigations revealed many cracks at the electrode after 20 cycles.^[107]

Figure 11. a) HRTEM images of Cr_2O_3 at fully lithiated state, and b) fully delithiated state, "Reprinted with permission from J. Hu, H. Li, X. Huang, L. Chen, Improve the electrochemical performances of Cr_2O_3 anode for lithium ion batteries, *Solid State Ionics* 177(26) (2006) 2791-2799, [107] Copyright © 2017 Elsevier".

Several methods have been presented to improve the electrochemical performance of Cr_2O_3 , e.g. the design of nanostructures, mesoporous structures, doping experiments, thin films, and synthesis of Cr_2O_3 /carbon nanocomposite and -hybrid structures.^{[107], [126]} Noteworthy, literature screening showed that additional capacities seem to play a very subordinate role for Cr_2O_3 . Only very few studies reported capacities over the theoretical value according to conversion reaction for Cr_2O_3 based negative electrodes at the first cycle. For instance, Abbas et al. presented Cr_2O_3 modified with CNT that showed an initial capacity of 1199 mAh g^{-1} (LiPF₆/EC/DEC). The additional capacity was attributed to SEI formation.^[127] Xu et al. synthesized graphene wrapped Cr_2O_3 hollow nanospheres that achieved 1460 mAh g^{-1} (LiPF₆/DMC/EC) at first cycle.^[128] Whereas to the best of our knowledge, capacities beyond the theoretical value of conversion reaction in the long-term for pure Cr_2O_3 could not be found (Table 5). Scenarios that might have an impact on the resulting capacity could be the preferred formation of chromium monoxide (CrO_{1-x}) instead of Cr_2O_3 during recharge,^[24] which reduces the overall exchange of $6 e^-$ according to conversion reaction. In addition, Cr_2O_3 electrodes show comparatively larger amounts of electrolyte decomposition products, leading to intense polymeric films that surround the electrode particles. This is possibly based in the relatively low

redox potential of $0.4 - 0.5 \text{ V}$ for the $\text{Cr}^{2+}/\text{Cr}^0$ couple.^[24] Thick films of electrolyte degradation products can retard lithium diffusion and weaken electrical contacts between the current collector and the active material.

The composition of SEI films on Cr_2O_3 electrodes (LiPF₆/EC/DMC) was investigated by Zheng et al. ROCO₂Li, oligomer and polyethylene-oxide-like species that decompose during lithiation were detected, and gaseous organic species such as $\text{H}_2\text{C}=\text{CH}_2$, CO_2 and CH_3 -containing compounds were released at the first cycle. In general, thermal decomposable species are found in the SEI layer of fully lithiated Cr_2O_3 electrodes to a much higher extend than known for graphite and hard carbon electrodes.^[129]

Further studies were conducted on a conversion electrode based on chromium oxide (named CBO) grown on stainless steel mesh tissues (LiPF₆/EC/DMC) by Tarascon's group. A solid layer surrounded by a jelly-like film was observed, and while the solid part consisted of inorganic species such as Li_2CO_3 , lithium methyl carbonate and lithium fluoride, the jelly-like film contained ethylene oxide-based oligomers. These oligomers had identical PEO units but differences in their termination groups such as carbonate, methoxy and hydroxyl groups (note, this study was done under extreme cycling conditions of 800 cycles at 55°C).^[62]

Table 5. Electrochemical performance against Li/Li⁺ of various chromium oxide based electrodes reported in literature.

Sample	Electrolyte, AM/CC/binder, C rate	1 st cycle capacity [mAh g ⁻¹]	Long-term cycling behavior	Ref.
Cr_2O_3 , particle size: ~38 nm	LiPF ₆ /EC/DEC/DMC, 70/15/15, 0.1 C	732.0 (discharge)	~100 mAh g ⁻¹ /100 cycles, stable cycling profile (100 cycles presented)	[130]
Bulk Cr_2O_3 commercial, Aldrich company, particle	LiPF ₆ /EC/DMC, 40/40/20, 0.1 C	1353 (discharge)	203 mAh g ⁻¹ /100 cycles, stronger fading until ~40 cycles, then relative stable (100 cycles presented)	[131]

size: 1 μm , BET: 6 $\text{m}^2 \text{g}^{-1}$				
Cr₂O₃ commercial , Beijing Chemicals Co. Ltd	LiPF ₆ /EC/DMC/DEC, 80/10/10, C/5	~580 (charge)	280 mAh g ⁻¹ /35 cycles, slight capacity fading (35 cycles presented)	[126]
Cr₂O₃ commercial , Sinopharm Chemical reagent Co. Ltd, Shanghai, China, particle diameter: 200 - 400 nm	LiPF ₆ /EC/DMC, 50/15/25/10 (Cr ₂ O ₃ /CB/PVdF/graphite), 0.05 C	1313 (discharge)	224 mAh g ⁻¹ /22 cycles, continuous fading (22 cycles presented)	[132]
Cr₂O₃ , BET: 179 $\text{m}^2 \text{g}^{-1}$	LiPF ₆ /EC/DEC, 8.5/1/0.5, 100 mA g ⁻¹	1120 (discharge)	523 mAh g ⁻¹ /200 cycles, continuous fading (200 cycles presented)	[127]
Cr₂O₃ film on Cr metal , thickness of Cr ₂ O ₃ film: 17.3 nm	5 $\mu\text{A cm}^{-2}$	1529 (discharge)	460 mAh g ⁻¹ /10 cycles	[133]
Mg-doped and carbon coated Cr₂O₃	LiPF ₆ /EC/DMC, 85/10/5, 0.2 mA cm ⁻²	832 (discharge)	~720 mAh g ⁻¹ /20 cycles (20 cycles presented)	[107]
Ni-doped and carbon coated Cr₂O₃	LiPF ₆ /EC/DMC, 85/10/5, 0.2 mA cm ⁻²	893 (discharge)	~820 mAh g ⁻¹ /20 cycles (20 cycles presented)	[107]
Mesoporous Cr₂O₃ , KIT-6 mesopore system, pore and wall size: ~10 nm	LiPF ₆ /EC/DMC, C/40 (at 55 °C)		~400 mAh g ⁻¹ /80 cycles, extended <i>U-shape</i> until ~60 cycles (80 cycles presented)	[24]
2D hexagonal mesoporous Cr₂O₃ , BET: 88 $\text{m}^2 \text{g}^{-1}$	LiPF ₆ /EC/DMC, 40/40/20, 0.1 C	1473 (discharge)	521 mAh g ⁻¹ /100 cycles, slight fading until ~40 cycles, then relative stable (100 cycles presented)	[131]
3D cubic mesoporous Cr₂O₃ , BET: 93 $\text{m}^2 \text{g}^{-1}$	LiPF ₆ /EC/DMC, 40/40/20, 0.1 C	1565 (discharge)	540 mAh g ⁻¹ /100 cycles, slight fading until ~40 cycles, then relative stable (100 cycles presented)	[131]
Mesoporous Cr₂O₃	LiPF ₆ /EC/DMC/DEC, 80/10/10, C/5	~480 (charge)	320 mAh g ⁻¹ /35 cycles, slight capacity fading (35 cycles presented)	[126]
G-Cr₂O₃ (with graphene) , Cr ₂ O ₃ content: 51.2 wt-%, particle size: ~25 nm for Cr ₂ O ₃	LiPF ₆ /EC/DEC/DMC, 70/15/15, 0.1 C	1114.2 (discharge)	~450 mAh g ⁻¹ /100 cycles, stable cycling profile (100 cycles presented)	[130]
G-Cr₂O₃-C2 (with graphene and carbon coating) , Cr ₂ O ₃ content: 41.9 wt-%, particle size: ~11 nm for Cr ₂ O ₃	LiPF ₆ /EC/DEC/DMC, 70/15/15, 0.1 C	1234.1 (discharge)	~550 mAh g ⁻¹ /100 cycles, stable cycling profile (100 cycles presented)	[130]
Cr₂O₃-C hierarchical core/shell nanospheres , carbon content: 3 wt-%	LiPF ₆ /EC/DMC/DEC, 80/10/10, C/5	688 (charge)	>600 mAh g ⁻¹ /35 cycles, slight capacity fading (35 cycles presented)	[126]
Mesoporous carbon Cr₂O₃ composite , BET: 505 $\text{m}^2 \text{g}^{-1}$, carbon content: 42 %	LiPF ₆ /EC/DMC/DEC, 80/10/10, 50 mA g ⁻¹		639 mAh g ⁻¹ /80 cycles, relative stable (80 cycles presented)	[134]
Interconnected graphene-Cr₂O₃ nanosheets , mass ratio of graphene to Cr ₂ O ₃ = 0.135	LiPF ₆ /EC/DMC, 80/10/10, 200 mA g ⁻¹		~850 mAh g ⁻¹ /50 cycles (theoretical capacity: 1020.7 mAh g ⁻¹)	[135]
Interconnected Graphene-Cr₂O₃ nanosheets , mass ratio of graphene to Cr ₂ O ₃ = 0.512	LiPF ₆ /EC/DMC, 80/10/10, 200 mA g ⁻¹		~700 mAh g ⁻¹ /50 cycles (theoretical capacity: 951.7 mAh g ⁻¹)	[135]
Graphene wrapped Cr₂O₃ hollow nanospheres , graphene content: 16.3 %	LiPF ₆ /DMC/EC, 80/10/10, 0.1 C	1460 (discharge)	580 mAh g ⁻¹ /100 cycles, stable cycling behavior (100 cycles presented)	[128]
Cr₂O₃-CNT_(0.08%) , BET: 306 $\text{m}^2 \text{g}^{-1}$	LiPF ₆ /EC/DEC, 8.5/1/0.5, 100 mA g ⁻¹	1199 (discharge)	995.3 mAh g ⁻¹ /200 cycles, stable cycling performance (200 cycles presented)	[127]
Cr₂O₃/C , carbon content: 16 wt-%, particle diameter: 200 - 400 nm	LiPF ₆ /EC/DMC, 70/10/10/10 (Cr ₂ O ₃ /C/CB/PVdF/gr	840 (discharge)	530 mAh g ⁻¹ /50 cycles, quite stable cycling performance (50 cycles presented)	[132]

aphite), 0.05 C

Please note: theoretical capacity of nanocomposite and -hybrid structures not clearly defined due to intrinsic lithium storage capacity of carbonaceous materials.

3.4.6. Nickel oxide based negative electrodes

The conversion reaction for nickel(II) oxide nanoparticles with Li⁺ is stated as $\text{NiO} + 2\text{Li}^+ + 2\text{e}^- \rightarrow \text{Ni} + \text{Li}_2\text{O}$ with a correlating theoretical capacity of 718 mAh g⁻¹.^{[78], [136]} However, difficulties have been experienced for pure NiO negative electrodes to achieve high reversible capacities in combination with high Coulombic efficiencies in lab-testing. This is mainly attributed to large volume changes during repetitive lithiation/delithiation associated with pulverization of the material and loss of electrical contacts (Table 6).^{[137], [138]} As already demonstrated for other TMOs, the synthesis of nickel oxide/carbon nanocomposite and -hybrid structures lead to intensively improved electrochemical performance against Li/Li⁺.^{[137], [139]} As often stated, the improvement is attributed to a synergistic effect between the two components. Zhou et al. provided a deeper understanding of the term *synergistic effect* exemplified by NiO/graphene sheet on sheet nanocomposites, synthesized by direct growth of NiO nanosheets on graphene sheets starting with dispersing of graphene in a Ni(NO₃)₂ solution. The

remaining oxygen functionalities on graphene (mostly epoxy rings and hydroxyl), served as preferential nucleation sites for NiO and supported a beneficial dispersion on the graphene substrate. As revealed by XPS, FTIR, Raman spectroscopy and first-principles calculations, the linkage between NiO and oxygenated graphene occurred via strong oxygen bridges (C-O-Ni) for that the oxygen was provided from hydroxyl groups or ring-opening reactions of epoxy functionalities attached to graphene. The calculated adsorption energies for Ni adatoms on oxygenated graphene, and especially the calculated high diffusion barriers for Ni adatoms on oxygenated graphene, demonstrated the easy binding character between NiO and graphene. The strong C-O-Ni linkage supports fast electron hopping from the graphene part to NiO associated with enhanced electrochemical performance against Li/Li⁺ as demonstrated by high reversible capacities of 883 mAh g⁻¹ at 50 cycles (50 mA g⁻¹), which is superior to physical mixtures of NiO and graphene that delivered 530 mAh g⁻¹ at 50 cycles under the same conditions.^[42]

Table 6. Electrochemical performance against Li/Li⁺ of various nickel oxide based electrodes reported in literature.

Sample	Electrolyte, AM/CC/binder, C rate	1 st cycle capacity [mAh g ⁻¹]	Long-term cycling behavior	Ref.
Bulk NiO commercial	LiPF ₆ /EC/DMC, 40/40/20, 0.1 C	924 (discharge)	188 mAh g ⁻¹ /50 cycles (50 cycles presented)	[140]
Porous NiO-Ni nanocomposite , pore size: 40 - 60 nm, NiO content: ~79.6 %	1 M lithium bis(perfluoroethylsulfonyl)imide/EC/DEC/EMC, CC and binder free, 286 mA g ⁻¹	503 (discharge)	397 mAh g ⁻¹ /50 cycles, stable curve (100 cycles presented)	[136]
Porous core-shell structured Ni/NiO , irregular porous structures with dimension of ~200 nm	LiPF ₆ /EC/DMC/EMC, CC and binder free, 156 mA g ⁻¹	997 (discharge)	646 mAh g ⁻¹ /65 cycles, stable curve (65 cycles presented)	[141]
NiO NSs , BET: 89 m ² g ⁻¹	LiPF ₆ /EC/DMC/EMC, 80/10/10, 50 mA g ⁻¹	1193 (discharge)	210 mAh g ⁻¹ /50 cycles, relative stable (50 cycles presented)	[42]
NiO nanoparticles particle size: 20 - 80 nm	LiPF ₆ /EC/DMC, 80/10/10, 0.5 C	1235.9 (discharge)	383.5 mAh g ⁻¹ /50 cycles, pronounced capacity fading (50 cycles presented)	[137]
Porous array NiO film	LiPF ₆ /EC/DEC, 1 C	1006 (discharge)	518 mAh g ⁻¹ /50 cycles, initially slight fading, then relative stable (50 cycles presented)	[138]
Dense NiO film	LiPF ₆ /EC/DEC, 1 C	960 (discharge)	287 mAh g ⁻¹ /50 cycles, fading until 30 cycles then relative stable (50 cycles presented)	[138]
Mesoporous NiO , BET: 96 m ² g ⁻¹	LiPF ₆ /EC/DMC, 40/40/20, 0.1 C	914, (discharge)	680 mAh g ⁻¹ /50 cycles, stable curve (50 cycles presented)	[140]
Porous NiO fibers , BET: 70.5 m ² g ⁻¹	LiPF ₆ /EC/DEC, 6/2/2, 40 mA g ⁻¹		638 mAh g ⁻¹ /50 cycles, stable curve (50 cycles presented)	[142]
NiO sheet-like structure with hexagonal holes , thickness: 24 ± 8 nm	LiPF ₆ /EC/DEC, 80/10/10, C/2	1138 (discharge)	675 mAh g ⁻¹ /40 cycles, capacity increase/decrease behavior with maximum at 928 mAh g ⁻¹ /~27 cycles (40 cycles presented), extra capacity attributed to interfacial charge storage, reversible side reactions (e.g. Li storage in carbon black and CuO at the surface of Cu current collector,	[37]

				conversion of LiOH to Li ₂ O and LiH)	
NiO nanoparticles , BET: 231.60 m ² g ⁻¹	LiPF ₆ /EC/DEC, 6/2/2, 0.2 C	~1500 (discharge)	~600 mAh g ⁻¹ /50 cycles (1 C), slight fading (50 cycles presented)		[143]
Sub-micro-sized NiO , BET: 30.05 m ² g ⁻¹	LiPF ₆ /EC/DEC, 6/2/2, 0.2 C	~900 (discharge)	~100 mAh g ⁻¹ /40 cycles (1 C), pronounced capacity fading (50 cycles presented)		[143]
NiO/C nanocapsules with onion-like carbon shell particle size: 10 - 30 nm	LiPF ₆ /EC/DMC, 80/10/10, 0.5 C	1689.4 (discharge)	1157.7 mAh g ⁻¹ /50 cycles (50 cycles presented)		[137]
NiO NS/graphene composite , BET: 188 m ² g ⁻¹	LiPF ₆ /EC/DMC/EMC, 80/10/10, 50 mA g ⁻¹	1478 (discharge)	883 mAh g ⁻¹ /50 cycles, relative stable (50 cycles presented), improved electrochemical performance attributed to synergistic effect (oxygen bridges) between NiO and graphene		[42]
NiO NS-graphene mixture , BET: 132 m ² g ⁻¹	LiPF ₆ /EC/DMC/EMC, 80/10/10, 50 mA g ⁻¹	1066 (discharge)	530 mAh g ⁻¹ /50 cycles (50 cycles presented)		[42]
NiO nanosheets grown on graphene nanosheets NiO nanosheets: 0.5 - 2 mm in size, 30 - 50 nm in thickness, NiO content: 22.8 %	LiPF ₆ /EC/DEC, 80/10/10, 0.1 C	1056 (charge)	1031 mAh g ⁻¹ /40 cycles, <i>type IV</i> (40 cycles presented)		[139]

Please note: theoretical capacity of nanocomposite and -hybrid structures not clearly defined due to intrinsic lithium storage capacity of carbonaceous materials.

Generally, not many reports about investigations of electrode/electrolyte interphases for NiO materials could be found. An interesting "TEM-grid-in-a-coin-cell" method for direct observation of interfacial changes for NiO nanosheets (LiPF₆/EC/DEC) was reported by Lin et al. In detail, electrode material was applied on a TEM grid, pressed against the bulk electrode material, and assembled into coin cell configuration together with the other cell components. This guarantees the same electrolyte environment for the material loaded on the TEM grid as for the whole electrode material, and parameters for

electrochemical testing can be accurately controlled for the investigated material. STEM imaging revealed an anode electrolyte interphase (AEI) on the surface of NiO and Ni. XAS and EELS confirmed the presence of Li₂CO₃, and HRTEM and FFT showed localized Li₂CO₃ nanocrystals. It was concluded that the AEI consists of Li₂CO₃ in an amorphous organic matrix (similarly to graphite negative electrodes), with a thickness that is subjected to changes in dependence of the SOC (Figure 12).^[37]

Figure 12. a) TEM image, b) Fast Fourier transform (FFT) pattern for the selected area boxed in a), c) STEM image of a NiO nanosheet during a discharging process, and NiO, Ni and AEI are indicated with arrows in the image (scale bar: 50 nm), d) EELS Li K-edge, C K-edge and O K-edge spectra for the AEI layer, and the assignment of peaks is indicated in the figure. A reference Li K-edge spectrum of Li₂CO₃ is provided in the figure. "Reprinted with permission from F. Lin, D. Nordlund, T.-C. Weng, Y. Zhu, C. Ban, R.M. Richards, H.L. Xin, Phase evolution for conversion reaction electrodes in lithium-ion batteries, Nature communications 5 (2014), Copyright © 2017 Nature Publishing Group, reference Li K-edge spectrum of Li₂CO₃ reprinted with permission from F. Wang, J. Graetz,

3.4.7. Copper oxide based negative electrodes

Among copper oxides, especially copper(II) oxide is subjected to intense research in the field of LIBs due to a theoretical capacity of 674 mAh g⁻¹ according to the conversion $\text{CuO} + 2\text{Li}^+ + 2\text{e}^- \rightarrow \text{Cu} + \text{Li}_2\text{O}$, whereas copper(I) oxide (Cu₂O) exhibit a lower theoretical capacity of 375 mAh g⁻¹.^{[78], [144]} Besides the relative higher theoretical capacity, CuO moved into the focus due to its chemical stability, non-toxicity, abundance and environmental benignity.^{[145], [146]} However, poor long-term cycling is often observed, and also capacities beyond the conversion reaction or capacity raise phenomena play a minor role for CuO based electrodes (Table 7). This electrochemical behavior is attributed to the poor electronic conductivity and large volume changes

(~174 %) during repetitive lithiation/delithiation.^{[147], [148]} In addition, it was suggested that CuO is not the end-product after recharging under particular conditions. Martin et al. applied XPS to investigate the redox mechanism during lithiation/delithiation of CuO thin films. Under the applied conditions (20 °C, scan rate of 5 μV s⁻¹, LiPF₆/EC/PC/DMC with 2 wt-% VC) Cu²⁺ could not be detected at the end of recharge to 3.5 V vs. Li/Li⁺, indicating irreversible steps for the reverse conversion reaction.^[149] Gangaja et al. did XPS analysis of CuO nanofiber composite electrodes and found large quantities of Cu₂O instead of CuO after first recharge.^[146] The formation of Cu₂O with its lower theoretical capacity possibly also contributes to decreased capacity values.

Table 7. Electrochemical performance against Li/Li⁺ of various copper oxide based electrodes reported in literature.

Sample	Electrolyte, AM/CC/binder, C rate	1 st cycle capacity [mAh g ⁻¹]	Long-term cycling behavior	Ref.
CuO nano hexagons , width: 570 - 650 nm, composed of nanorods with sizes of 10 - 12 nm	LiPF ₆ /EC/DMC, 80/10/10, 215 mA g ⁻¹	1007 (discharge)	~575 mAh g ⁻¹ /100 cycles	[147]
CuO nanoparticles , particle size: 35 - 40 nm, particles form an interconnected network	LiPF ₆ /EC/DMC, 70/10/20, 1 C	~860 (discharge)	310 mAh g ⁻¹ /100 cycles, stabilized capacity of ~120 mAh g ⁻¹ for 1000 cycles at 5 C	[146]
CuO/Cu₂O composite hollow polyhedrons , BET: 9 m ² g ⁻¹	LiPF ₆ /EC/DEC, 50/30/20, 100 mA g ⁻¹	727 (discharge)	740 mAh g ⁻¹ /250 cycles (theoretical capacity: ~520 mAh g ⁻¹), additional capacity is attributed to polymeric gel-like film	[150]
CuO thin films , thickness: ~1.6 μm, consists of bumps/gullies with micro-structured protuberances	LiPF ₆ /EC/DMC, CC and binder free, 100 mA g ⁻¹	900 (discharge)	703 mAh g ⁻¹ /100 cycles, relative stable (100 cycles presented), additional capacity attributed to unique microstructure features and interfacial lithium storage by rough surfaces	[151]
Cu₄O₃ microspheres , BET: ~3 m ² g ⁻¹	LiPF ₆ /EC/DMC, 75/15/10, 0.1 C	878 (discharge)	508 mAh g ⁻¹ /50 cycles (theoretical capacity: 529 mAh g ⁻¹)	[152]
Pompon-like hierarchical CuO hollow microspheres , BET: 18.5 m ² g ⁻¹	LiPF ₆ /EC/DMC/EMC, 80/15/5, 0.1 C	1278.7 (discharge)	683.7 mAh g ⁻¹ /50 cycles, slight capacity fading (50 cycles presented)	[153]
CuO nanoribbons arrays thickness: ~10 nm	LiPF ₆ /EC/DMC/DEC, CC and binder free, 175 mA g ⁻¹	866 (discharge)	608 mAh g ⁻¹ /275 cycles, relative stable with slight capacity increase (275 cycles presented)	[154]
CuO hollow nanoparticles/graphene-nanosheet composites , CuO content: 65 wt-%	LiPF ₆ /EC/DMC, 80/10/10, 50 mA g ⁻¹	1248 (discharge)	743 mAh g ⁻¹ /50 cycles, capacity increases gradually, attributed to interfacial interactions (50 cycles presented)	[148]
CuO/graphene nanocomposite , CuO content: ~74 %	LiPF ₆ /EC/DMC/DEC, 80/10/10, 65 mA g ⁻¹	~900 (lithiation)	~600 mAh g ⁻¹ /100 cycles, relative stable (100 cycles presented)	[155]
CuO/rGO nanocomposite , particle size: 40 - 65 nm, BET: 37.7 m ² g ⁻¹ , synthesized with 10 wt-% GNS	LiPF ₆ /EC/DMC, 80/10/10, 0.1 mA cm ⁻²	1043.3 (discharge)	516.4 mAh g ⁻¹ /45 cycles, relative stable (45 cycles presented)	[156]

CuO/graphene composite , particle size CuO: ~30 nm, CuO content: ~88 wt-%	LiPF ₆ /EC/DMC, 85/10/5, 67 mA g ⁻¹	817 (discharge)	423 mAh g ⁻¹ /50 cycles, slight capacity fading (50 cycles presented)	[157]
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Please note: theoretical capacity of nanocomposite and -hybrid structures not clearly defined due to intrinsic lithium storage capacity of carbonaceous materials.

Xiang et al. demonstrated the impact of various nanostructured CuO morphologies (more specifically their differences in specific surface areas associated with differences in SEI formation), on the electrochemical performance against Li/Li⁺. The higher the pH value (from 9.5 to 11.5, adjusted with ammonia) during a self-assembled synthesis approach starting with an aqueous solution of Cu(Ac)₂·H₂O, the CuO morphology tends towards more and more 3D shapes, resulting in leafs, shuttles, flowers (composed of 2D nanosheets), dandelions (composed of 2D nanofeathers), and caddice clews (composed of nanowires). In this order, the various CuO materials displayed first discharge capacities of 740 mAh g⁻¹, 773 mAh g⁻¹, 847 mAh g⁻¹, 927 mAh g⁻¹, and 952 mAh g⁻¹, with initial Coulombic efficiencies of 69.1 %, 69.5 %, 71.1 %, 62.1 % and 62.5%, respectively (LiPF₆/EC/DME). For CuO leafs and shuttles, only their surfaces are in contact with the electrolyte, resulting in lesser active sites for Li⁺ accommodation. Whereas for the hierarchical nanostructures (shuttle, flower, dandelion), the specific surface area becomes larger, associated with higher CuO/electrolyte contact area and more active sites for Li⁺ accommodation. However, a large CuO/electrolyte contact area provides also increased area for SEI formation, resulting in more SEI for the CuO dandelions and caddice clews, and supposed to be responsible for the lower initial Coulombic efficiencies of these CuO hierarchical nanostructures.^[158]

Gangaja et al. applied *ex situ* XPS to investigate the composition of SEI formed on CuO nanofiber composite electrodes (LiPF₆/EC/DMC) and confirmed LiF, Li₂CO₃ and Li₂O with variations in quantity over lithiation/delithiation processes (note: these samples were exposed to environmental conditions for less than 2 min before transfer to XPS chamber).^[146]

Martin et al. applied XPS and AFM to investigate SEI species and morphology on lithiated CuO thin film during initial lithiation from 3.5 to 0.8 V against Li/Li⁺ (LiPF₆/EC/PC/DMC + 2 wt-% VC). In general, a layered SEI structure was confirmed with a LiF-enriched inner part and a Li₂CO₃-enriched outer part. In

addition, intense morphological changes of the electrode surface were observed, viz. round shaped nodules (~400 nm in diameter) that progressively formed and covered the electrode surface. The formation of these nodules started simultaneously with the formation of the Li₂CO₃-enriched layer below 1.4 V, and both, the nodules disappeared and the Li₂CO₃ efficiently dissolved after the initial charge process, as revealed by AFM and XPS (a LiF-enriched deposit remained on the electrode). These observations led to the assumption that formation and disappearance of the nodules is strongly connected with formation and dissolution of SEI species. The formation and disappearance of the nodules was still present for subsequent cycles, however the quantity of remaining Li₂CO₃ increased with cycle number leading to thickening of residual deposit. Two hypotheses were presented for the nodules formation: 1) the nodules are built up by solely electrolyte degradation products, or 2) the nodules exhibit a core-shell structure with a lithiated active material core and a shell made of electrolyte degradation products (Figure 13). The second hypothesis might be supported by the volume changes in the active material during lithiation, which could lead to extrusion processes of active material, generating the core. However, the authors demonstrated that the theoretical volume changes of mixed possibly active phases in the potential range in which the nodules formation take place, is negligible. Thus, the formation of large nodules should be mainly related to huge amounts of SEI species, this was also supported by XPS results that demonstrated the efficient dissolution of Li₂CO₃.^[159] At this point it should be mentioned that types of intermixing of SEI and active material in nanosized TMO electrodes were also described by others, e.g. Tian et al. that found a penetration of the SEI layer into the bulk electrode material (α-Fe₂O₃ thin film electrode, LiClO₄/PC) upon repeated charge/discharge. In this work, also morphological changes that are non-uniformly distributed over the electrode surface in the nanoscopic scale were described.^[110]

Figure 13. Scheme illustrating the two different mechanisms proposed (hypotheses 1 and 2) to explain the possible origin of the large spherical nodules formed at the electrode surface during the first discharge, "Reprinted with permission from L. Martin, H. Martinez, D. Poinot, B. Pecquenard, F. Le Cras, Direct observation of important morphology and composition changes at the surface of the CuO conversion material in lithium batteries, Journal of Power Sources 248 (2014) 861-873, Copyright © 2017 Elsevier".

Klein et al. investigated additive-free CuO thin film electrodes in lithium and sodium half-cell configuration (LiPF₆/EC/DMC, and NaFSI/EC/DMC), and found that the applied alkaline ion has significant impact on the SEI formation. In general, surface film formation was more pronounced in the CuO/Na system. Comparison after the 10th cycle revealed a film thickness of ~6 μm for the CuO/Na cell, and ~1.5 μm for the CuO/Li cell. Differences in compositions were found, such as mainly organic species (mostly hydrocarbons) for CuO/Li, with a layer-like structure (more organic in the outer part and more inorganic in the inner part). Whereas the CuO/Na system showed a homogeneous distribution of inorganic compounds such as carbonates. In addition, a pronounced decrease of the surface film to a huge extent (remaining film ~1 μm) was observed during charging (Figure 14).^[22]

Figure 14. Schematic model for SEI evolution and composition in CuO/Na- and CuO/Li-systems, "Reprinted with permission from F. Klein, R. Pinedo, P. Hering, A. Polity, J.r. Janek, P. Adelhelm, Reaction Mechanism and Surface Film Formation of Conversion Materials for Lithium-and Sodium-Ion Batteries: An XPS Case Study on Sputtered Copper Oxide (CuO) Thin Film Model Electrodes, The Journal of Physical Chemistry C 120(3) (2016) 1400-1414, Copyright © 2017 American Chemical Society".

3.4.8. Contribution of transition metal nanoparticles and SEI species to additional capacities

Conversion reaction of nanosized TMOs is assumed to result in metallic nanoparticles finely dispersed in Li₂O. The role of these

metallic nanoparticles in processes of interfacial film formation has been discussed in literature.

For instance, Guo et al. observed additional capacities for $\text{Co}_3\text{O}_4/\text{PPy}$ electrodes (PPy: polypyrrole, $\text{LiPF}_6/\text{EC}/\text{DMC}$) from lithium storage below 0.7 V. It was suggested that the additional capacity originates from reversible decomposition of SEI species catalyzed by metallic cobalt.^[71] Yu et al. observed additional capacities for $\text{CoO-Li}_2\text{O}$ composites ($\text{LiPF}_6/\text{EC}/\text{DEC}$) as negative electrodes in LIBs, attributed to a polymer/gel-like film, as the result of kinetically activated electrolyte degradation enabled by metallic cobalt nanoparticles.^[160]

Su et al. did test series including $\text{Fe}_3\text{O}_4@\text{C}$ microspheres, $\text{Fe}@\text{C}$ microspheres (carbon content 22.6 %) and electrodes with only carbon ($\text{LiPF}_6/\text{EC}/\text{EMC}/\text{DMC}$) to investigate a possible electrocatalytic role of Fe nanoparticles in the conversion of species found in SEI films. $\text{Fe}@\text{C}$ microspheres, actually assumed to be inert towards lithium storage, exhibited 1379 mAh g^{-1} as initial discharge capacity and 447 mAh g^{-1} after 40 cycles (50 mA g^{-1}). Phase changes were absent after discharge/charge processes, indicating the stability of iron nanoparticles during cycling. The observed capacities were higher than for pure carbon electrodes ($\sim 270 \text{ mAh g}^{-1}$ at 40 cycles). In addition, significant different CV curves were obtained (Figure 15). For $\text{Fe}@\text{C}$ electrodes an intense and broad peak appeared between 0.3 and 0.8 V. For $\text{Fe}_3\text{O}_4@\text{C}$ microsphere electrodes, the peak located at similar position was attributed to the reduction of $\text{Fe}^{3+}/\text{Fe}^{2+}$ to Fe. Since no higher valence iron species are present in the $\text{Fe}@\text{C}$ system, the peak was attributed to the formation of SEI. It was suggested that iron nanoparticles are supposed to activate or promote the electrolyte decomposition.^[20] Similar electrochemical behavior was reported for Ni/C hierarchical composites (nickel nanoparticles highly dispersed in N-containing carbon nanosheets, $\text{LiPF}_6/\text{EC}/\text{EMC}/\text{DMC}$). Although nickel nanoparticles are seen as inert towards the reaction with lithium, an unexpected high reversible capacity of 1051 mAh g^{-1} after 30 cycles, and 635 mAh g^{-1} after 100 cycles (200 mA g^{-1}) were observed and ascribed to the electrochemically catalytic behavior of Ni nanoparticles in the process of the reversible

formation/decomposition of some species in SEI films.^[161] Su et al. observed capacities over the theoretical value for CoCO_3/GNS composites ($\text{LiPF}_6/\text{EC}/\text{EMC}/\text{DMC}$). Besides the conversion reaction, a new electrochemical catalytic conversion reaction that also involves the anion was proposed. C^{4+} in CO_3^{2-} is reduced to C^0 or other low valence C species catalyzed by metallic cobalt, and contributes to the observed additional capacity.^[28] Similar observations were reported for pure CoCO_3 electrodes ($\text{LiPF}_6/\text{EC}/\text{EMC}/\text{DMC}$).^[162] According to Ding et al., CO_3^{2-} can be reduced to Li_xC_2 ($x = 0, 1, 2$) during electrochemical processes.^[29] Li_2C_2 formation in SEIs originating from CO_3^{2-} was also suggested in earlier literature by Eshkenazi et al. (investigation of SEI formed on carbonaceous materials).^[17] Besides metallic nanoparticles, also Fe_3C nano shells are reported to catalyze reversible redox processes of some SEI species leading to enhanced capacity output.^[163] Further investigations regarding the role of SEI compounds and metallic nanocatalysts in additional capacity phenomena were conducted using layered hydroxide cobalt acetate (LHCA) nanoplates face-to-face anchored to GNS ($\text{LiPF}_6/\text{EC}/\text{EMC}/\text{DMC}$). These systems delivered an initial discharge capacity of 2526 mAh g^{-1} and a reversible capacity of 1035 mAh g^{-1} after 40 cycles at 200 mA g^{-1} (GNS content: 32.0 wt-%). At 350 mA g^{-1} the observed Li uptake was 2.29 times the theoretical value based on conversion reaction for the 1st and 2nd cycles, and 1.90 times at 100-120 cycles. The authors attributed the additional capacity mainly on electrocatalytic conversion of LiOH and lithium acetate (LiAc), which are well known SEI species and for the here discussed system also provided during lithiation and decomposition of LHCA resulting in Co, LiOH and LiAc. The metallic Co nanoparticles serve as electrocatalyst for further reaction of LiOH and LiAc with Li resulting in $\text{Li}_2\text{O}/\text{LiH}$ and acetaldehyde, respectively. The conversion from acetate to acetaldehyde was confirmed with FT-IR.^[164] The reaction of LiOH with Li leading to $\text{Li}_2\text{O}/\text{LiH}$ catalyzed by metallic Ru confirmed through solid state NMR and theoretical calculations was also reported by Hu et al.^[30]

Figure 15. (l) CV curves of pure C, and (r) Fe@C for the initial 3 cycles. "Reprinted with permission from L. Su, Y. Zhong, Z. Zhou, Role of transition metal nanoparticles in the extra lithium storage capacity of transition metal oxides: a case study of hierarchical core-shell $\text{Fe}_3\text{O}_4/\text{C}$ and Fe@C microspheres, *Journal of Materials Chemistry A* 1(47) (2013) 15158-15166, Copyright © 2017 Royal Society of Chemistry".

4. Summary and Outlook

This review article covers interfacial phenomena and additional capacity occurrences beyond the theoretical values calculated according to the classical conversion reaction for nanosized TMOs as negative electrodes in LIBs. Particularly, reports on oxides of cobalt, iron, manganese, ruthenium, chromium, nickel, and copper including nanocomposite and -hybrid structures of these oxides in half-cell configuration with electrolytes based on lithium salts and organic carbonates are presented. The origin of additional capacities in the long-term (up to ~50 - 200 cycles) is attributed to several hypotheses based on interfacial phenomena and material dimensions in the nanometer regime, with the following distribution: For approximately half of the presented additional capacity occurrences, a contribution of interfacial interphases (SEI, polymer/gel-like film) is suggested. Additional lithium storage capabilities by unique nano-architectures with high specific surface areas, nanocavities, and/or interconnected meso- and/or nanopore systems are suggested to have a contribution in approximately one third of the reported cases. Contributions of interfacial lithium storage are mentioned in approximately one fifth of all occurrences (please note: distribution according to suggestions/assumptions from presented literature in this review article; multiple assignments are possible). In nanocomposite and -hybrid structures of TMOs with carbon derivatives (primarily sp^2 hybridized carbons), additional capacities are also attributed to synergistic effects between nanosized TMO and the carbon species. In this context, *synergistic effects* are for instance the formation of strong oxygen linkages between TM and the carbon part (TM-O-C) that allows for fast electron hopping, and hence supports enhanced conductivity and electrochemical performance.^[42] For manganese based oxides, the reoxidation of Mn^{2+} to higher oxidation states was reported in the presence of carbon. This might contribute to the overall improved capacity, since MnO was identified in some test series as the product of recharge, although initially higher oxidized manganese species

were utilized as electrode materials, which reduces the theoretical capacity for subsequent cycles.^{[76], [111]} Newer literature suggests a capacity contribution of SEI species that are subjected to chemical reactions, for instance reduction of C^{4+} in CO_3^{2-} to C^0 and/or other low valence C species, or the reversible reaction of LiOH with lithium leading to Li_2O and LiH .^{[28], [29], [30]} To a very small extend also capacity contributions through interactions with further cell compounds were suggested, such as additional lithium storage in acetylene black or CuO at the surface of the current collector (even though half-cell systems without conductive carbon additives/binder show additional capacity occurrences).

Additional capacities are mainly observed for negative electrodes based on nanosized oxides of cobalt and iron (in pristine form and in their nanocomposite and -hybrid structures with carbonaceous species). In addition, remarkable high capacities are found for manganese oxides/carbon nanocomposites, especially with N-doped carbon derivatives, attributed to a synergy effect of N-doping and C-hybridization.^[115]

Interestingly, the different utilized TMO types seem to tend towards particular capacity profile shapes over a monitored area starting from the 2nd cycle to approximately 50 - 200 cycles. Cobalt oxides often show a *type I (mound-shape)* capacity profile with an initial increase and subsequent decrease and a clear defined capacity maximum. Operating temperature and C rate were found to have an impact on this capacity profile shape. For instance, Tarascon's group reported that cycling at 55 °C compared to 20 °C led to capacity enhancement, and to an appearance of a capacity maximum that shifts towards increased cycle numbers the higher the C rate.^[75] In contrast to cobalt oxides, iron oxide based electrodes tend towards a *type IV (horizontal-shape)* capacity profile without any significant minimum or maximum. Besides that, *type II (upward-shape)* capacity profiles are also found for several cases of additional capacity occurrences when the electrode material contains iron oxides. Manganese oxide based electrodes show a trend

towards *type III (U-shape)* capacity profiles, exhibiting an initial decrease followed by an increase with a clear defined capacity minimum. Interestingly, also doping of Fe_2O_3 with manganese leads to the *type III (U-shape)* capacity profile, although iron oxide based electrodes usually show a trend towards *IV (horizontal-shape)* or *type II (upward-shape)*,^[36] and indicating that the presence of manganese promotes such a capacity output behavior. The mechanism leading to the *U-shape* remains speculative. It might be based on mixed effects, such as manganese cluster aggregation in secondary MnO_x particles and formation of defects and deformations.^[76] At this point it needs to be mentioned that a pronounced *U-shape* in the capacity profile of mesoporous hollow spheres of Co_3O_4 was also found. In this case, the *U-shape* was associated with high-rate lithiation-induced reactivation of the active material.^[92]

Pristine oxides of ruthenium, chromium, nickel and copper are often reported to show poor long-term cycling with pronounced capacity fading. Theoretical capacities based on conversion reaction are hardly achieved in lab experiments, primarily attributed to large volume changes during lithiation/delithiation associated with pulverization of the material and loss of electric contacts. However, ruthenium oxide shows extremely high Coulombic efficiencies and metallic conductivity, hence it is considered as a model material to investigate lithium storage, preferentially at the initial cycle. Especially for chromium oxides, comparatively huge quantities of electrolyte degradation products have been reported leading to retardation of lithium diffusion. In addition, the preferred formation of chromium monoxide (CrO_{1-x}) instead of Cr_2O_3 during recharge possibly contributes to the reduced capacity output.^[24] Similar difficulties

are observed for CuO electrodes in some cases, in which re-oxidation preferentially leads to Cu_2O that shows a significantly lower theoretical capacity compared to CuO .^{[146], [149]} Pure nickel oxides also show poor long-term cycling behavior, but can be intensively improved by embedding of NiO into a carbonaceous matrix.

Besides the impact of the TMO type, also structural and morphological aspects seem to have a significant impact on the overall capacity output, since reduced fading, stabilization of capacity curves and even additional capacity occurrences are mainly found in materials with nano-dimensions, high specific surface areas and/or hierarchical meso- and/or nanopore networks, whereas bulk materials tend towards a strong capacity fading behavior over long-term cycling. A stable and homogenous SEI is found to be supportive for improved electrochemical performance, hence interfacial design of nanosized TMO/Li systems and tuning of pore diameters and/or layer spacings are understood as beneficial approaches towards optimized electrochemical performance.

For calculation of theoretical capacities, interpretation of lithiation/delithiation curves, and estimation of C rates, the classical conversion reaction remains the most utilized concept for nanosized TMOs. However, this is a schematic concept that might not display the full picture and further lithium storage and capacity providing processes, e.g. based on electrode/electrolyte interphases (SEI, polymer/gel-like film), grain boundaries, interfacial lithium accommodation, and/or unique nano-architectures, should be regarded for discussions of the overall capacity output.

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Keywords: Solid electrolyte interphase • polymer/gel-like film • additional capacity • batteries • electrode materials

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REVIEW

The origin of additional capacities for nanosized transition metal oxides is a subject of intense debate. This review provides an up-to-date summary with special emphasis on scenarios based on interfacial phenomena and material dimensions in the nanometer regime. In addition, a first attempt is made to systematically classify capacity profiles of nanosized transition metal oxides with additional capacity occurrences.

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Review on interfacial phenomena/capacities beyond conversion reaction occurring in nanosized transition metal oxide based negative electrodes in lithium ion batteries