The continuing development of Magnéli phase titanium sub-oxides and Ebonex® electrodes

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**Abstract**

Magnéli phase titanium sub-oxides were identified (via X-ray diffraction) in the 1950s as a distinct series of electrically conducting compounds having the general formula TiₙO₂ₙ₋₁, where 3 < n < 10. Early research on the characterisation of materials based on TiₙO₂ₙ₋₁ has been well documented. This concise review, which is illustrated by data from the literature and our own laboratory, concerns more recent research on Magnéli phase titanium oxide materials. A brief overview of chemical and physical properties is followed by the applications of electrode materials based on these titanium oxides. Energy conversion technologies (particularly batteries and fuel cells) are shown to be a continued area of research that particularly suits the relatively high electrical conductivity and chemical stability inherent in these materials.

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**1. Introduction**

The Magnéli phases of titanium oxide, which have been commercially recognised under the Ebonex® trade name [1–4], comprise a series of distinct compounds having the generic formula TiₙO₂ₙ₋₁, where n is an integer between three and ten (and more typically between four and six). These materials are relatively robust in aggressive media and exhibit high conductivity; for example, Ebonex® has a projected half-life of 50 years in 4 mol dm⁻³ H₂SO₄ at room temperature [5]. The electrical conductivity varies depending on the sub-oxide (‘n’ value) but is of the same order of magnitude as carbon. Due to the methods used in manufacturing Magnéli phase materials, it is difficult to prepare the separate phases in a pure form; the materials usually contain a mixture of stoichiometries. As a result, the electrical and chemical properties of the separate phases can be difficult to obtain with a high degree of...
Fig. 1. The relative electrical conductivities of the more common Magnéli phase titanium sub-oxides [6,7]. Log10 (conductivity, \(\sigma/\text{S cm}^{-1}\)) is plotted vs. the coefficient, \(n\), in \(\text{Ti}_n\text{O}_{2n-1}\).

Fig. 2. The different orientations of TiO\(_2\) octahedra in Magnéli phase materials; edge-, face- and corner-sharing of oxygen.

Fig. 3. Edge-sharing TiO\(_2\) and Ti\(_4\)O\(_7\) octahedra sheets showing the face sharing shear plane which is present in Ti\(_4\)O\(_7\).

Table 1

<table>
<thead>
<tr>
<th>(\text{Ti}<em>n\text{O}</em>{2n-1}) phase(s)</th>
<th>Electrical conductivity ((\sigma/\text{S cm}^{-1}))</th>
<th>Log10 ((\sigma/\text{S cm}^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Ti}_3\text{O}_5)</td>
<td>630</td>
<td>2.8</td>
<td>[12]</td>
</tr>
<tr>
<td>(\text{Ti}_4\text{O}_7)</td>
<td>1035</td>
<td>3.0</td>
<td>[7]</td>
</tr>
<tr>
<td>(\text{Ti}_5\text{O}_9)</td>
<td>1995</td>
<td>3.3</td>
<td>[6]</td>
</tr>
<tr>
<td>(\text{Ti}<em>6\text{O}</em>{11})</td>
<td>631</td>
<td>2.8</td>
<td>[6]</td>
</tr>
<tr>
<td>(\text{Ti}<em>7\text{O}</em>{15})</td>
<td>63</td>
<td>1.8</td>
<td>[6]</td>
</tr>
<tr>
<td>(\text{Ti}<em>8\text{O}</em>{15})</td>
<td>25</td>
<td>1.4</td>
<td>[6]</td>
</tr>
<tr>
<td>(\text{Ti}_4\text{O}_7 + \text{Ti}<em>6\text{O}</em>{15})</td>
<td>410</td>
<td>2.6</td>
<td>[7]</td>
</tr>
<tr>
<td>(\text{Ti}_3\text{O}_5 + \text{Ti}_4\text{O}_7)</td>
<td>330</td>
<td>2.5</td>
<td>[7]</td>
</tr>
<tr>
<td>(\text{Ti}_4\text{O}_7 + \text{Ti}<em>6\text{O}</em>{15})</td>
<td>500</td>
<td>2.7</td>
<td>[7]</td>
</tr>
</tbody>
</table>
vary significantly depending on exact sub-oxide (‘n’ number). During production, all the sub-oxides can be derived from the same feedstock so reaction conditions must be carefully controlled to give the desired stoichiometry for the final material. Factors that influence the degree of reduction and compositional gradients include the composition of the reaction environment, the diffusion of reducing agent through the feedstock, particle size, feedstock density, temperature profile during reaction and the time-scale of processing.

The different phases can be readily identified by X-ray diffraction. The following reflections can be used to distinguish the presence of mixed phases using Cu Kα radiation: \( \theta = 10.39^\circ \) for \( \text{T}_4 \text{O}_7, \theta = 11.01^\circ \) for \( \text{Ti}_2 \text{O}_5 \) and \( \theta = 11.42^\circ \) for \( \text{Ti}_6 \text{O}_{11} \) [12]. Fig. 4 shows the expected peak positions for the powder XRD patterns of \( \text{TiO}_2 \) starting material along with \( \text{Ti}_6 \text{O}_{11}, \text{Ti}_5 \text{O}_9 \) and \( \text{Ti}_4 \text{O}_7 \) phases [13]. Raman spectroscopy has also been used to differentiate the Magnéli phases [14]. In particular, this technique has been used to investigate the charge ordered states of the metallic conducting (>150 K) and semi-conducting (<120 K) phases of \( \text{Ti}_4 \text{O}_7, \text{Ti}_5 \text{O}_9 \) and \( \text{Ti}_6 \text{O}_{11} \) phases.

### 2.2. Physical form

Ebonex®-type materials can be processed into a variety of physical forms; powders, porous and non-porous three-dimensional solids, together with composites, are all readily achievable. There is also evidence for naturally occurring Magnéli phase titanium sub-oxides in mudstone deposits [15]. Fig. 5 shows photographic images of some Ebonex® materials: (A) powder, (B) sintered tile and (C) polymer composite tile. Production of three-dimensional forms may be achieved either by processing pre-produced Magnéli phase powders or from pre-shaped precursor materials (e.g. reduction of sintered \( \text{TiO}_2 \) monoliths). A flow chart defining the various forms of Magnéli oxides is presented in Fig. 6.

#### 2.3. Doped materials

The ability to create custom made materials for specific applications is increased by doping of the Magnéli phases. Doping, however, is less readily achievable for these materials compared to other systems, such as carbon or metallic alloys. Increased conductivity or catalytic properties are particularly desirable. Gusev et al. compared standard Magnéli phases with vanadium, niobium and iron doped sub-oxide materials [7,12] demonstrating that the doping can reduce the conductivity compared to the pure phases. A recent patent [16] has compared commercial Ebonex® and in-house prepared \( \text{Ti}_4 \text{O}_7 \) to cerium doped \( \text{Ti}_4 \text{O}_7 \) (\( \text{CeO}_0.4 \text{Ti}_3.6 \text{O}_7 \)) showing that, when used as an additive for the positive electrode active material within NiMH rechargeable batteries, the materials resulted in different electrode resistances. Electrodes containing the additive had a lower resistance than the equivalent standard electrode. Differences were observed between commercial Ebonex® and ‘in-house’ prepared \( \text{Ti}_4 \text{O}_7 \) material and between \( \text{CeO}_0.4 \text{Ti}_3.6 \text{O}_7 \) prepared by two different processes. Different processes for manufacturing the Magnéli phases can significantly affect the electrode resistance. Using a one-step synthesis to produce Ce-doped Magnéli phases (heating a mixture of \( \text{CeO}_2, \text{TiO}_2 \) and Ti powders at 1200 °C for 4 h under \( \text{N}_2 \)) the resistance of the electrode was reported to be 24% lower than a similar material made using a two-step process ((1) combining \( \text{Ti}_4 \text{O}_4 \) and Ti powders at 1300 °C for 4 h under \( \text{N}_2 \) then (2) adding \( \text{CeO}_2 \) and heating at 1300 °C for a further 4 h). This highlights the importance of process conditions; materials characteristics and the composition of synthesised materials and suggests that particle morphology, together with phase composition, controls the properties of these materials.

### Table 2

<table>
<thead>
<tr>
<th>Structure</th>
<th>Composition</th>
<th>Pre-treatments</th>
<th>Process conditions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porous, monolithic</td>
<td>( \text{Ti}_4 \text{O}_7 )</td>
<td>(monophasic)</td>
<td>Mouldings were sintered in air at 1323 K for 24 h followed by reduction under a nitrogen atmosphere at 1323 K for 4 h.</td>
<td>[58]</td>
</tr>
<tr>
<td>Powder</td>
<td>( \text{Ti}_4 \text{O}_7 )</td>
<td>None</td>
<td>A mixture of ( \text{TiO}_2 ) and Ti metal was ground in an evacuated silica tube at 1423 K over one week.</td>
<td>[59]</td>
</tr>
<tr>
<td>Pressed pellet</td>
<td>( \text{Ti}<em>4 \text{O}</em>{2n-1} )</td>
<td>3 ≤ 8 ≤ 10</td>
<td>The intermediate material was cured at 1423 K for 3 days in a sealed silica tube.</td>
<td>[60]</td>
</tr>
<tr>
<td>Sintered pellet</td>
<td>( \text{Ti}_4 \text{O}_7 )</td>
<td>Intermediate material was made from ( \text{TiO}_2/\text{Ti} ) metal mixtures by heating under argon in a furnace (&lt;1473 K).</td>
<td>The sintered pellets were reduced under a 93% ( \text{Ar} ), 7% ( \text{H}_2 ) atmosphere for 3.5 h at 1270–1340 K.</td>
<td>[61]</td>
</tr>
<tr>
<td>Rod or tile</td>
<td>( \text{Ti}_4 \text{O}_7, \text{Ti}_6 \text{O}_5, \text{Ti}_5 \text{O}_9 )</td>
<td>None</td>
<td>( \text{TiO}_2 ) was reduced in a hydrogen furnace at 1453 K for 8 h.</td>
<td>[62]</td>
</tr>
<tr>
<td>Tile</td>
<td>( \text{Ti}_4 \text{O}_7 ) (70%), ( \text{Ti}_6 \text{O}_5 ) (30%)</td>
<td>( \text{TiO}_2 ) powder (5–50 μm) was mixed with a petroleum-based organic binder, Mobiler S (3–4%). The mixture was ball milled then pressed at 5 tons per square inch. The binder was removed by heating at 523–573 K before the block was fired at 1573 K for 3 h.</td>
<td>The prepared ceramic tile was heated in a hydrogen atmosphere at 1503 K for 6 h.</td>
<td>[63]</td>
</tr>
</tbody>
</table>
2.4. Coated materials

Magnéli phase conductive ceramics make suitable support materials for several catalytic coatings and the rutile-type surface structure can provide good adhesion of surface layers. Materials that also adopt a rutile configuration, for example PbO₂, can adhere particularly well. This is an important feature for longevity of the coating and essential where the toxicity of any electrode dissolution could cause a problem. Active materials may be applied via numerous methods, including thermal decomposition (oxidation) [17], reduction (wet chemistry [18,19] or the use of an H₂ atmosphere [13]) and condensation [20]. Electrodeposition is, perhaps, the most common method used to apply coatings to Magnéli phase materials. Typical electrodeposits include Pb (cathodic) and PbO₂ (anodic). Both the Pb and PbO₂ layers follow the underlying morphology of the Ebonex®/composite substrate and can adhere well to the substrate. Deposited layers with a thickness ranging from 1 μm to several millimetres can prove particularly suitable for battery applications.

3. Applications

3.1. ‘As-prepared’ and catalyst coated materials

Monolithic Magnéli phase materials can be used as electrodes in a wide range of electrochemical processes. Research applications include the production of glyoxylic acid [21], oxidation of flue gases [22,23], preparation of pyrite (FeS₂) [24] and the oxidation of trichloroethylene [25]. Industrial applications include battery technologies [26], remediation of foul water [27] and cathodic protection of steel in concrete [4,26,28].

Magnéli phase materials provide a practical substrate for catalyst layers. The latter can be either particulate or bulk coatings. Table 3 summarises the synthesis and applications of some of these materials. Lead dioxide has been used as an electrode for the catalytic oxidation of organic species [29] and can be anodically deposited onto Ebonex® from aqueous plating solutions [30,31]. Amorphous deposits containing α- and β-PbO₂ can be electroplated from lead nitrate (Pb(NO₃)₂) in nitric acid solution [29–31]. However, selection of appropriate electrolyte composition, pH and current density can yield pure α-PbO₂ (PbO in NaOH at pH > 13; Pb(CH₃SO₂)₂ in KOH at pH > 13; or PbO in HClO₄ at pH 5.8) or pure β-PbO₂ (PbCO₃ in HClO₄ at pH 0.04) [30]. The PbO₂ coatings can be extremely stable with reduction only taking place at potentials more negative than 0.75 V vs. SHE. PbO₂ coatings also have low corrosion rates of circa 700 μm per year [31].

The majority of research in recent years has focussed on platinum coatings. Careful choice of experimental conditions allows the production of platinum-on-Ebonex® electrodes which are stable and show similar electrochemical activity to bulk Pt electrodes [32,33]. Table 4 gives some examples of platinum catalysts.
### Table 3
Magnéli phase titanium oxides as conductive supports for non-platinum-based catalysts. NG = not given.

<table>
<thead>
<tr>
<th>Deposited material</th>
<th>Method</th>
<th>Conditions</th>
<th>Application</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon film</td>
<td>Thermal reduction of TiO₂/polyvinyl alcohol mixtures</td>
<td>973–1373 K for 1 h under N₂ flow (50 Ml/min)</td>
<td>Photocatalyst: decomposition of iminocadetetriaacetate and phenol</td>
<td>[64]</td>
</tr>
<tr>
<td>Ru film</td>
<td>Electrodeposition</td>
<td>–1.4 V vs. SCE for 1 h</td>
<td>NG</td>
<td>[17]</td>
</tr>
<tr>
<td>RuO₂ film</td>
<td>Thermal decomposition of RuCl₃</td>
<td>653 K for 10 min</td>
<td>NG</td>
<td>[17]</td>
</tr>
<tr>
<td>Co–Te–O</td>
<td>Condensation</td>
<td>10⁸ Pa</td>
<td>Fuel cells</td>
<td>[20]</td>
</tr>
<tr>
<td>Pd</td>
<td>Electrodeposition</td>
<td>3.0 mol dm⁻³ PdCl₂, 1.0 mol dm⁻³ HCl</td>
<td>Flu gas treatment (oxidation of sulphur dioxide)</td>
<td>[65]</td>
</tr>
<tr>
<td>PbO₂</td>
<td>Electrodeposition</td>
<td>0.4 mol dm⁻³ PbNO₃, 10 mA cm⁻² for 30 min</td>
<td>Water purification</td>
<td>[29]</td>
</tr>
<tr>
<td>PbO₂</td>
<td>Electrodeposition</td>
<td>Various nitrate electrolytes</td>
<td>NG</td>
<td>[31]</td>
</tr>
<tr>
<td>PbO₂</td>
<td>Electrodeposition</td>
<td>Various acidic and alkali electrolytes</td>
<td>Cr⁺ oxidation</td>
<td>[30,66]</td>
</tr>
</tbody>
</table>

### Table 4
Magnéli phase titanium oxides as conductive supports for platinum-based catalysts [32].

<table>
<thead>
<tr>
<th>Catalyst form</th>
<th>Method of catalyst preparation</th>
<th>Reagents and conditions</th>
<th>Applications considered</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particles</td>
<td>Electrodeposition</td>
<td>Pt(NH₃)₂(NO₂)₂</td>
<td>Redox electrode</td>
<td>[32,33]</td>
</tr>
<tr>
<td>Nanoparticles</td>
<td>H₂ reduction</td>
<td>H₂ atmosphere at 573 K</td>
<td>Water hydrolysis (fuel cells)</td>
<td>[37,39,67]</td>
</tr>
<tr>
<td>Pt and Pt/Co nanoparticles</td>
<td>Aqueous reduction</td>
<td>Pt(ethylenediamine)Co(ethylenediamine)NaBH₄</td>
<td>Oxygen evolution</td>
<td>[19]</td>
</tr>
<tr>
<td>Film</td>
<td>Electrodeposition</td>
<td>K₂PtCl₆, 2–5 mA cm⁻² (1 h)</td>
<td>Trichloroethylene and chloroform reduction (water decontamination)</td>
<td>[35]</td>
</tr>
<tr>
<td>Pt/Ru/Os/Rh mixed particles</td>
<td>Aqueous reduction</td>
<td>H₂PtCl₆, RhCl₃, RuCl₃, OsCl₃, IrBr₃</td>
<td>Oxygen reduction/water oxidation (fuel cells)</td>
<td>[68]</td>
</tr>
<tr>
<td>Particles</td>
<td>Electrodeposition</td>
<td>PdCl₂, CH₃COOH (Sn–Pd pre-treatment)</td>
<td>Oxidation of organics (e.g. aliphatic/aromatic alcohols and formaldehyde)</td>
<td>[18]</td>
</tr>
<tr>
<td>Nanoparticles</td>
<td>H₂ reduction</td>
<td>Pt(NH₃)₂(NO₂)₂ H₂ atmosphere at 1173 K (1 h)</td>
<td>Electrocatyst (PEM fuel cells)</td>
<td>[13]</td>
</tr>
<tr>
<td>Film</td>
<td>Electrodeposition</td>
<td>H₂PtCl₆, 1.8 V vs. SCE (1 h)</td>
<td>General catalysis requiring a Pt surface</td>
<td>[69]</td>
</tr>
</tbody>
</table>

Analysis indicates that at high positive potentials (water hydrolysis region) it is possible to oxidise the lower Magnéli phases. Kao et al. observed the irreversible conversion of Ti₄O₇ to Ti₆O₁₁ while repeatedly cycling the potential of an Ebonex® electrode between 0.8 and 1.7 V vs. SCE in sulphuric acid [5]. In the case of catalyst-loaded materials, this approach could effectively be used to passivate the electrode surface at areas where no catalyst was present and thus reduce the likelihood of side reactions taking place on the substrate during use.

A further (non-electrochemical) example of the diversity of applications for which Magnéli phase titanium sub-oxides have been considered is given by United States patent application US2007/0163612A1 which suggests their use as catalyst supports for cigarette filters [34].

### 3.2. Remediation of aqueous waste and contaminated water

The robust characteristics of Magnéli phase materials make them suitable for electrochemical treatment of many contaminants, such as halogenated organic species [35], which are typically stable compounds with long half-lives in the natural environment or sulphites [22,23,36], which are common in industrial effluents.

Decomposition of trichloroethylene (TCE) and chloroform (CF) have been shown to be pseudo-first order at Ebonex® based electrode [35]. Fig. 7 shows current efficiencies for the reduction of TCE and CF plotted vs. cathode potential [35]. TCE reduction was carried out at a Pt-coated Ebonex® electrode in a pH 7 electrolyte, initially containing 0.1 mol dm⁻³ K₂SO₄ and 1.0 mmol dm⁻³ TCE. CF reduction was carried out at a Pd-coated Ebonex® electrode in a pH 7 electrolyte, initially containing 0.05 mol dm⁻³ KCl and 1.0 mmol dm⁻³ CF.

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taining 0.1 mol dm\(^{-3}\) \(\text{K}_2\text{SO}_4\) and 1.0 mmol dm\(^{-3}\) \(\text{TCE}\). CF reduction was carried out at a Pd-coated Ebonex® electrode in a pH 7 electrolyte, initially containing 0.05 mol dm\(^{-3}\) \(\text{KCl}\) and 1.0 mmol dm\(^{-3}\) CF. Current efficiencies approaching 100% were observed at low overpotentials (−0.3 V and −0.5 V vs. SHE for CF and TCE, respectively). The decrease in current efficiency at higher overpotentials corresponded to water decomposition becoming a competing side reaction. Reduction in current efficiency also occurred as the reactant concentration decreased leading to mass transport effects.

High current efficiencies (>80%) have also been demonstrated for the oxidation of sulphur dioxide [22,23]. Fig. 8 shows the current efficiency for the continuous running of a sieve-flow reactor during the oxidation of sulphur dioxide from simulated flue gas. The effect of current density and acid concentration are shown [22].

**Fig. 8.** Current efficiency for the continuous running of a sieve-flow reactor during the oxidation of sulphur dioxide from simulated flue gas. The effect of current density and acid concentration are shown [22].

3.3. Fuel cells

Many catalysed Magnéli materials have been aimed at fuel cell applications. Electrocatalytic films of Co–Te–O on Ebonex® have shown an acceptable performance for oxygen evolution and oxygen reduction reactions – of interest for regenerative fuel cells and batteries [20].

Analogous to the platinum on carbon black catalysts currently used in PEM fuel cell technologies, Magnéli phase titanium oxides can be used as the catalyst support for platinum. Pt nanoparticles on Ebonex® show enhanced oxygen reduction compared to polycrystalline platinum electrodes [37]. Fig. 9 shows cyclic voltammograms for platinum-on-Ebonex® catalysts [38,39]. The voltammograms show that Magnéli materials can be successfully used as a catalyst support material for applications in both acidic and alkali media. Compared to equivalent platinum-on-carbon catalysts, these materials appear to show improved catalyst utilisation efficiencies and enhanced electrocatalytic activity [38]. More complex catalyst–electrode combinations have also been investigated; Fig. 10(A) shows a cyclic voltammogram of a platinum/gold/Ebonex® electrode in a HClO\(_4\) electrolyte [37]. The voltammogram demonstrates good hydrogen adsorption/desorption and PtO\(_x\) formation/reduction activity with the electoractive area being calculated as 36 m\(^2\) g\(^{-1}\) Pt. Fig. 10(B) presents a cyclic voltammogram at a platinum/cobalt/Ebonex® electrode in KOH electrolyte [19]. This voltammogram differs from the typical Pt response. An anodic peak at circa 200 mV corresponds to the formation of cobalt(II) species. Further oxidation to cobalt(III) occurs at circa 1150 mV. These cobalt oxides suppress hydrogen formation while enhancing oxygen evolution.

In addition, a number of patents have cited Ebonex® or Magnéli phase titanium oxides as materials suitable for catalyst supports, bipolar electrodes or flow field plate applications in fuel cells:

- US 5,281,496 and 5,173,215 describe methods of applying platinum to various materials, including carbon and Magnéli phase titanium sub-oxides, for use in catalyst layers for oxygen reduction electrodes [42].
- US 6,517,962B1 and United States patent application US 2007/0248752A1 describe the use of catalysed Magnéli phase titanium sub-oxides as materials suitable for catalyst supports, bipolar electrodes or flow field plate applications in fuel cells: [45].
- US 6,790,554B4 describes the use of various materials, including carbon and Magnéli phase titanium sub-oxides, for use in catalyst layers for oxygen reduction electrodes [42].
- US 6,517,962B1 and United States patent application US 2004/0157110A1 describe the use of catalysed Magnéli phase titanium sub-oxides as electrode materials which would be tolerant to voltage reversal in fuel cell applications [43,44].
- US 6,790,554B4 describes the use of various materials, including Ebonex®, as substrates for bipolar fuel cell electrodes [45].
- US 5,635,039 describes design of MEA’s based on metallic sub-oxides, for use in catalyst layers for oxygen reduction electrodes [42].
- US 5,784,196 describes methods of applying platinum to various materials, including carbon and Magnéli phase titanium sub-oxides, for use in catalyst layers for oxygen reduction electrodes [42].
- US 5,281,496 and 5,173,215 describe methods of applying platinum to various materials, including carbon and Magnéli phase titanium sub-oxides, for use in catalyst layers for oxygen reduction electrodes [42].
- US 6,517,962B1 and United States patent application US 2007/0248752A1 describe the use of catalysed Magnéli phase titanium sub-oxides as electrode materials which would be tolerant to voltage reversal in fuel cell applications [43,44].
- US 6,790,554B4 describes the use of various materials, including Ebonex®, as substrates for bipolar fuel cell electrodes [45].
- US 5,635,039 describes design of MEA’s based on metallic sub-oxides, for use in catalyst layers for oxygen reduction electrodes [42].

The literature contains several studies suggesting that Magnéli phase materials are suitable for use in fuel cells; however, these tend to be short term, ‘proof of concept’ studies. Focused trials are required to show that these materials can operate for extended, maintenance-free periods under operational conditions in fuel cell stacks.
3.4. Batteries

Magnéli phase sub-oxides of titanium can be utilised in batteries as either electrode materials or as additives to the active materials. Significant work has been carried out on the applications of Ebonex® in static lead-acid batteries. Added to the positive paste of lead-acid batteries, Ebonex® particles have been shown to improve formation efficiency [5]. In particulate form (powder, granule or fibre), the conductive Magnéli phase materials are claimed to improve current distribution through the paste material. This effect is most beneficial for the positive electrode, where the PbO₂ active material is considerably less conductive than metallic Pb at the negative electrode. Traditionally, lead-acid batteries use heavy lead-alloy grids as current collectors. In addition to their heavy weight, the grids are prone to corrosion during operation. Titanium sub-oxides are considerably lighter and their corrosion resistance has led to the development of viable bipolar lead-acid battery technology [1].

Bipolar batteries are constructed with the cells are arranged in series such that the positive electrode of one cell acts as the negative electrode of the adjacent cell and vice-versa. In this configuration, the current density through the cells is more uniform across the electrode surface than in traditional designs, where the current must flow into and out of the cell via a current collector at the top of each electrode. Fig. 11 compares bipolar and conventional configurations for a 3-cell, 6 V lead-acid battery. The arrows show the current flow through the cells.

Composite Ebonex® electrodes can offer higher impact resistance and easier processing compared to pure Ebonex® sheets. The advantages of a bipolar construction include lower materials use in cell packaging and higher active material utilisation [47]. Fig. 12 presents utilisation efficiency data of the active mass for bipolar Ebonex® compared to traditional battery configurations [1]. At a 10 h discharge rate, the bipolar configuration had approximately twice the active mass utilisation efficiency compared to a traditional lead-acid battery. The batteries tested were of different voltages and capacities (4 V, 7 A h Ebonex® vs. 6 V, 1.2 A h conventional). It would be expected, however, that even for batteries having the same capacities and nominal voltage, the active mass utilisation would be higher for the bipolar configuration.

Ebonex® has also been investigated for use in nickel metal hydride (NiMH) technologies, where it was used as an additive for the positive, nickel electrode. It was found to increase performance by suppressing oxygen evolution as well as by increasing the conductivity of the electrode [16]. Additional doping of the Ti₄O₇ parent lattice with Ce ions further enhanced the observed performance benefits. Fig. 7 shows the reduction in electrode resis-
4. Commercial development

Variations of phase composition and morphology (inherent to the different synthetic routes for manufacturing the Magnéli phases) have, particularly in the early stages of the materials’ development, caused some batch-to-batch deviations in performance characteristics. Coupled to intermittent availability over the past 30 years the anticipated development of commercial applications has been restricted.

The most obvious commercial outlets are in energy conversion technologies (batteries and fuel cells) and electrochemical reactors. The ceramic nature of these materials can be a problem in terms of robustness for such applications. In part, this limitation can be mitigated by their incorporation into pastes and composites, for example with carbon powder and polymer binders.

Commercially, Ebonex® is currently marketed for a limited number of applications:

4.1 Atraverda: are in the process of developing and bringing to market bipolar batteries which use Ebonex® composite electrodes [26]. The relatively high electrical conductivity and chemical resistance to sulphuric acid make Ebonex® an ideal material for such bipolar electrodes. Incorporation of the ceramic material into a composite enhances the physical robustness to provide vibration and shock resistance to the batteries while still maintaining adequate electrical conductivity between the anode and cathode faces of the bipolar plate.

4.2 Atranova: offer systems based on Ebonex® technology for applications such as remediation of waste/foul water, disinfection, electrowinning of metals, fuel cells and land remediation. In particular, case studies include flow reactors for the reduction of COD levels in pig slurry and industrial effluent containing oils and greases. These flow reactors offer robust and more compact solution compared to biological based treatment facilities. Reduction of COD and TSS levels by more than 90% are reported along with a reduction of associated Moden costs [27].

4.3 Vector Corrosion Technologies: supply Ebonex® for use in the cathodic protection of concrete [4]. Their long service life, the ability to operate at high current densities and a gas venting design enables Magnéli phase ceramic electrodes to be embedded within structures giving a maintenance-free system. Applications include both new builds and restoration/remediation of historical structures based on either metal frame masonry or steel reinforced concrete construction.

5. Non-Magnéli phase materials

There are a number of possible alternatives to the Magnéli phase titanium oxides for electrochemical applications. Carbon, which is an extremely common choice of material for electrodes, can be used in a number of forms, such as graphite, vitreous (glassy), compos-ite and doped diamond [48,49]. Boron doped diamond (BDD) has received a great deal of interest recently and has been investigated as an electrode material for electrosynthesis, water remediation (particularly oxidation of organic contaminants), energy conversion technologies and biological sensors [50,51]. Some metal oxides and doped oxides are also suitable for electrochemical applications [52]. In particular, doped titanium dioxide has attracted interest as a catalyst support material [53]. Platinum deposited on niobium-doped titania has recently been compared to HiSpec-4000 as an alternative catalyst for PEM fuel cells [54]. Ex-situ voltammetry for the niobium-doped titania showed lower activity compared to the HiSpec-4000. The in situ performance, following prolonged polari-sation (1.4 V) of MEAs made with each catalyst support, showed a lower drop-off for the niobium-doped titania, which might indicate an increased cycle life for devices made with this material.

Fig. 13 shows voltammograms for Ebonex® based electrodes in aqueous acid media. No anodic or cathodic reactions were observed between circa -0.5 and 2.5 V vs. RHE. At more negative potentials, along with hydrogen evolution, some redox activity was observed corresponding to changes in the oxidation state of titanium atoms.
Magnéli oxides of titanium are ideal for such applications due to their high surface area and their ability to accommodate large volumes of electrolyte. Phase materials have focused on electrode substrates for batteries and fuel cells. Bipolar batteries using Magnéli phase materials are well known and have been investigated for numerous electrochemical applications, including the use of ionic liquid electrolytes. Some redox activity is observed at very positive and negative potentials [11] and some studies have indicated that reversible polarisation of Magnéli phase electrodes can occur. This results in a lag effect in the electrode response when the potentials are reversed [55]. Despite this, these materials are intrinsically electrochemically stable and compete well with carbon-based electrodes. As specialist ceramic materials, the Magnéli phases are cost competitive with other nickel application electrodes, such as BDD, which are produced in low volumes.

6. Future developments

Recent research and development of Ebonex® and Magnéli phase materials has focused on electrode substrates for batteries along with catalyst supports for fuel cells and effluent treatment. Magnéli oxides of titanium are ideal for such applications due to their electrical conductivity and chemical resistance. Unlike other titanium oxides [53,56,57], the Magnéli oxides have not been manufactured as nanoparticles or nanotubes. Their defect structure does not lend itself to single walled nanostructures, however, multi-walled, thicker nanostructures should be achievable. The increased surface area of such structures would improve their suitability as catalyst support materials, in particular, for fuel cell applications. Other areas for continued investigation include: composite material matrices, nanostructured morphologies, long-term stability in electrochemical devices and anodes in surface finishing (including the use of ionic liquid electrolytes).

7. Conclusions

(1) Ebonex® and Magnéli phase materials are well known and have been investigated for numerous electrochemical applications which could utilise their electrical conductivity and chemical inertness. The commercial development of these materials has been slower than anticipated, however, as specialist ceramic electrodes there are expanding niche markets.

(2) These materials appear particularly suitable for bipolar battery and fuel cell technologies. Bipolar batteries using Ebonex® are currently being commercialised, while several literature references cite favourable results using Ebonex® as a catalyst support material for oxygen reduction reactions.

(3) Long-term testing and characterisation under operational conditions in fuel cells are still required to show viability for commercialisation.

(4) Doped Magnéli phases show promise for fine-tuning chemical and physical properties to suit specific applications, e.g. as catalyst support materials.

References

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