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"Perovskitization"-Assisted Electrochemical Reduction of Solid TiO₂ in Molten CaCl₂**

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The present inability to increase on-board hydrogen storage beyond 6 wt% of the storage materials and/or devices suggests that a longer time is needed before commercially viable hydrogen-powered vehicles join the battle against global warming. This situation would not be quite so constraining, however, if car manufacturers could replace steel components by titanium ones as both are equally strong but titanium is about 40% lighter (and more corrosion resistant). A lighter titanium car would then allow an additional load capacity for the heavy hydrogen-storage system. However, titanium (\approx \$8000 per ton of sponge from the Kroll process) is far more expensive than steel (\approx \$150 per ton of steel from carbothermic reduction; steel producers consequently emit about 5×10^{11} kg of CO₂ per annum into the atmosphere).

The discovery^[1a,b] of direct electrochemical reduction of solid TiO₂ (an insulator) to Ti metal in molten CaCl₂ promises an alternative to the Kroll process, which consumes far more energy (45–55 kWh per kg of Ti) than the industrial production of other common metals (for example, 4–6 kWhkg⁻¹ for steel and 12–14 kWhkg⁻¹ for Al).^[1-3] It also suggests innovative approaches to other metallic and semimetallic materials directly from the respective oxide powders by either electrolytic^[1,4] or metallothermic means.^[3,5] Industrial pilot tests of the electrolytic route have started,^[6] but the most urgent need is to increase the electrolysis speed and current efficiency, both of which are currently unsatisfactory, probably owing to the slow process of removing dissolved oxygen from the metal phase.^[1-6] However, this should not really be the case because the particles in the produced Ti pellet are usually 10–20 µm in

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size^[1] and it has been demonstrated that the removal of oxygen from a 1–2-mm thick Ti foil takes only a few hours using the same method.^[1b,3d]

In all reported studies of electroreduction of solid oxides, such as TiO_2 ,^[1b,d,4a,7,8a] Nb₂O₅,^[4b,c] Cr₂O₃,^[1e,4d,8b] ZrO₂,^[4e,f] NiO,^[8b] SiO₂,^[4g,h,8c,d] and various mixed oxides,^[1c,f,4e] oxygen ionization $(MO_x + 2xe \rightleftharpoons M + xO^{2-})$ or $MO_x + x Ca^{2+} +$ $2xe \rightleftharpoons M + xCaO$) has been confirmed to be the overall cathodic reaction, although the kinetic steps involved in the process were found to be much more complex. In particular, for TiO₂, Nb₂O₅, ZrO₂, and Cr₂O₃, calcium-enriched oxide or perovskite phases of various compositions are often observed in partially reduced cathodes. However, the mechanism of formation of these intermediate products and their influence on the reduction process are not fully understood.^[1c,4a,7] For electroreduction of TiO₂ to Ti metal, there were also arguments for calcium deposition being a necessary step (Ca^{2+} + $2e \rightleftharpoons Ca; TiO_2 + 2Ca \rightleftharpoons Ti + 2CaO)$,^[3,5] although such claims disagree with results from in-depth cyclic voltammetric investigations.^[1d,7a]

Herein, we demonstrate a novel concept of perovskitization-assisted electroreduction of TiO₂ to Ti metal in molten CaCl₂. The result of this process is a significantly increased electrolysis speed and efficiency. In this context, "perovskitization" refers to the interaction or reaction between solid TiO_x ($1 \le x \le 2$) and calcium oxide or cation driven by chemical or electrochemical potentials, leading to structural transformation into perovskite phases that may have a general formula of Ca₀TiO_x ($x/\delta \ge 2$).

Due to electric neutrality, the injection of electrons into a solid oxide can lead to either removal of oxygen anions,^[1,4,7] which is needed for producing metals, or uptake of metal cations from the electrolyte into the oxide phase.^[1a-e,4a,7] The latter occurs in Li-ion batteries and has been used to synthesize LiTiO₂ and LiTi₂O₄ in molten LiCl;^[8a] similar processes are to be expected in molten CaCl₂.

Figure 1 A presents a cyclic voltammogram (CV) of TiO₂ (curve a) in molten CaCl₂. Details of the Mo/oxide-powder working electrode and the Ag/AgCl reference electrode have been described elsewhere.^[8] The CV exhibits three main reduction peaks at -0.23 V (c1), -0.41 V (c2), and -1.13 V (c3). Peak c3 possibly includes two unresolved processes, as implied by the inflexion at -1.02 V. In recent studies of thin TiO₂ coatings,^[1d,7a] these features were attributed to TiO₂ \rightarrow Ti₃O₅(c1) \rightarrow Ti₂O₃(c2) \rightarrow TiO \rightarrow Ti(c3), respectively.^[1d,7a] In particular, potentiostatic electrolysis at potentials around peaks c1 and c2 produced perovskite, which was claimed to result from the chemical reaction (1) where the O²⁻ ion results from partial electroreduction of TiO₂.^[7a]

$$TiO_2 + Ca^{2+} + O^{2-}(or \ CaO) \rightleftharpoons CaTiO_3$$
(1)

In this work, SEM and EDX analyses of the Mo–TiO₂ electrode after potentiostatic electrolysis also revealed that the product at potentials more-negative than peak c3 was Ti metal. However, at more-positive potentials, particularly around peaks c1 and c2, various titanate/titanite or perovskite phases were observed, but their O/Ti atomic ratio remained close to 2 and the Ca/Ti ratio was ≤ 0.5 . We therefore believe



Figure 1. A) CVs of the Mo/perovskite-powder electrode at 850 °C. The powder was ground from perovskitized pellets of mixed TiO₂ and CaO with a Ca/Ti ratio of 0 (a), 0.25 (b), 0.5 (c), and 1.0 (d). Scan rate: 20 mV s^{-1} . The insert shows the consecutive CVs of the Mo–TiO₂ electrode in a narrower potential range. B) XRD spectra of synthetic CaTiO₃ before (a) and after electrolysis at 3.2 V and 850 °C for 10 (b), 30 (c), 60 (d), 120 (e), and 240 min (f). Spectrum (g) was measured from a partially reduced TiO₂ pellet. C) Current–time plots of the electrolysis of TiO₂ (dashed line, 1.0 g pellet) and CaTiO₃ (solid line, 1.7 g pellet) at 3.2 V and 850 °C. The inserts are (a) the CaTiO₃ pellet wrapped by Mo wires as an assembled cathode, and (b) the cross-section of a partially reduced TiO₂ pellet with the layered interior structure of (EDX analyses) 1: Ti metal; 2: perovskite, O/Ti = 1.49; 3: perovskite, O/Ti = 1.89. All results were obtained in molten CaCl₂.

electrochemical reactions (2) and (3) also occur.^[1b-e, 4a, 7a]

$$\mathrm{TiO}_{2} + 2ae \to \mathrm{TiO}_{x} + a\mathrm{O}^{2-} \ (x = 2-a, \ 0 \le a \le 0.5)$$

$$\operatorname{TiO}_{x} + \delta \operatorname{Ca}^{2+} + 2\delta e \rightleftharpoons \operatorname{Ca}_{\delta} \operatorname{TiO}_{x} \ (0 \le \delta \le 0.5)$$

$$(3)$$

Continuous cycling of the potential to more-negative regions than peak c3 caused the current to decrease due to oxygen removal being irreversible in pure molten CaCl₂ that contains very few oxygen ions.^[1d,7a] However, if limited to less-negative potentials, stable CV currents were observed.^[1d] In particular, potential cycling around peaks c1 and c2 caused the two to merge, accompanied by the appearance of a reoxidation peak between 0.0 and -0.1 V, (insert, Figure 1A). This behavior agrees with reactions (2) and (3).^[1d,7a]

The SEM and EDX results also showed intermediate phases containing Ti and O (O/Ti \leq 1), but no Ca, at potentials slightly more positive than peak c3. This can be explained by the perovskite decomposing when the oxygen content is lowered to a certain level, probably O/Ti = 1.^[4a] Therefore, the electroreduction of TiO₂ may involve reactions (1)–(3) as well as reactions (4)–(7). Reaction (4) is a

$$TiO_x + CaO \rightarrow CaTiO_y \ (1 + x = y \le 3)$$
(4)

$$CaTiO_{y} + 2\beta e \rightleftharpoons TiO_{z} + CaO + \beta O^{2-} \ (\beta = y - z - 1)$$
(5)

$$\operatorname{Ca}_{\delta}\operatorname{TiO}_{x} + 2\gamma e \rightleftharpoons \operatorname{TiO}_{z} + \delta\operatorname{CaO} + \gamma \operatorname{O}^{2-}(\gamma > \delta, z \le 1)$$
(6)

$$\operatorname{TiO}_{z} + 2 \, z \, e \to \operatorname{Ti} + z \, \mathrm{O}^{2-} \tag{7}$$

more general form of reaction (1). Obviously, combinations of reactions (1)–(7) can lead to other reaction types^[4a] but these should have the same overall thermodynamic consequences.

When electrolyzing the large TiO_2 porous preforms that are presently used in industrial tests, in situ perovskitization, represented by reactions (1), (3), and (4), causes expansion in the solid phase and slows ion transport in the pores existing between the oxide particles.^[1c,d,7] In previous work^[1c,7b] and herein, it was observed that, before full reduction, electrolyzed TiO₂ pellets, even at voltages higher than 3.0 V, always have layered structures, as shown in Figure 1 Cb. EDX analyses revealed a large amount of Ca in the inner layers whose O/Ti ratios were, however, different (core > intermediate layer). The XRD spectra of these partially reduced TiO₂ pellets indicate the presence of a perovskite phase (see Figure 1 B g and Table 1).

On the basis of these findings and analyses, we can conclude that in situ perovskitization proceeds inevitably by both electrochemical and chemical reactions during the electroreduction of solid TiO_2 in molten CaCl_2 . The perovskite phases formed can be further reduced to Ti at more-negative potentials, but they also retard the electroreduction kinetically. Therefore, if in situ perovskitization can be avoided, electrolysis of TiO_2 preforms should be faster.

We achieved ex situ partial and full perovskitization by sintering a pressed mixture of TiO_2 and CaO or $Ca(OH)_2$ powders at 1300°C (see Figure 2A and Experimental Sec-

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Table 1: XRD phase analyses of different electrolysis products.

TiO ₂ , 900°C	3.0 V, 0.5 h	perovskite (81.3%) + Ti ₂ O ₃ (18.7%)
	3.0 V, 2 h	perovskite (83.7%) + Ti ₂ O ₃ (10.6%) + Ti ₃ O ₅ (5.7%)
	3.0 V, 4 h	perovskite (89.9%) + TiO (11.1%)
TiO ₂ , 900°C	2.8 V, 1 h	perovskite (50.7%; <i>31.2%</i>) ^[a] + TiO ₂ (49.3%; 68.8%) ^[a]
	2.8 V, 2 h	perovskite (65.6%) ^[a] + Ti ₃ O ₅ (18.2%) ^[a] + unknown (16.2%) ^[a]
CaTiO ₃ , 850°C	2.8 V, 5 h	Ti (87.2%) ^[a,b] + unknown (12.8%) ^[a]
	2.6 V, 5 h	Ti (51.8%) ^[a,b] + perovskite (38.8%) ^[a] + unknown (9.4%) ^[a]
	2.4 V, 11.5 h	Ti (50.1%) ^[a,b] + perovskite (37.7%) ^[a] + unknown (12.2%) ^[a]

[a] The presence of some unknown phases prevented the XRD spectrum quantitative analysis software from determining the proportions of the different phases observed. The numbers in italics were estimated from the area of the strongest XRD peak of each phase and are presented here as approximate references with caution. Use of the total area of three of the strongest peaks of each phase led to similar results. [b] The electrolyzed CaTiO₃ samples listed in the table fell apart into a powder after washing in water, and contained up to 7 wt% oxygen as measured by LECO. Their XRD spectra exhibit all the main titanium peaks, although these were shifted to lower diffraction angles close to those of the standard Ti_xO ($x \ge 2$) phases. The negative shifts of the Ti peaks are understandable because of lattice expansion caused by dissolved oxygen. The XRD spectra of typical fully and partially electrolyzed CaTiO₃ samples are presented in the Supporting Information.

tion). The CVs of the synthetic powder are also shown in Figure 1A. The currents on these CVs are normalized against peak c3. It can be seen that peaks c1 and c2, which lead to in situ perovskitization according to the above discussion, have been effectively supressed. Figure 1 C compares the currenttime plots recorded during electrolysis of similar CaTiO₃ and TiO₂ pellets under identical conditions. Interestingly, the current in TiO₂ is obviously larger than that in CaTiO₃ for the first 20 min. This may be due to reactions (2) and (3) occurring with TiO₂ but not with CaTiO₃. XRD analyses of the electrolysis products at different times (Figure 1B) revealed that the metal phase grows at the expense of the perovskite phase, and at least one early and one later intermediate phase appear and vanish with time (see the peaks enclosed in the vertical rectangles in Figure 1B and also data in Table 1 and Figure S3 in the Supporting Information). These results may indicate that CaTiO₃ is reduced to Ti via relatively stable intermediate Ti^{III} and/or Ti^{II} states, thereby supporting reactions (5) and (6).^[7a] The oxygen content in the CaTiO₃ pellet electrolyzed for 265 min at 3.2 V was lower than the detection limit of EDX over relatively large areas inspected by SEM (Figure 2), and was only 2800 ppm according to fusion elemental analysis. In contrast, an identical TiO₂ pellet electrolyzed for 265 min showed a very thin metallic surface but its interior still contained layered perovskite phases similar to those shown in Figure 1Bg and 1 Cb. Complete reduction of the TiO_2 pellet to Ti metal (2100 ppm oxygen) took about 600 min. Clearly, the faster reduction of CaTiO₃ occurs because in situ perovskitization is avoided. The removal of CaO [reaction (5)] may also leave a more porous structure and very fine TiO_z particles, both of which help to speed up the electrolysis.

Three more points are worth mentioning. First, the CVs of simply mixed TiO₂ and CaO powders show some, although limited, changes of peaks c1 and c2. Second, in the presence of trace amounts of Mg (<0.3 wt%), Mg-containing phases (often crystallites) were detected in partially reduced TiO₂ electrodes by SEM and EDX.^[8c,d] The highest atomic ratios were Mg/Ti \approx 0.5 and O/Ti \approx 1.5, in agreement with a process

similar to reaction (3) that deserves more general investigation.^[8a] Third, although electrolysis of CaTiO₃ was faster, the current efficiency still remained low (28 % for CaTiO₃ vs. 15 % for TiO₂). The large background current (Figure 1 C) due to electronic conduction in the melt^[9] and cell configuration might be responsible, and these are being addressed separate-ly.^[1g]

Finally, the reduction of TiO₂ preforms by Ca vapor was recently reported to be quicker in the presence of CaO or CaCl₂.^[3b] However, the additives were used as a flux (for by-product) and the trace CaTiO₃ phase in the sintered (800 °C) preform was ignored. More recently, the electrochemical reduction of solid Nb₂O₅ in the presence of small amounts of carbon (<5 wt %), CaCO₃,

and/or CaO (<20 wt%) has been reported.^[10] Nonetheless, the function of the additives was claimed to be the creation of O^{2-} vacancies in the oxide phase, and only small amounts of the calcium niobate phases were detected by XRD in the sintered oxide pellets. The effect of these calcium niobate phases was regarded to be detrimental to the reduction.^[10a]

In summary, we have demonstrated, for the first time, that ex situ perovskitization can significantly increase the speed and efficiency of the electroreduction of solid TiO₂ in molten CaCl₂. We anticipate that the fast reduction of CaTiO₃ can also be applied to extract Ti metal directly from natural perovskite, and from the by-product of steel making from ilmenite (FeTiO₃), which is often enriched in Mg and/or Ca. This process may also, in principle, be applied for the electroreduction of other oxides, such as ZrO₂, Nb₂O₅, and Ta₂O₅.

Experimental Section

Synthesis: The conventional synthesis of CaTiO₃ is by a solid-state reaction between TiO2 and CaCO3 or CaO at temperatures of about 1350°C. This phase has also been prepared by other techniques, including organometallic, liquid-mix, and mechanochemical methods. In this work, partial and complete chemical perovskitization of TiO₂ was achieved as described below. The TiO2 powder (AR grade; particle size: 0.1-0.2 um, Kemi'ou Reagent Plant, Tianiin, China) was thoroughly ball-milled (overnight) with a prescribed amount of CaO or Ca(OH)₂ (AR grade, Fengcheng Reagent Plant, Shanghai, China) in the presence of distilled water (enough to turn the mixture into a thin slurry). The mixture was dried in air at 120°C (overnight), diepressed into small cylindrical pellets (6 MPa), and then sintered at 1300°C for 5 h. The color change (white to brown) and SEM and XRD analyses showed that, depending on the Ca/Ti atomic ratio (0 to 1) in the mixture, the sintered pellet (diameter: ≈ 2.0 cm; thickness: 0.2-0.3 cm) had been partially or fully converted into porous CaTiO₃ (perovskite), as shown in Figures1Ba and 2A. The porosity was estimated to be 40–50% on the basis of the pellet's mass and volume, and the densities of the oxides (CaTiO₃: 4.02 g cm^{-3} ; TiO₂: 4.23 g cm⁻³). Pure TiO₂ pellets were also prepared similarly but were sintered at lower temperatures (900-1000 °C) for shorter times



Figure 2. SEM images of the interior of a $CaTiO_3$ pellet before (A) and after (B) electrolysis (3.2 V, 850 °C, 265 min, molten $CaCl_2$). The EDX spectrum measured over the image area of (B) is also shown.

(2 h). The pellets were used directly in the assembled cathode (see Figure 1 Ca) for constant-voltage electrolysis in a two-electrode cell.

Constant-voltage electrolysis: Molten dried $CaCl_2$ was used as the electrolyte in the electrolysis experiments and the subsequent cyclic voltammetry and chronoamperometry studies. Two commercial $CaCl_2$ salts were used in this work: the anhydrous salt (AR grade, the content of Mg and alkali metals was about 0.3% counted by sulfate, Silian Reagent Plant, Shanghai, China) and the dihydrate salt (ACS grade, the content of Mg and alkali metals was less than 0.005 wt.%, Shanghai Bioengineering Co. Ltd,).

The CaCl₂ salt in a graphite crucible (inner diameter: 9.0 cm; height: 23.5 cm) was placed in a sealable stainless-steel reactor, which was assembled in a vertical programmable furnace (Wuhan Experimental Furnace Plant). The furnace temperature was first raised to and maintained at 200–300 °C for more than 12 h, then to 450 °C for 2 h under argon, and finally to the working temperature (850–900 °C).

After melting, pre-electrolysis of the freshly prepared molten salt at 2.6–2.8 V was applied to remove some redox-active impurities from it. A graphite rod (diameter: 2.0 cm; length: 20 cm) and a steel wire (diameter: 2.9 mm; length: ≈ 60 cm) were used as the anode and cathode, respectively. Pre-electrolysis lasted until the current reached a low and stable value, that is, the background or residual current, which was found to depend strongly on temperature, cell voltage, and the purity of the CaCl₂ salt.

The oxide pellet was either wrapped with molybdenum wires or sandwiched between two molybdenum meshes to form the assembled cathode (Figure 1 C a). After pre-electrolysis, the steel-wire cathode was replaced by the assembled oxide cathode and electrolysis was carried out at 2.4–3.2 V. During all pre-electrolysis and electrolysis processes, the electrolytic cell was sealed in the stainless-steel retort and was continuously purged with an argon flow.

After termination of the constant-voltage electrolysis at a prescribed time, the cathode was removed from the molten salt, cooled in argon, and then washed with water in air to dissolve the solidified salt on the cathode. The electrolyzed pellets were visually inspected for color and dimension changes, and then broken into two halves whose cross-sections were examined under optical and scanning electron microscopes. For powder X-ray diffraction and fusion elemental analyses, the electrolyzed pellets were manually ground into a powder with a mortar and pestle, further washed with water, and dried at about 120 °C in air or vacuum before further analysis.

Cyclic voltammetry and chronoamperometry: The recently reported Mo–oxide powder electrodes^[8a,b] and a quartz-sealed Ag/ AgCl reference electrode^[8c] were used to perform cyclic voltammetry and chronoamperometry (potentiostatic electrolysis) in molten CaCl₂. Typically, the Mo-cavity powder electrode^[8b] and the oxide-powder-modified Mo electrode^[8a] were loaded with 0.1–1.0 mg of oxide powder. The sub-micrometer TiO₂ powder was used either

directly or pre-mixed with the CaO powder before loading onto the electrode. The perovskite powders were obtained by finely grinding the respective perovskite pellets that were prepared as described above.

About 45 g of dried $CaCl_2$ was filled into a small graphite crucible (inner diameter: 1.8 cm; height: 25 cm), dehydrated, and pre-electrolyzed as described above. The graphite crucible also functioned as the counter electrode. The three-electrode cell was then sealed in a quartz tube, which was placed in a furnace and heated to the working temperature (850 °C). During the experiments, argon was continuously fluxed through the quartz tube. Cyclic voltammetry was performed with a CHI 605A Electrochemical System (Shanghai Chenhua, China). After chronoamperometric experiments for a prescribed time, the Mo–oxide powder electrodes were washed with distilled water, dried, and examined by SEM and EDX.

Spectroscopic analysis: The XRD patterns were obtained with a D8 Advance X-ray diffractometer (Bruker, Germany) with $Cu_{K\alpha 1}$ radiation ($\lambda = 1.5406$ Å) at 40 kV and 40 mA. The scan rate of 2 θ was 4 deg min⁻¹. Micrographic and composition analyses were performed with a FEI Sirion Field Emission Gun SEM system equipped with a CCD camera and an EDAX GENESIS 7000 energy-dispersive X-ray spectrometer (EDX). Products were also sent to the Materials Test and Inspection Research Institute of Wuhan Iron and Steel (Group) for analysis of their oxygen content with an Oxygen Determinator (model RO-416DR, LECO, USA).

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- a) D. J. Fray, T. W. Farthing, Z. Chen, PCT Patent, WO9964638,
 1998; b) G. Z. Chen, D. J. Fray, T. W. Farthing, *Nature* **2000**, 407,
 361; c) G. Z. Chen, D. J. Fray, *Light Met.* **2004**, 881; d) G. Z.
 Chen, D. J. Fray, *J. Electrochem. Soc.* **2002**, 149, E455; e) G. Z.
 Chen, E. Gordo, D. J. Fray, *Metall. Mater. Trans. B* **2004**, 35, 223;
 f) A. J. Muir Wood, R. C. Copcutt, G. Z. Chen, D. J. Fray, *Adv. Eng. Mater.* **2003**, *5*, 650; g) D. J. Fray, PCT Patent, WO2004018735A1, **2002**.
- [2] D. Yan, Energy Saving of Non-ferrous Metall. 2004, 21, 12 (in Chinese).
- [3] a) I. Park, T. Abiko, T. H. Okabe, J. Phys. Chem. Solids 2005, 66, 410; b) T. H. Okabe, T. Oda, Y. Mitsuda, J. Alloys Compd. 2004, 364, 156; c) T. H. Okabe, D. R. Sadoway, J. Mater. Res. 1998, 13, 3372; d) T. H. Okabe, M. Nakamura, T. Oishi, K. Ono, Metall. Mater. Trans. B 1993, 24, 449.
- [4] a) C. Schwandt, D. J. Fray, *Electrochim. Acta* 2005, *51*, 66;
 b) X. Y. Yan, D. J. Fray, *Metall. Mater. Trans. B* 2002, *33*, 685;
 c) X. Y. Yan, D. J. Fray, *J. Electrochem. Soc.* 2005, *152*, D12;
 d) E. Gordo, G. Z. Chen, D. J. Fray, *Electrochim. Acta* 2004, *49*, 2195;
 e) G. Z. Chen, D. J. Fray, *Light Met.* 2001, 1147;
 f) K. S. Mohandas, D. J. Fray, poster presentation at *EUROMAT* 2005, 5–8 Sept. 2005, Federation of European Materials Societies, Prague, Czech Republic;
 g) T. Nohira, K. Yasuda, Y. Ito, *Nat. Mater.* 2003, *2*, 397;
 h) K. Yasuda, T. Nohira, K. Amezawa, Y. H. Ogata, Y. Ito, *J. Electrochem. Soc.* 2005, *152*, D69.
- [5] a) K. Ono, R. O. Suzuki, *JOM* 2002, 54, 59; b) R. O. Suzuki, K. Teranuma, K. Ono, *Metall. Mater. Trans. B* 2003, 34, 287; c) R. O. Suzuki, *J. Phys. Chem. Solids* 2005, 66, 461.
- [6] a) http://www.darpa.mil/dso/thrust/matdev/titanium.htm; b) S. Ashley, Sci. Am. 2003, 289, 38.
- [7] a) K. Dring, R. Dashwood, D. Inman, J. Electrochem. Soc. 2005, 152, E104; b) K. Dring, M. Jackson, R. Dashwood, H. Flower, D. Inman in Cost-Affordable Titanium—A Symposium Dedicated to Professor Harvey Flower (Eds.: F. H. Froes, M. A. Imam, D.

Communications

Fray), Minerals, Metals & Materials Soc., Warrendale, 2004, p. 95.

- [8] a) K. Jiang, X. H. Hu, H. J. Sun, D. H. Wang, X. B. Jin, Y. Y. Ren, G. Z. Chen, *Chem. Mater.* 2004, *16*, 4324; b) G. H. Qiu, M. Ma, D. H. Wang, X. B. Jin, X. H. Hu, G. Z. Chen, *J. Electrochem. Soc.* 2005, *152*, E328; c) P. Gao, X. B. Jin, D. H. Wang, X. H. Hu, G. Z. Chen, *J. Electroanal. Chem.* 2005, *579*, 321; d) X. B. Jin, P. Gao, D. H. Wang, X. H. Hu, G. Z. Chen, *Angew. Chem.* 2004, *116*, 751; *Angew. Chem. Int. Ed.* 2004, *43*, 733.
- [9] a) U. Stohr, W. Freyland, *Phys. Chem. Chem. Phys.* 1999, *1*, 4383;
 b) G. Z. Chen, D. J. Fray, *J. Appl. Electrochem.* 2001, *31*, 155.
- [10] a) Q. Xu, L. Q. Deng, Y. Wu, T. Ma, J. Alloys Compd. 2005, 396, 288; b) L. Q. Deng, Q. Xu, T. Ma, B. Li, Y. C. Zhai, Acta Metall. Sin. (Chin. Ed.) 2005, 41, 551.