Porous TiB_2 electrodes for the alkali metal thermoelectric convertor

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Porous TiB_2 electrodes for the alkali metal thermoelectric convertor have been developed and tested. The electric performance of these new electrodes turned out to be superior to that of other electrodes known so far, like TiN or Mo. Because of its low reactivity, TiB_2 (like TiN) can be expected to show a long-time stable operation. The performance of TiB_2 electrodes of different sizes is described, using current–voltage relationships and impedance measurements.

1. Introduction

The alkali metal thermoelectric convertor (AMTEC) is an electrochemical heat engine which converts heat directly into electricity without moving parts [1]. This is done by expanding sodium at 800–1000°C via the sodium-ion conducting ceramic separator beta-alumina into a compartment with low sodium vapour pressure, corresponding to temperatures of 250 to 350°C.

The negative electrode of the AMTEC is the hot sodium metal itself, whereas the positive electrode is a sophisticated arrangement of porous conductive materials. Being a three-phase boundary, consisting of beta-alumina, sodium gas and electron conductor, the positive electrode has to supply the electrons necessary to reduce the sodium ions to sodium gas. Besides good conductivity, the positive electrode must exhibit also a "proper" porosity for letting the sodium gas pass with tolerable pressure losses. Such electrodes have been made, for example, from thin (about 1 μm thick), porous layers of molybdenum [1, 2], precious metals [3] and TiN [4, 5]. As these thin layers alone are not able to draw high currents, a current collector mesh has to be put on top of the electrode.

A comparison of different electrodes is difficult, because of the unknown influence of the current collector and to an even larger extent because of the different size of the electrodes. For example, it seems to be a general rule that small electrodes give higher power densities than larger electrodes of otherwise identical composition. This "small electrode effect" is the main reason why the data reported in the literature for the power density vary, e.g. for Mo electrodes at 800°C from about 0.2 to 0.8 $W\,cm^{-2}$. The larger values have been obtained with electrode areas of $< 1\ cm^2$. Electrodes for technical use, however, must be larger than 30 cm^2. The reason for this size-effect, which has been investigated in detail [6], is mainly the potential drop in the electrode layer. This can be improved by using current collectors with a higher density of current collector contacts. Recently, a compilation of data of different electrode types was presented, taking into account the various electrode areas [7]. This is shown in Table I.

The long-term behaviour of the metal electrodes described above (especially of Mo) is not satisfactory. The decrease of power density of Mo electrodes with time has been attributed to the evaporation of an active Na–Mo–O compound [8]. Because of such effects, chemically stable electrodes like TiN, NbN and TiC have been investigated [5]. As candidates, Mo_2C, NbC, WC, ZrC and ZrN have been proposed, but not investigated so far [9]. However, most of these nonmetallic electrode materials exhibit a relatively high specific resistance. As a consequence they must be made very thick, which in turn decreases the open porosity, obstructs the flow of the sodium gas and leads to reduced power density. Therefore, we looked for chemically stable materials with high electronic conductivity. Table II shows a list of candidate materials.

We chose to investigate TiB_2 because of its chemical stability ($\Delta G = -246 \pm 20\ kJ\,mol^{-1}$ [10], its low resistivity (near to Mo) and its expansion coefficient, which matches well with that of the β''-Al_2O_3 tube (which is $7.8 \times 10^{-6}\ K^{-1}$).

2. Experimental procedure

The β''-Al_2O_3 tubes of 25 mm diameter and 200 mm length were sputtered with TiB_2 using a TiB_2 target (Leyboldt–Heraeus). The tubes were of our own manufacture and had a wall thickness of 1.3 mm. The sputtering power was 500 W at an Ar pressure of 8×10^{-3} mbar. The distance between target and tube was about 50 mm and the sputtering time was 0.5 to 3 h, depending on the layer thickness. The thickness was varied between 0.5 to 4 μm and the area on to which TiB_2 was sputtered was varied from 0.8 to 30 cm^2.

The tubes were tested in special cell arrangements shown in Fig. 1. By filling the tube only about half with sodium, the temperature around the rubber seal can be held below 150°C. The sodium was heated by a

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heater to 800°C. The amount of sodium used corresponded to about 15 A h of current flow. This was sufficient for the present investigations (Na was not recirculated). The current collector generally consisted of Mo mesh placed on the sputter layer and wrapped with Mo wire.

Current–voltage curves were determined at temperatures from 600 to 800°C. Impedance measurements were carried out between 0.1 Hz and 10 kHz, using a commercial impedance spectrometer with potentiostatic control (Zahner Electronic, Kronau, Germany).

3. Results

Figs 2 and 3 show SEM pictures of TiB_2 sputter layers on a glass substrate and on a β''-Al_2O_3 tube, respectively. The deposit shows a columnar structure, which is also characteristic for Mo and TiN electrodes and which is important for low-pressure losses at high sodium flow rates.

Fig. 4 shows current–voltage relationships at different temperatures and Fig. 5 shows the corresponding power–voltage curves. It can be seen that a maximum current density of about 1.3 A cm^{-2} and a maximum

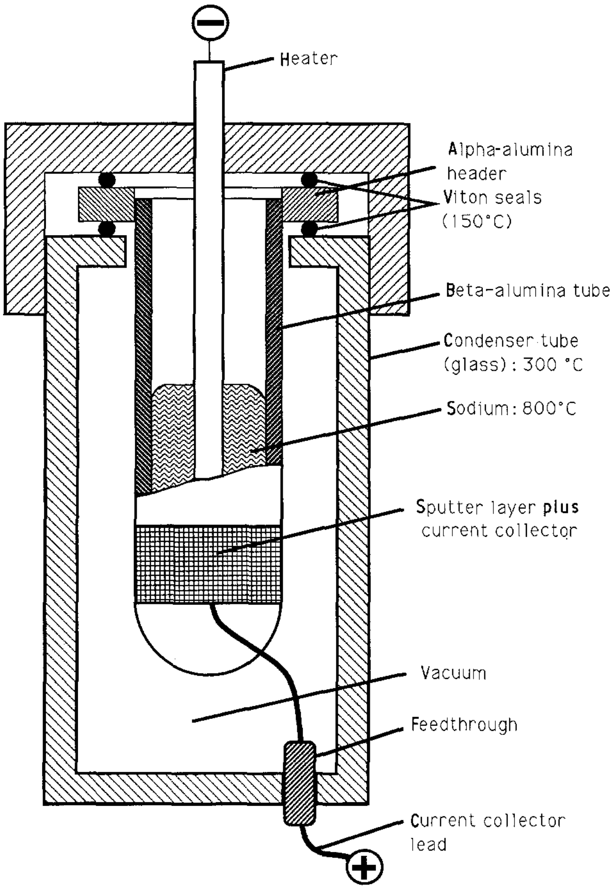

Figure 1 Experimental AMTEC cell for temperatures of up to 800°C.

TABLE I Power densities of state-of-the-art AMTEC electrodes for different electrode areas (from 7)

Electrode	Temperature (°C)	Area (cm^2)	Power density (W cm^{-2})
Rh–W	930	4.7	0.64
	900	4.7	0.52
	800	4.7	0.27
Mo	760	9.4	0.19
	760	4.7	0.25
	760	0.9	0.36

TABLE II Candidate materials for AMTEC electrodes

Material	Melting point (°C)	Expansion coefficient at 25°C (10^{-6} K^{-1})	Specific resistance at 25°C (10^{-7} Ωm)
TiC	3140	7.4	7.5
ZrC	3420	6.7	6
TaC	3880	6.3	3
WC	2780	5.2	5.3
NbC	3500	6.6	7.4
SiC	2700	6.0	> 2000
Mo_2C	2690	5.0	13
ZrN	2980	6.5	3
NbN	2050	10.0	20
ZrB_2	2990	6.8	1
TiB_2	2900	7.4	1
Mo	2620	5.1	0.5
TiN	2950	9.4	3

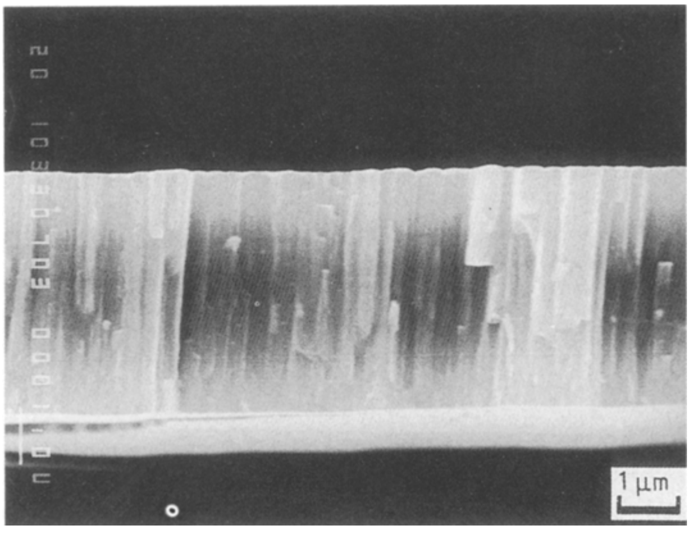

Figure 2 TiB_2 sputter layer (about 4 μm thick) on a glass substrate.

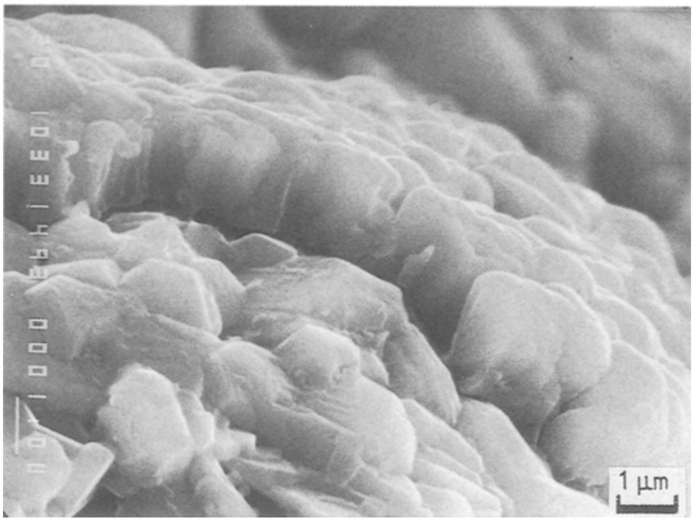

Figure 3 TiB_2 sputter layer (about 1 µm thick) on a β''-Al_2O_3 substrate.

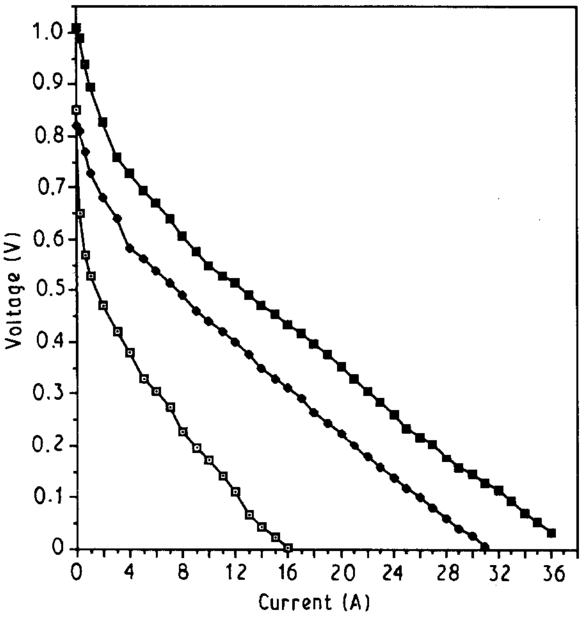

Figure 4 Current–voltage curves for TiB_2 electrodes (area 30 cm^2, 1 µm sputter layer) at different temperatures: (□) 600°C, (◆ 700°C, (■) 800°C.

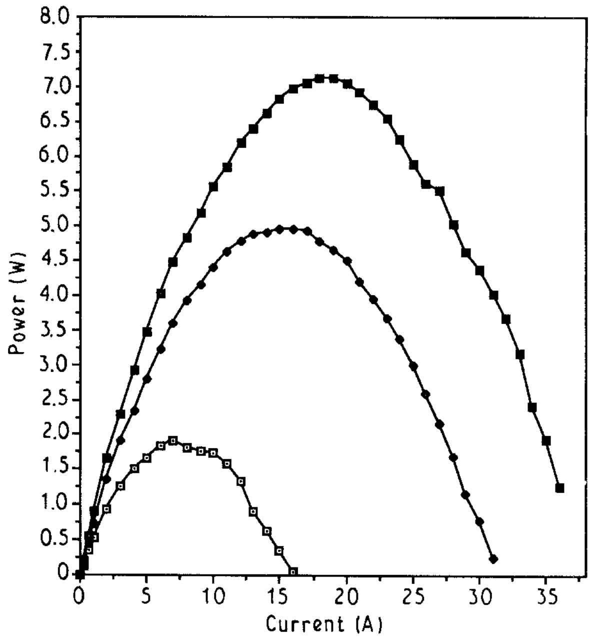

Figure 5 Current–power curves for TiB_2 electrodes (area 30 cm^2, 1 µm sputter layer) at different temperatures: (□) 600°C, (◆) 700°C, (■) 800°C.

power density of 0.24 W cm^{-2} could be achieved with these large-area electrodes.

The optimal thickness of the TiB_2 sputter layer could be shown to be between 1 and 2 µm (Fig. 6). The decrease of performance for a thinner electrode is probably due to the higher sheet resistance, and the decrease in the case of a thicker electrode might be connected with higher vapour pressure losses because of lower porosity.

As has been observed already with other AMTEC electrode materials [6, 7], there is a strong dependence of the power density on the electrode area. It is therefore important to always specify the electrode area when figures on power density are being presented. Fig. 7 shows that also with TiB_2 there is a strong dependence of the power density on the electrode area. Small electrodes can reach almost 0.4 W cm^{-2} with the standard current collector. As can be seen by comparing these values with Table I, the TiB_2 electrode performs better than the Mo and about equally as well as Rh–W electrodes.

Impedance spectroscopy was used for determination of the ohmic resistance and of the capacity of the electrode at high frequencies. These values can give information about layer resistance and layer structure (thickness, porosity). A complete analysis as done by Williams *et al.* [11] was not within the scope of this investigation. An example of a Nyquist plot of a TiB_2 electrode at open circuit and at 800°C is given in Fig. 8. As in other publications [11] the plots are usually depressed semicircles shifted on the real axis. This means that there is a frequency-independent ohmic resistance R_0 and an electrochemical process, represented (as a very rough approximation) by a resistance R_D and a capacity C_D in parallel. The values of R_0 and C_D (as obtained by a fit-program) are shown in Table III for different electrodes. The values of R_D are not presented because of the great scatter to these values

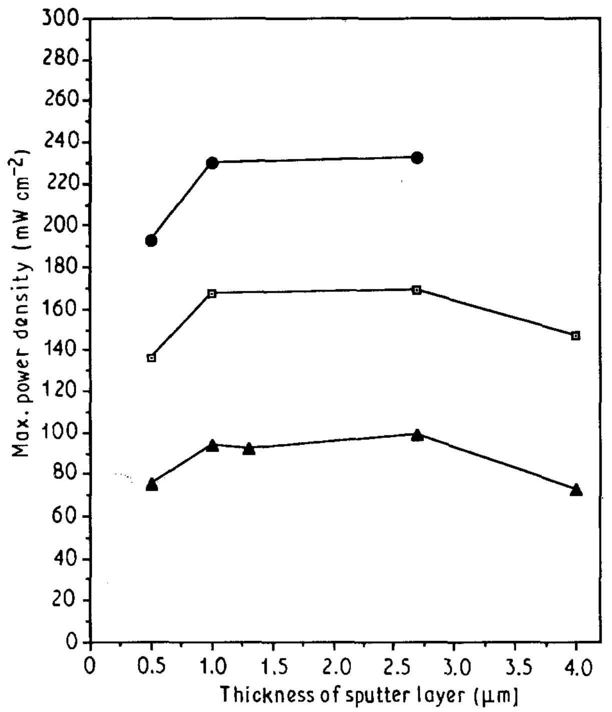

Figure 6 Maximum power density of TiB_2 electrodes (area 30 cm^2) as a function of the thickness of the sputter layer at different temperatures: (▲) 600°C, (⊡) 700°C, (●) 800°C.

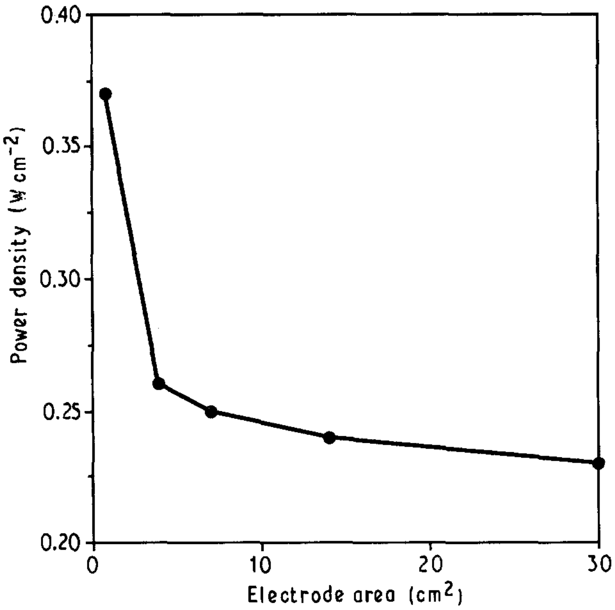

Figure 7 Maximum power density of TiB_2 electrodes (1 μm sputter layer) at 800°C as a function of the size of the electrode area.

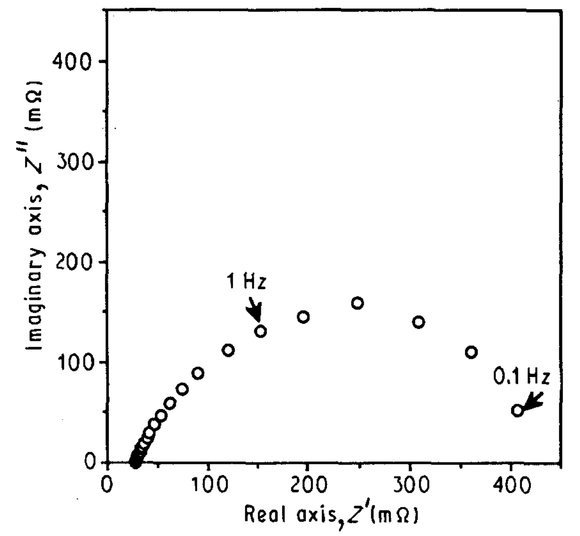

Figure 8 Impedance spectrum of a 30 cm^2 TiB_2 electrode (thickness of sputter layer 0.5 μm) at 750 °C at frequencies from 0.1 Hz to 1 kHz.

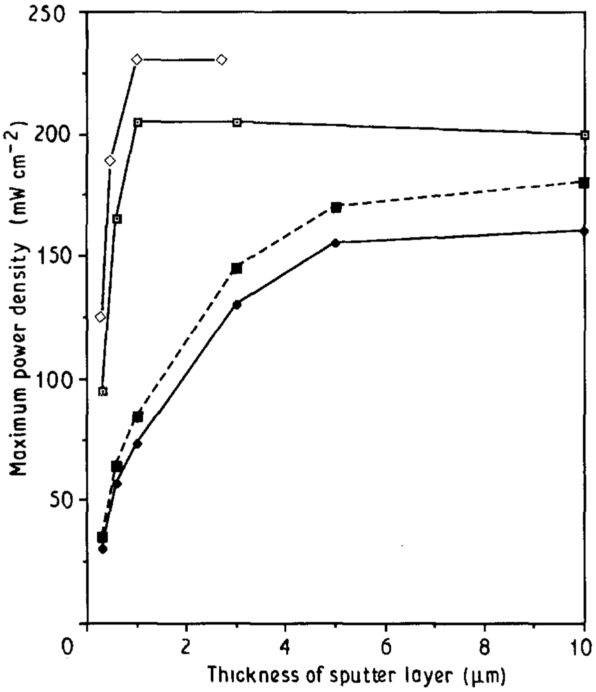

Figure 9 Comparison of the maximum power density of different electrode materials (area 30 cm^2) as a function of the layer thickness: (◇) TiB_2 at 800°C, (⊡) Mo at 800°C, (◆) TiN at 750°C (measured), (■, ---) TiN at 800°C (extrapolated).

at the lower frequencies (R_0 and C_D are determined at high frequencies). The resistance R_0 is the sum of the ohmic resistance of the β″-Al_2O_3 tube, the electrode, the current collector and the current leads.

3.1. Stability

The stability of TiB_2 in contact with β″-Al_2O_3 was determined by heating up a mixture of TiB_2 and β″-Al_2O_3 powder to a temperature of 1000°C. After 100 h, X-ray analysis revealed only the spectra of the original substances and no new phases.

Also at AMTEC operating conditions, the stability of TiB_2 proved to be good. The potential of a test cell operated at 750°C remained completely stable at 0.83 V at a current of 0.5 A for more than 10 h. This time limit was given by the finite amount of sodium inside the tube. SEM inspection after this test showed that the TiB_2 sputter layer had remained fully intact.

4. Discussion

As shown in Fig. 9 for 30 cm^2 electrodes, TiB_2 performs better than Mo and TiN. It is important to note that both Mo and TiB_2 reach their maximum power density already at a small thickness, whereas TiN layers must be at least 5 μm thick. This is due to the relatively large electronic resistance of TiN.

TABLE III Impedance of different AMTEC electrodes (30 cm^2) at 750°C

Thickness (mm)	Mo		TiB_2		TiN	
	R_0 (Ω cm^2)	C_D (mF cm^{-2})	R_0 (Ω cm^2)	C_D (mF cm^{-2})	R_0 (Ω cm^2)	C_D (mF cm^{-2})
0.3	1.66	1.2				
0.5	0.57	4.3	0.82	9.3		
1.0	0.58	10.0	0.87	14.5		
4.0			0.69	75.0	0.70	97.0
11.0	0.6	25.0				

The values of the power density shown in Fig. 9 were obtained with our standard current collector. With improved collectors, which provide more frequent and more intimate contacts to the sputter layer, power densities of up to 0.42 W cm^{-2} have been obtained [12] for Mo with 30 cm^2 electrodes. For TiB_2 electrodes, these improved current collectors will be used also in the future.

The impedance data (Table III) show that the ohmic resistance R_0 tends to decrease with increasing thickness of the sputter layer. However, it is not clear yet why TiB_2 shows higher values than Mo, although the power densities of TiB_2 were higher than of Mo. This may be connected with better sodium flow conditions in the case of TiB_2 when current is drawn. The capacity shows a clear tendency to higher values with thicker layers. At a given thickness, the absolute values, however, are higher with TiB_2 than with Mo and even more so with TiN. This behaviour indicates that with the Ti compounds a higher specific surface is active for the reduction of sodium ions than with Mo.

5. Conclusions

The investigations described above show that the intermetallic compound TiB_2 is a good candidate for AMTEC electrodes. With this material a higher power density than with Mo electrodes can be achieved. It can be expected that – because of its chemical inertness – the stability of TiB_2 will be superior to that of metal electrodes. Further investigations are necessary in order to reveal the role of the electronic resistance and of the porosity of such layers.

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References

1. N. WEBER, *Energy Conversion* **14** (1974) 1.
2. B. L. WHEELER, R. M. WILLIAMS, B. JEFFRIES-NAKAMURA, J. L. LAMB, M. E. LOVELAND, C. P. BANKSTON and T. COLE, *J. Appl. Electrochem.* **18** (1988) 410.
3. R. M. WILLIAMS, B. JEFFRIES-NAKAMURA, M. L. UNDERWOOD, B. L. WHEELER, M. E. LOVELAND, S. J. KIKKER, J. L. LAMB, T. COLE and C. P. BANKSTONE, *J. Electrochem. Soc.* **136** (1989) 893.
4. J. R. McBRIDE, P. F. NOVAK, D. J. SCHMATZ, W. B. COPPLE, J. T. BROCKWAY, N. ARNON and G. A. GRAB, in Proceedings of 24th IECEC, Washington, DC, August 1989, p. 683.
5. O. ASAKAMI, K. SHIBATA, T. HASHIMOTO, H. NAKATA, K. TSUCHIDA and A. KATO, in Proceedings of 26th IECEC, Boston, 1991, p. 469.
6. R. KNÖDLER, K. REISS, and B. WESTHOVEN, *J. Mater. Sci. Lett.* **11** (1992) 343.
7. M. L. UNDERWOOD, R. M. WILLIAMS, B. JEFFRIES-NAKAMURA and M. A. RYAN, in Proceedings of 26th IECEC, Boston, 1991, p. 475.
8. R. M. WILLIAMS, C. P. BANKSTONE, S. K. KHANNA and T. COLE, *J. Electrochem. Soc.* **133** (1986) 2253.
9. O. ASAKAMI, K. TSUCHIDA, H. TOGAWA and A. KATO, *J. Mater. Sci. Lett.* **8** (1989) 1141.
10. H. WENDT, K. REUHL and V. SCHWARZ, *Electrochim. Acta* **37** (1992) 237.
11. R. M. WILLIAMS, M. E. LOVELAND, B. JEFFRIES-NAKAMURA, M. L. UNDERWOOD, C. P. BANKSTONE, H. LEDUC and J. T. KUMMER, *J. Electrochem. Soc.* **137** (1990) 1709.
12. R. KNÖDLER, H.-P. BOSSMANN, A. KRANZMANN and F. HARBACH, *J. Electrochemical Soc.* **139** (1992) 3029.

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