



ELSEVIER

Journal of Power Sources 92 (2001) 163–167

JOURNAL OF
POWER
SOURCES

www.elsevier.com/locate/jpowersour

Cyclic voltammetric studies of the effects of time and temperature on the capacitance of electrochemically deposited nickel hydroxide

E.E. Kalu^{a,*}, T.T. Nwoga^a, V. Srinivasan^b, J.W. Weidner^b^aDepartment of Chemical Engineering, FAMU-FSU College of Engineering, Tallahassee, FL, 32310, USA^bDepartment of Chemical Engineering, University of South Carolina, Columbia, SC, 29208, USA

Received 15 May 2000; accepted 3 June 2000

Abstract

A cyclic voltammetric (CV) technique was used to study the combined effects of annealing temperature and time on the pseudocapacitance of thermally treated electroprecipitated nickel hydroxide thin films. Through the analysis of the areas of the CVs cycled between 0 and 0.35 V (versus Ag/AgCl) it is shown that the optimal treatment condition for maximum film capacitance occurs at 300°C for 3 h. On the other hand, using the anodic and cathodic peak currents of the CVs cycled between 0 and 0.5 V (versus Ag/AgCl), the maximum film capacitance is also shown to occur at a thermal treatment condition of 300°C and 3.5 h (or 320°C and 3.2 h for linear approximations). The two methods demonstrate simple ways of extracting useful information on the electrochemical performance properties of thin films. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Pseudocapacitance; Capacitor; Thermal annealing; Cyclic voltammetry; Electroprecipitated; Nickel oxide

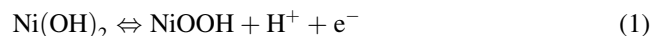
1. Introduction

The increased research activity in the development of electrochemical capacitors (ECs) is motivated by its possible use in high-power devices such as lasers and electric vehicles (for acceleration). Most commercially available ECs are based on electrochemical double layer charging (EDLC) or charge separation. These EDLCs are limited by the ranges of their maximum capacitances (10–40 $\mu\text{F}/\text{cm}^2$) [1], electrochemical stability of the electrolytes and under utilization of the electrode surface area due to the presence of non-wettable micropores [2]. The utilization of faradaic pseudocapacitances of high area noble metal oxides of ruthenium and iridium is an alternative way of overcoming some of the limitations associated with EDLCs. However, the cost of the noble metal oxides are prohibitive, hence the interest in low cost metal oxides such as nickel oxide for redox type supercapacitors.

Nickel oxide can be prepared by thermal treatment of electrodeposited [3,4] or sol–gel prepared [5] nickel hydroxide thin film. Following a thermal treatment, electrodeposited or sol–gel prepared nickel oxide behaves as a pseudocapacitor. A thermal treatment of nickel hydroxide

is also undertaken in the preparation of nickel oxide thin film for electrochromic or ‘smart window’ applications [6–8]. In comparison to the thermal treatment reported for supercapacitor applications [3,4], the annealing time for electrochromic applications is relatively short (15 min). It is further known that the annealing temperatures for smart window thin films are often lower than those reported for supercapacitor nickel oxide thin film. The heat treatment of electrochromic film is known to alter its water content and crystallinity and this in turn alters the electrochromic properties of the film [8]. Similar observations are made when the thermally treated films are used as supercapacitors.

An examination of the cyclic voltammograms of nickel oxide films obtained from a short annealing time at either a high ($\geq 300^\circ\text{C}$) or low ($\leq 300^\circ\text{C}$) temperature, shows pronounced characteristic peaks associated with reaction (1).



However, when the annealing time is prolonged at a high temperature, the size of the characteristic peaks is reduced and pseudocapacitive behavior of the film becomes pronounced. It was only recently that the relationship between some of the thermal treatment variables (temperature, time, heating rate) and the deposited film performance properties was examined [3]. It was found that the capacitance of the thin film is maximized at 300°C and that surface redox

* Corresponding author. Tel.: +1-850-410-6327; fax: +1-850-410-6150.
E-mail address: ekalu@eng.fsu.edu (E.E. Kalu).

reaction accounts for the pseudocapacitance of nickel oxide film instead of large surface area [9]. How long and at what temperature can Ni(OH)₂ thin film be annealed as to completely eliminate the characteristic peaks associated with reaction of Eq. (1) and obtain a pseudocapacitive film? The objective of the present study is to utilize cyclic voltammetric technique and investigate the effects of time and annealing temperature on the capacitance of nickel oxide film prepared by the electrochemical method. The expected outcome of the work is the prescription of optimum annealing conditions (both time and temperature) for maximizing the capacitance of electrodeposited nickel hydroxide thin film.

2. Experimental

Thin film of nickel hydroxide was electrodeposited at 25°C from a bath containing 1.8 M Ni(NO₃)₂ and 0.075 M NaNO₃ in a solvent of 50 vol.% ethanol at a cathodic current density of 5 mA/cm² using a procedure described in detail by Streinz et al. [10,11]. The active surface area of the gold foil used as the working electrode was 1.0 cm² and the current density was applied for 25 min. The deposited films were washed in deionized water and initially cycled between 0 to 0.5 V (Ag/AgCl) in a 3 wt.% KOH solution to stabilize the films. The stabilized film was then washed with deionized water and annealed in air convection oven for a specified time and temperature. Five isothermal-hold or annealing temperatures and three hold-time periods were examined. The samples were heated linearly from room temperature to the target temperature at a rate of 5°C/min, then held at that temperature for the specified annealing time. At the end of the hold time, the sample was cooled at 5°C/min to room temperature.

In one group of experiments, following the end of the annealing time, the film was cycled from 0 to 0.35 V 10 times in 3 wt.% KOH to achieve a steady state. In another group of experiments, following the end of annealing time, the films were cycled from 0 to 0.5 V (Ag/AgCl) in 3 wt.% KOH for 20 times to examine the ease of conversion of nickel oxide back to nickel hydroxide. The final cycle in both groups of experiments were saved and used for analysis. The electrochemical measurements (galvanostatic charge/discharge and cyclic voltammetric) were conducted in a three-cell arrangement with platinum foil as the counter electrode and Ag/AgCl reference electrode. A computer controlled EG & G Model 273 potentiostat/galvanostat was used for the experiments and the data analysis was carried out with Corrview (Scribner Associates, NC, USA). The total surface charge, q (and total capacitance) of the film was estimated by integrating the area under the CVs using the software. The scanning rates for all reported cyclic voltammetric experiments were kept constant at 20 mV/s. A 3.0 wt.% potassium hydroxide solution was used for all CV runs.

3. Results and discussion

Two groups of CV experiments with different voltage ranges were conducted with the annealed thin films. In one group of runs, the annealed film was cycled between 0 and 0.35 V while in the second group, the voltage range was between 0 and 0.5 V.

Fig. 1 shows the voltammogram obtained for as-deposited thin film. The voltammogram shows a well-resolved anodic peak at 0.387 V and a cathodic peak at 0.238 V. The oxidation peak is associated with the formation of nickel oxy-hydroxide while the reduction peak is associated with the conversion of the oxy-hydroxide back to hydroxide. Apart from the apparent oxidation-reduction peaks, the voltammogram shows that as the film is cycled from 0 towards the anodic direction, a purely capacitive current is obtained between 0 and 0.325 V. This suggests that a reversal of the CV at 0.325 V may give a voltammogram that is purely due to the capacitance of the film rather than due to the redox (faradaic) reaction peaks observed in Fig. 1. This is the basis of the first group of experiments cycled between 0 and 0.35 V.

Fig. 2 shows several thin film samples annealed for 1 h at different temperatures and cycled between 0 to 0.35 V (versus Ag/AgCl). Although the current-potential responses of Fig. 2 do not resemble that of an ideal capacitor where $dI/dV = 0$, they do show that nickel oxide thin film behaves as non-ideal capacitor when cycled between 0 to 0.35 V. Fig. 2 also shows that the annealing temperature for any given time changes the magnitude of the film's capacitance (area under the I - V curve). The surface charge density, q (C/cm²) obtained from the integration of the area under the I - V curve is proportional to the capacitance of the film since

$$C(V_f - V_{i0}) = q = \frac{1}{\nu} \int_{V_{i0}}^{V_f} I(V) dV \quad (2)$$

where C is the total capacitance, I the current density (A/cm²), ν the sweep rate (V/s), V_{i0} , the initial and V_f the final voltages (V). The integral on the right hand side of Eq. (2) is

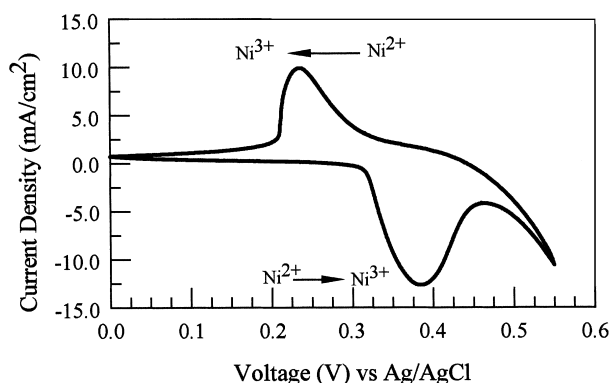


Fig. 1. Cyclic voltammetry for electroprecipitated nickel hydroxide (as-deposited) in 3% KOH. The scan rate was 20 mV/s. Anodic current is negative.

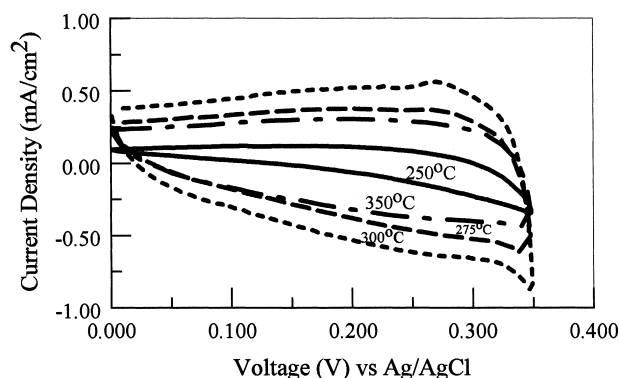


Fig. 2. CVs of electroprecipitated nickel hydroxide following 1 h annealing time at different temperatures. The scan rate was 20 mV/s. Anodic current is negative.

the area under the CV. Thus, the total surface charge, (or total capacitance) of the deposit material can be estimated by evaluating the area under the capacitive current-voltage curve portion of a CV (without faradaic reaction peaks).

Typically, mass of nickel hydroxide deposited under the present experimental condition was $c = 35 \mu\text{g}$. However, when annealed, the electrodeposited nickel hydroxide film's mass changes as it is converted into nickel oxide. Following the thermal treatment, the mass of the deposited thin (active) film can be represented by

$$m_{ij} = m_0 - \beta f(T_i - T_0)t_j \quad (3)$$

where m_{ij} is the mass of the film following a thermal treatment at temperature T_i for time t_j , β is the mass change per unit energy input (inverse of heat capacity), T_0 is the annealing temperature below that no mass change occurs, while $f(T_i - T_0)$ is a function of the annealing temperature. The function $f(T_i - T_0)$, measures the fraction of energy input per unit time that is specifically or efficiently employed for the reactions that result in the thin film weight loss. For a sample prepared under similar conditions, the film's total capacitance can then be estimated as

$$C_{ij} = \alpha_{ij}(m_0 - \beta f(T_i - T_0)t_j) = \frac{1}{v(V_f - V_{i0})} \int_{V_{i0}}^{V_f} I(V) dV \quad (4)$$

where C_{ij} is the total capacitance after thermal treatment at temperature T_i and time t_j and α_{ij} is the specific capacitance of the film at the specified conditions. The specific capacitance is a more desirable parameter for comparative purposes, however from Eq. (4), it is seen that accurate measure of the weight loss function is needed for the evaluation of the specific capacitance. Since $f(T_i - T_0)$ is not always accurately known (including the present work), the proportional relationship between the total capacitance or total surface charge (q) and the specific capacitance justifies the use of either total capacitance or total surface charge for comparative purposes for similarly prepared and treated thin films (as in this work).

It is justified on the premise that not until the NiO thin film achieves its maximum active surface area, the deposit's weight loss affects its capacitance in the inverse direction (i.e. increases the capacitance) to the mass loss. Considering that the loss of both water of hydration and defect water from the electrodeposited nickel hydroxide constitute about 20–40 % of the weight of as-deposited film [9], the use of Eq. (4) for comparing similarly deposited samples is in order.

Fig. 2 shows that the annealing temperature of the thin film changes the film's capacitance. It appears from the observation of the CVs that the capacitance of the film increases as the annealing temperature increases. Using Eq. (4) and same voltage limits for all the CVs in Fig. 2 (to remove any biases), the total capacitance (or charge) of the film is estimated and observed to increase with temperature reaching a maximum at 300°C and then decreasing from this maximum value. This is similar to the result obtained by Srinivasan and Weidner [9] for an annealing time of 3 h and estimated specific film capacitance. The agreement of the trend observed in this work and that in [9] further justifies the use of Eq. (4).

Fig. 3 compares the total capacitance obtained from films that were annealed for different lengths of time and cycled between 0 and 0.35 V (Ag/AgCl) at 20 mV/s. Three regions can be delineated in the figure:

1. The region (below 280°C) at which the capacitances of the films annealed for 5 h are greater than those annealed for 1 h but less than those annealed for 3 h.
2. In the second region (between 280 and 320°C), the 5 h annealed samples have the least capacitances followed by the 1 h films and then the 3 h films. In this region, maximum capacitance is reached for each annealing time.
3. The third region shows a decrease in the films' capacitance with increase in temperature for all the samples. There is insufficient data for all times to compare the data trends in this region (with respect to the annealing time). However, based on the work of Srinivasan and Weidner [9] at 300°C and 3 h annealing

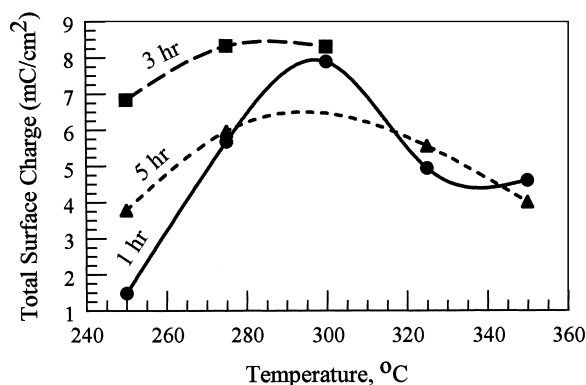


Fig. 3. Dependence of nickel oxide thin film's total capacitance on the annealing time and temperature. CV scan rate was 20 mV/s.

time, it is clear that within the third region, irrespective of annealing time, the total capacitance decreases with increase in temperature.

Fig. 3 further shows that at each annealing time, an optimal annealing temperature for the maximization of the film capacitance exists. The maximum capacitance is obtained within the same temperature range of 290–320°C for all the annealing times studied. For the 3 h annealing time, the optimal temperature is 300°C. It appears that below the optimal annealing temperature, the film's active area is minimized while for temperatures above the optimal temperature, sintering and crystallization effects set in and impact negatively on the active area of the film. Thus, the optimal annealing temperature is then the temperature at which the oxide's active surface area is maximized. These observations are made with respect to a given annealing time. In summary, the CV data obtained by cycling the annealed film in a region where no faradaic reaction occurs on the surface of the film (0–0.35 V) (Fig. 2) is used to construct a relationship between film capacitance and temperature (Fig. 3). The optimal annealing temperature and time are obtained from such relationship. Within the potential region, non-faradaic adsorption of OH⁻ and possibly double layer charging occur. And the optimal annealing conditions are 300°C and 3 h annealing time.

In addition to its effect on the microstructure, thermal annealing affects the electrochemical properties of the electrodeposited Ni(OH)₂ films. This is because as the annealing temperature and time increase, more Ni(OH)₂ active ingredient is converted to NiO. Since the electrochemical rate of the reaction or current is proportional to the quantity of active ingredient, a decrease in Ni(OH)₂ present in the film is reflected on the magnitude of the CV current. Since the Ni(OH)₂ oxidation peak occurs beyond the 0.35 V potential range used for the previous analysis, then the films are cycled between 0–0.5 V (versus Ag/AgCl) in order to examine the effects of annealing on the electrochemical properties of the thin film.

To examine the effect of annealing temperature on the characteristic peaks of the nickel hydroxide films, cyclic voltammograms were obtained for films heated at different temperatures for different times. The voltammograms of films that were heat-treated for 5 h and cycled between 0 and 0.5 V at 20 mV/s are shown in Fig. 4. The figure shows that as the annealing temperature of the thin film sample increases, the treatment necessitates a subsequent change in the size of the anodic and cathodic peaks associated with the nickel hydroxide-nickel oxy-hydroxide reactions. Thus, as the thermal treatment temperature increases, the thin film changes its electrochemical response from that of a battery to that of a capacitor. This behavior is associated with the thermal dehydration of the electroprecipitated nickel hydroxide film and its subsequent conversion to nickel oxide.

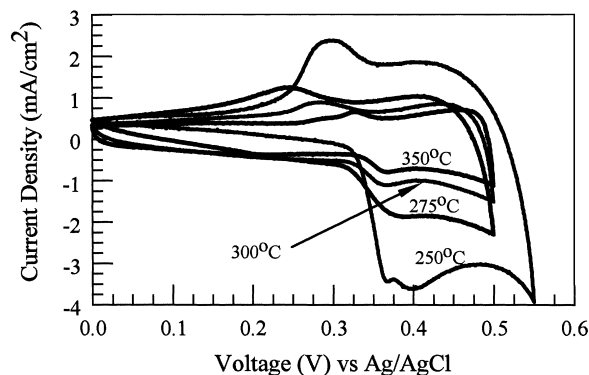


Fig. 4. CVs for nickel hydroxide thin film at different annealing temperatures and 5 h annealing time. The films were cycled from 0–0.5 V at 20 mV/s and anodic current is negative.

In theory, this suggests that as long as there is unconverted Ni(OH)₂, the characteristic electrochemical peak associated with Ni(OH)₂ will be observed as the film is cycled from 0 to 0.5 V (Ag/AgCl).

Fig. 5 shows the relationship between the peak current and the annealing temperatures for 5 h holding time. The figure shows that as the annealing temperature increases, both cathodic and anodic current peaks decrease. This implies that the higher the annealing temperature (at a given annealing time), the more the nickel hydroxide active ingredient is converted to nickel oxide and hence the larger the capacitance of the film. As the annealing temperature increases, the cathodic and anodic peak currents continue to decrease until a temperature is reached at which only non-faradaic (capacitive) current exists. It then suggests that there must be a theoretical temperature at which the capacitance of the film is maximized. At that temperature, all Ni(OH)₂ is converted to NiO (i.e. faradaic electrochemical rate = 0) and the film behaves like an ideal capacitor. It behaves like an ideal capacitor because in the absence of Ni(OH)₂, no NiOOH is formed as the film is cycled between 0 and 0.5 V. As an ideal capacitor, both the anodic and cathodic currents are equal in magnitude and symmetrical about the zero current axis (i.e. an ideal capacitor) at the point in question. No bulk faradaic process occurs in the film at the temperature at which the two

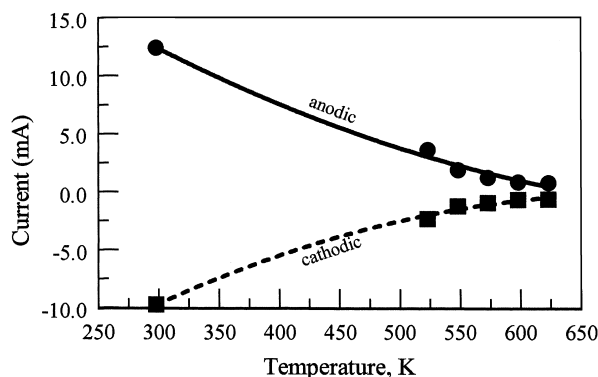


Fig. 5. Variation of peak current with annealing temperature for 5 h annealing time. Scan rate was 20 mV/s.

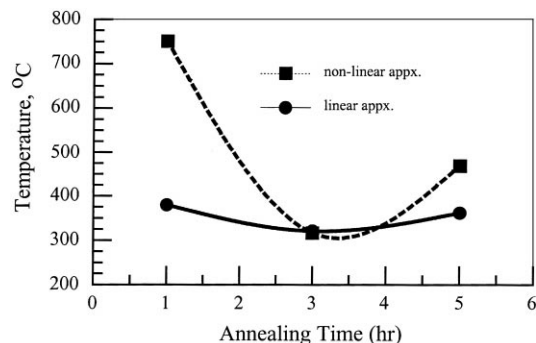


Fig. 6. Optimal annealing temperature and time for electroprecipitated nickel hydroxide thin film. Scan rate was 20 mV/s.

peak currents are equal in magnitude. Hence, the only phenomena that take place on the film surface are capacitive and surface non-faradaic processes such as the adsorption of OH^- .

We can postulate then that at any annealing temperature above or at the decomposition temperature of nickel hydroxide (reaction 5), an optimal time exists at which the hydroxide is completely annealed and converted to the oxide film without sintering. The corollary is that at a given annealing time, an optimal temperature exists at which the hydroxide film is annealed completely to an oxide film without sintering. At this optimal temperature and time, all the oxide's properties are maximized — it has maximum capacitance, the anodic and cathodic peaks of the oxide's cyclic voltammogram are equal and at their minima.

With the data such as in Fig. 5, we explore to verify the postulations. Correlation (linear and non-linear) relationships between the anodic and cathodic peak currents and annealing temperatures are constructed for each annealing time. Equating the anodic and cathodic correlations and solving for the temperature, we obtain the optimal temperature for each annealing time. The optimal temperatures obtained for the different annealing times are shown in Fig. 6. Similar to the findings made with films cycled from 0 to 0.35 V, both the linear and non-linear approximations in the figure show that the minimum annealing temperature for optimal capacitance occurs in the 3 h neighborhood. Whereas the non-linear approximation yielded an optimal condition of 300.2 °C and 3.48 h, the linear approximation gave 320.6 °C and 3.18 h. For other annealing times between 1 to 5 h studied in the present work, the results suggest that higher annealing temperatures are required.

We cannot construct figures analogous to Fig. 5 using the data obtained from cycling the film between 0 and 0.35 V (Fig. 2). This is because, within the 0–0.35 V potential range, there is not a well-defined faradaic reaction peak that is attributable to the bulk nickel hydroxide film. Except for the OH^- adsorption and double layer charging, the electrodeposited film is electrochemically inactive within

the potential range. Figs. 5 and 6 suggest that if the faradaic reaction of Eq. (1) is eliminated through the reaction process shown in Eq. (5), then the whole electrodeposited film behaves like a capacitor. This is an increase in potential range of operation of the capacitor from 0.35 to 0.5 V.

4. Conclusion

The effect of heat treatment on the electrochemical properties of electroprecipitated nickel hydroxide is studied using cyclic voltammetry. It is shown that both annealing time and temperature are critical factors in the optimization of the capacitance of the deposit. Two potential ranges of the film's operation were examined and analyzed. Irrespective of the potential range at which the oxide is cycled, it is shown that the optimal conditions for the maximization of film's capacitance lie between 3 and 3.5 annealing hours at temperature range of 300–320 °C. The two methods demonstrate simple ways of extracting useful information from CVs on the performance properties of thin films for possible applications in electrochemical power sources.

Acknowledgements

The authors gratefully acknowledge financial support from the US Department of Energy/EPSCoR cooperative agreement no. DE-FC02-91ER75666. The University of South Carolina assisted in meeting the publication costs of this article.

References

- [1] A.J. Bard, L.R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, Wiley, New York 1980.
- [2] S.T. Mayer, R.W. Pekela, J.L. Kaschmitter, *J. Electrochem. Soc.* 140 (1993) 446.
- [3] E.E. Kalu, V. Srinivasan, T. Nwaoga, J.W. Weidner, in: W.R. Cieslak, K.M. Abraham, W.A. Adams, G. Halpert, et al. (Eds.), *Selected Battery Topics, PV 98–15*, The Electrochemical Society Proceedings Series, Pennington, NJ, 1999, p. 639.
- [4] V. Srinivasan, J.W. Weidner, *J. Electrochem. Soc.* 144 (1997) L211.
- [5] K.C. Liu, M.A. Anderson, *J. Electrochem. Soc.* 143 (1996) 124.
- [6] K. Hinokuma, A. Kishimoto, T. Kudo, *J. Electrochem. Soc.* 141 (1994) 176.
- [7] A. Guerfi, R.W. Paynter, L.H. Dao, *J. Electrochem. Soc.* 142 (1995) 3457.
- [8] C. Natarajan, H. Matsumoto, G. Nogami, *J. Electrochem. Soc.* 144 (1997) 121.
- [9] V. Srinivasan, J.W. Weidner, *J. Electrochem. Soc.* 147 (2000) 880.
- [10] C.C. Streinz, A.P. Hartman, S. Motupally, J.W. Weidner, *J. Electrochem. Soc.* 142 (1995) 1084.
- [11] C.C. Streinz, S. Motupally, J.W. Weidner, *J. Electrochem. Soc.* 143 (1995) 4051.