A Sol-Gel Process for the Synthesis of NiCo_2O_4 Having Improved Specific Capacitance and Cycle Stability for Electrochemical Capacitors

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High performance nickel cobaltite (NiCo_2O_4) with ultrahigh capacitance is synthesized by a facile sol-gel process and then calcined at 300°C. The structure and morphology is characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscope (TEM), and nitrogen adsorption/desorption experiments. A mesoporous structure with high specific surface area is obtained. Electrochemical properties are investigated by cyclic voltammetry (CV), galvanostatic charge/discharge, and electrochemical impedance spectroscopy (EIS). The NiCo_2O_4 exhibits excellent electrochemical performance. The highest specific capacitance of 1128 F g^{-1} is achieved at a current density of 5 mA cm^{-2} and 92.5% of the initial specific capacitance remained after 1000 cycles. NiCo_2O_4 prepared by this scale-able route could be a promising electrode material for electrochemical capacitors. © 2012 The Electrochemical Society. [DOI: 10.1149/2.057208jes] All rights reserved.

Manuscript submitted February 22, 2012; revised manuscript received May 18, 2012. Published 00 00, 2012.

As energy storage devices having properties intermediate to those of batteries and electrostatic capacitors, electrochemical capacitors (ECs) exhibit the desirable properties of high power density, fast charging, excellent cycling stability, small size, and low mass, which make them one of the most promising candidates for next generation power devices.¹⁻⁴ On the other hand, ECs deliver a low and unsatisfactory energy density.⁵ Current research work on ECs has been mainly focused on the enhancement of energy density to make it comparable to that of batteries.^{6,7} Generally, faradaic pseudo capacitors based on metal oxides or conducting polymers that can be doped electrochemically have a higher energy density than electrochemical double-layer capacitors (EDLCs) based on carbon materials.⁸⁻¹⁰ Conducting polymer materials are considered to have relatively lower specific capacitances and also poor electrochemical stability.¹¹⁻¹³ Metal oxides have been considered to be one of the most promising materials for ECs.¹⁴⁻¹⁶

As a typical metal oxide electrode material, RuO_2 has a high capacitance, reversible charge/discharge features, and good electrical conductivity, all of which make it the focus of research and development of supercapacitors having the potential to achieve higher energy and power densities.¹⁷⁻¹⁹ Unfortunately, its high cost renders this material unsuitable for commercialized in many applications. Thus, development of alternative electrode materials having improved characteristic and performance is the next logical step.²⁰⁻²² Transition metal oxides possess multiple oxidation states/structures that enable rich redox reactions for pseudo capacitance and have drawn much attention in recent years.²³ Interestingly, mixed metal oxides²⁴⁻²⁶ and binary metal oxide/hydroxides,^{27,28} which have been reported to exhibit a higher performance than single component oxides/hydroxides, seem to be one of the most promising electrode materials for ECs.

One of the binary metal oxide, NiCo_2O_4 adopts a spinel structure in which nickel occupies the octahedral sites and cobalt distributes over both octahedral and tetrahedral sites.²⁹ It is expected to offer rich redox reactions and is highly considered in energy-conversion/storage systems due to its better electronic conductivity and higher electrochemical activity than those of nickel oxides and cobalt oxides.³⁰ Recently, some studies have been carried out on the supercapacitive performance of NiCo_2O_4 .^{23,31,32} However, a high degree of crystallinity and low level of electrochemical active sites was introduced into the synthesis by the high calcination temperature used, which leads to a low specific capacitance. In contrast, Chen and co-workers³¹ have

synthesized NiCo_2O_4 crystals by a sol-gel method then calcined the product at 400°C. The highest specific capacitance of 217 F g^{-1} they achieved is, however, lower than that reported for NiO and Co_3O_4 . Lu et al.²³ have synthesized NiCo_2O_4 aerogels at 200°C and a specific capacitance of 719 F g^{-1} was obtained. Unfortunately, the synthesized NiCo_2O_4 aerogel is a composite of Ni(OH)_2 , NiO , Co_3O_4 , and NiCo_2O_4 according to the XRD characterization. Its higher specific capacitance was not only contributed by the NiCo_2O_4 phase, but also by Ni(OH)_2 , NiO , and Co_3O_4 . Hence, the exploitation of pure NiCo_2O_4 , using an sol-gel technique, raises the expectation of a facile and scale-able synthesis of a high specific capacitance NiCo_2O_4 .

An appropriate mesostructure, which is expected to enhance the electrochemical performance owing to the shape-selective properties and large surface area,³³⁻³⁶ is essential to improve the performance of electrode materials. Here, we report a porous NiCo_2O_4 single phase fabricated by a sol-gel process then calcined at a moderate temperature of 300°C. The effects of calcination temperature on product phase were investigated. The as-prepared NiCo_2O_4 exhibits a higher specific capacitance than NiO and Co_3O_4 , showing high performance electrode material of ECs. On the one hand, this can be attributed to the low crystallinity and large specific surface area of the as-prepared NiCo_2O_4 , which result in a high activity and an effective utilization of the active materials. On the other hand, it benefits from feasible oxidation states/structures of NiCo_2O_4 contributed by both nickel and cobalt ions. Moreover, the excellent rate capability and cycle stability of the as-prepared material is also demonstrated.

Experimental

Materials.— Analytical grade $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$, KOH, propylene oxide, and absolute alcohol were purchased from Sinopharm Chemical Reagent Co. Ltd. and used as received without any further purification.

Fabrication of the NiCo_2O_4 .— The NiCo_2O_4 was synthesized using a modified version of the procedure described in a previous report.²³ In a typical process, 0.225 g $\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.37 g $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 2.5 mL ethanol and stirred for 5 min, then 2.0 g propylene oxide was added and the mixture was stirred at room temperature (25°C) for another 12 h. The resulting solution was then stirred at 75°C to promote gelation. The product was dried at 60°C for 12 h then heated in an air atmosphere at 200, 250, 300, or 350°C for 5 h. The resulting samples were washed with ethanol and distilled water several times then dried at 80°C for 12 h. For

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comparison, NiO and Co₃O₄ were synthesized by the same procedure. The mechanism of gelation can be explained as the following reaction sequence:

where M represents nickel or cobalt ions, A[−] represents Cl[−] or NO₃[−] ions. In this procedure, the propylene oxide acts as an acid scavenger through protonation of the epoxide oxygen and subsequent ring opening by the nucleophilic, anionic conjugate base.³⁹

Structure characterization.— The microstructure and morphology of the as-prepared NiCo₂O₄ was characterized by transmission electron microscope (TEM, JEOL, JEM-2010, Japan) and field emission scanning electron microscope (SEM, JEOL, JSM-6701F, Japan). The pore properties, including the BET surface area and pore size distribution were investigated volumetrically by nitrogen adsorption/desorption experiments (ASAP 2020). Crystallite structures were determined by X-ray diffraction (XRD) using a Rigaku D/MAX 2400 diffractometer (Japan) with Cu Kα radiation (λ = 1.5418 Å) operating at 40 kV and 60 mA.

Electrode preparation and electrochemical measurements.— The working electrodes were prepared as follows. 80 wt% of NiCo₂O₄ was mixed with 7.5 wt% of acetylene black and 7.5 wt% of conducting graphite in an agate mortar until a homogeneous black powder was obtained. To this mixture, 5 wt% of poly (tetrafluoroethylene) was added together with a few drops of ethanol. The resulting paste was pressed at 10 MPa into a nickel foam (ChangSha Lyrin New Material Co. Ltd., 90 PPI, 2 mm) then dried at 80°C for 12 h. Each carbon electrode contained approximately 8 mg of electroactive material and had a geometric surface area ≈ 1 cm².

A typical three-electrode glass cell equipped with a working electrode, a platinum foil counter electrode, and a saturated calomel reference electrode (SCE) was used for electrochemical measurements of the as-prepared working electrodes. All electrochemical measurements were performed using an electrochemical working station (CHI660C, Shanghai, China) in 2 M KOH aqueous solution at 25°C. The corresponding specific capacitance was calculated from the following equation:

$$C_m = \frac{C}{m} = \frac{I \times \Delta t}{\Delta V \times m} \quad [1]$$

where C_m (F g^{−1}) is the specific capacitance, I (A) is discharge current, Δt (s) is the discharge time, ΔV (V) represents the potential drop during discharge process, and m (g) is the mass of the active material.

Results and Discussion

Structure characterization.— XRD was employed to determine optimum calcination temperature of the pure NiCo₂O₄ phase. Fig. 1 shows XRD patterns of four samples calcined at various temperatures. When samples were calcined at 200 or 250°C, the (111) peak and (400) peak of NiCo₂O₄ (JCPDS No. 20-0781) were observed, indicating that the NiCo₂O₄ phase was successfully obtained. Unfortunately, the diffraction peaks of NiO (JCPDS No. 04-0835) and Co₃O₄ (JCPDS No. 42-1467) also appeared, i.e. the as-fabricated samples were a NiO/NiCo₂O₄/Co₃O₄ composite rather than the pure NiCo₂O₄ phase sought. A pure NiCo₂O₄ crystalline phase was obtained at a calcination temperature of 300°C. The resultant diffraction peaks were in good accordance with the standard pattern for face-centered cubic spinel NiCo₂O₄, the absence of NiO and Co₃O₄ characteristic peaks affirming phase-purity of NiCo₂O₄ crystal and suggesting that 300°C is optimum suitable temperature for fabricating pure NiCo₂O₄. On further increasing the calcination temperature to 350°C, the NiCo₂O₄ coexists with NiO and Co₃O₄ phases, the Co₃O₄ crystalline phase even

Figure 1. XRD patterns of the NiCo₂O₄ following calcination at various temperatures.

becoming dominant due to its sharper and narrower diffraction peaks compared to NiCo₂O₄. Appearance of the diffraction peaks for NiO and Co₃O₄ show that 350°C is too high for formation pure NiCo₂O₄ crystal, or else that a higher calcination temperature may lead to the decomposition of NiCo₂O₄ to NiO and Co₃O₄ phases and also the growth of the resulting Co₃O₄ crystals. The unit cell dimension of the spinel structure NiCo₂O₄ crystal, *a*, was determined from the observed d-spacing for the (111) and (400) planes using the formula for a cubic lattice:

$$a = d\sqrt{h^2 + k^2 + l^2} \quad [2]$$

where *h*, *k*, and *l* are the Miller indexes. The calculated value of *a* corresponding to (111) and (400) planes, which ranges between 0.8080 and 0.8238 nm, is very close to that of 0.8110 nm given in the JCPDS 20-0781 file for NiCo₂O₄.

The surface morphology of the fabricated NiCo₂O₄ was investigated by SEM measurement. As shown in Fig. 2a, a loosely packed porous structure consisting of interconnected nanoparticles, tens of nanometers in size, was clearly visible. This is in accordance with

Figure 2. (a) SEM image of NiCo₂O₄. (b, c) TEM and (d) HRTEM images of porous NiCo₂O₄.

the results of TEM imaging shown in Fig. 2b. Fig. 2c exhibits the porous structure of NiCo_2O_4 with a pore size approximately 10 nm. The high-resolution TEM (HRTEM) image shown in Fig. 2d reveals an interplanar spacing of 0.2803 nm for the (220) plane of spinel NiCo_2O_4 , which is close to that of 0.2869 nm given in the JCPDS 20-0781 file. The results suggest that the as-fabricated NiCo_2O_4 has a porous structure which will enhance the facility of ion transportation and maintain the smooth electron pathways facilitating rapid charge/discharge reactions and is a promising candidate for EC electrode materials.

The porous characteristics of NiCo_2O_4 were further investigated by N_2 adsorption/desorption. Fig. 3a and 3b show the N_2 adsorption/desorption isotherms and corresponding BJH pore size distributions. As seen from Fig. 3a, the existence of the hysteresis loops indicates the porous structure of NiCo_2O_4 . In Fig. 3b, NiCo_2O_4 exhibits a narrow pore-size distribution at 3.28 nm and a wide pore size distribution around 6.24 nm, suggesting a hierarchical porous structure. The sample shows a specific surface area of $32.7 \text{ m}^2 \text{ g}^{-1}$ and an average pore size of 11.1 nm.

Electrochemical characterization.— CV, chronopotentiometry, EIS, and cycle measurements were employed to evaluate electrochemical capacitive performance of NiCo_2O_4 electrodes.

Fig. 4a shows the CV of a pure NiCo_2O_4 electrode at different scan rates. A pair of redox peaks is visible in each voltammogram, suggesting that the measured capacitance is mainly based on the redox mechanism. The anodic peak current is increasing at 0.2 V, and that for the corresponding cathodic peak is evident at approximately 0.18 V, indicating that the oxidation reaction and reduction reaction of active material began at 0.2 and 0.18 V, respectively. This was attributed to the redox reactions of Ni (II)/Ni (III). According to the literature,^{38,39} anodic peaks located at approximately 0.35 V in the CV curves at a scan rate of 10 mV s^{-1} was also contributed

Figure 3. (a) N_2 adsorption/desorption isotherms and (b) pore size distribution curve of the as-synthesized NiCo_2O_4 .

Figure 4. Electrochemical properties of porous NiCo_2O_4 . (a) CV curves and (b) charge/discharge curves of NiCo_2O_4 . (c) Complex-plane impedance plots of Co_3O_4 , NiO , and NiCo_2O_4 . (d) Cycling performance of the as-synthesized NiCo_2O_4 .

by the transition of the redox couple Co (II)/Co (III), indicating that both nickel and cobalt ions were involved in energy storage. Based on the results of Fig. 4a, it is evident that the CV curves of NiCo₂O₄ electrode at different scan rates display a high redox peak current.

To further understand the rate capability and to estimate the specific capacitance of the NiCo₂O₄ electrode, charge/discharge measurements were performed. Fig. 4b shows charge/discharge curves of the NiCo₂O₄ electrode at a current density ranging from 5 to 50 mA cm⁻². The calculated specific capacitances of NiCo₂O₄ electrode are 1128, 1068, 988, 937, 888, and 833 F g⁻¹ corresponding to the discharge current densities of 5, 10, 20, 30, 40, and 50 mA cm⁻², respectively. The specific capacitance gradually decreased at higher current density due to the incremental (IR) voltage drop and insufficient active material involved in redox reaction at a higher current density. However, the as-fabricated NiCo₂O₄ possesses excellent capacitance at all the current densities evaluated and shows a good rate capability. Even at a high current density of 50 mA cm⁻², nearly 74% of the initial capacitance value remains. We believed that the porous structure of NiCo₂O₄ provides a larger surface area and a high density of active sites. The porous structure also allows rapid transportation of electrolyte ions into bulk materials, improving the rate capability of the electrodes.

Figure 4c displays the EIS of NiO, NiCo₂O₄, and Co₃O₄ electrodes, respectively. The inset shows the semicircle evident at high-frequency. All the impedance spectra were similar, being composed of one semicircle at high-frequency followed by a linear component at low frequency. The internal resistances (R_b) of Co₃O₄, NiO, and NiCo₂O₄ electrodes, obtained from the intercept of the plots on real axis, are very similar (0.94, 1.07, and 1 Ω , respectively.). However, the semicircle for the NiCo₂O₄ electrode is smaller than that of Co₃O₄ and NiO, revealing a lower pseudo charge transfer resistance (R_{ct}) which dues to the good electrical conductivity of NiCo₂O₄. At lower frequencies, the straight line represents the diffusive resistance (Warburg impedance) of the electrolyte ions diffusion in host materials. Each spectrum has higher angles above 45°, corresponding to the lower Warburg impedance. Interestingly, the Warburg impedance of the NiCo₂O₄ electrode is lower than that of NiO, which is attributable to the effective porous structure of NiCo₂O₄ facilitating ionic transportation.

The excellent cycle stability of the as-fabricated NiCo₂O₄ electrode at a current density of 20 mA cm⁻² is demonstrated in Fig. 4d. The specific capacitance of the electrode increased over the first 100 cycles due to complete activation of the active materials. After 100 cycles, the capacitance gradually decreased at higher cycle numbers such that 92.5% of the initial specific capacitance was remained after 1000 cycles. The results reveal the excellent stability of the NiCo₂O₄ electrode as high-performance electrochemical pseudo capacitors.

To further illustrate the excellent electrochemical properties and the suitability of the synthesized NiCo₂O₄ as an electrode material for ECs, the specific capacitance of NiO and Co₃O₄ electrodes at various current densities were measured for comparison. As shown in Fig. 5, the specific capacitances of NiCo₂O₄ are much higher than that of NiO and Co₃O₄. There are three contributions to the excellent supercapacitive performance of NiCo₂O₄. The first is the higher electrochemical performance of NiCo₂O₄ compared to NiO and Co₃O₄ because of the possible increase in feasible oxidation states contributed by both constituent metal ions. The second is the high utilization of active material and excellent reversibility in faraday reactions resulting from its unique morphology and hierarchical mesoporous structure. The third is the high electrical conductivity of NiCo₂O₄ which improves the rate capability of the electrodes. The highest specific capacitance of 1128 F g⁻¹ is relatively close to that of 1580 F g⁻¹ reported for RuO₂.⁴⁰ Taking advantage of its excellent electrochemical capacitive properties, low cost, and easy fabrication, sol-gel synthesized NiCo₂O₄ is a promising alternative material to RuO₂ in next-generation supercapacitors.

Figure 5. Specific capacitances of Co₃O₄, NiO, and NiCo₂O₄ at a controlled current density.

Conclusion

A promising electrode material, NiCo₂O₄ is successfully synthesized by a sol-gel process followed by calcining at 300°C. It exhibits a high specific capacitance, excellent rate capability, and good cycle stability. A high specific capacitance of 1128 F g⁻¹ is achieved at a current density of 5 mA cm⁻² and 92.5% of the initial specific capacitance was remained after 1000 cycles. The excellent electrochemical capacitive performance, low cost, and easy fabrication of the as-prepared NiCo₂O₄ render it a promising electrode material for electrochemical capacitors.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 21163010), the Key Project of Chinese Ministry of Education (No. 212183), and the Natural Science Funds for Distinguished Young Scholars of Gansu Province (No. 1111RJDA012).

References

- J. R. Miller, R. A. Outlaw, and B. C. Holloway, *Science*, **329**, 1637 (2010).
- D. Pech, M. Brunet, H. Durou, P. Huang, V. Mochalin, and Y. Gogotsi, *Nat. Nanotechnol.*, **5**, 651 (2010).
- T. Brezinskii, J. Wang, S. H. Tolbert, and B. Dunn, *Nat. Mater.*, **9**, 146 (2010).
- L. Q. mai, F. Yang, Y. L. Zhao, X. Xu, L. Xu, and Y. Z. Luo, *Nat. Comms.*, **2**, 381 (2011).
- Q. T. Qu, S. B. Yang, and X. L. Feng, *Adv. Mater.*, **23**, 5574 (2011).
- W. Chen, Z. L. Fan, L. Gu, X. H. Bao, and C. L. Wang, *Chem. Commun.*, **46**, 3905 (2010).
- J. Bae, M. K. Song, Y. J. Park, J. M. Kim, M. L. Liu, and Z. L. Wang, *Angew. Chem. Int. Ed.*, **50**, 1683 (2011).
- R. Kotz and M. Carlen, *Electrochim. Acta*, **45**, 2483 (2000).
- J. S. Huang, B. G. Sumpter, and V. Meunier, *Angew. Chem. Int. Ed.*, **47**, 520 (2008).
- J. W. Lang, X. B. Yan, and Q. J. Xue, *J. Power Sources*, **196**, 7841 (2011).
- S. J. Ding, T. Zhu, J. S. Chen, Z. Y. Wang, C. L. Yuan, and X. W. Lou, *J. Mater. Chem.*, **21**, 6602 (2011).
- H. L. Wang, H. S. Casalongue, Y. Y. Liang, and H. J. Dai, *J. Am. Chem. Soc.*, **132**, 7472 (2010).
- L. B. Kong, M. C. Liu, J. W. Lang, M. Liu, Y. C. Luo, and L. Kang, *J. Solid State Electrochem.*, **15**, 571 (2011).
- L. B. Kong, J. W. Lang, M. Liu, Y. C. Luo, and L. Kang, *J. Power sources*, **194**, 1194 (2009).
- Y. Y. Gao, S. L. Chen, D. X. Cao, G. L. Wang, and J. L. Yin, *J. Power sources*, **195**, 1757 (2010).
- J. K. Lee, G. P. Kim, K. H. Kim, I. K. Song, and S. H. Baeck, *J. Nanosci. Nanotechnol.*, **10**, 3676 (2010).
- Z. S. Wu, D. W. Wang, W. C. Ren, J. P. Zhao, G. M. Zhou, F. Li, and H. M. Cheng, *Adv. Funct. Mater.*, **20**, 3595 (2010).
- W. Sugimoto, H. Iwata, Y. Yasunaga, Y. Murakami, and Y. Takasu, *Angew. Chem. Int. Ed.*, **42**, 4092 (2003).

- 322 19. C. Y. Lee and A. M. Bond, *Langmuir*, **26**, 16155 (2010). 341
323 20. G. X. Hu, C. H. Tang, C. X. Li, H. M. Li, Y. Wang, and H. Gong, *J. Electrochem.* 342
324 *Soc.*, **158**, A695 (2011). 343
325 21. C. Z. Yuan, X. G. Zhang, L. H. Su, B. Gao, and L. F. Shen, *J. Mater. Chem.*, **19**, 5772 344
326 (2009). 345
327 22. W. Lee, T. Ahn, D. Soundararajan, J. M. Ko, and J. D. Kim, *Chem. Commun.*, **47**, 346
328 6305 (2011). 347
329 23. T. Y. Wei, C. H. Chen, H. C. Chien, S. Y. Lu, and C. C. Hu, *Adv. Mater.*, **22**, 347 348
330 (2010). 349
331 24. G. Y. Zhao, C. L. Xu, and H. L. Li, *J. Power Sources*, **163**, 1132 (2007). 350
332 25. S. H. Kim, Y. I. Kim, J. H. Park, and J. M. Ko, *Int. J. Electrochem. Sci.*, **4**, 1489 351
333 (2009). 352
334 26. J. P. Liu, J. Jiang, C. W. Cheng, H. X. Li, J. X. Zhang, H. Gong, and H. J. Fan, *Adv.* 353
335 *Mater.*, **23**, 2076 (2011). 354
336 27. J. K. Chang, M. T. Lee, C. H. Huang, and W. T. Tsai, *Mater. Chem. Phys.*, **108**, 124 355
337 (2008). 356
338 28. J. Jayalakshmi and K. Balasubramanian, *Int. J. Electrochem. Sci.*, **3**, 1196 (2008). 357
339 29. B. Cui, H. Lin, J. B. Li, X. Li, J. Yang, and J. Tao, *Adv. Funct. Mater.*, **18**, 1440 358
340 (2008). 359
30. M. R. Tarasevich and B. N. Efremov, in *Electrodes of Conductive Metallic Oxides Part A* (Ed: S. Trasatti), Elsevier, USA (1982). 341
31. Y. Q. Wu, X. Y. Chen, P. T. Ji, and Q. Q. Zhou, *Electrochim. Acta*, **56**, 7517 (2011). 343
32. H. W. Wang, Z. A. Hu, Y. Q. Chang, Y. L. Chen, H. Y. Wu, Z. Y. Zhang, and 344
Y. Y. Yang, *J. Mater. Chem.*, **21**, 10504 (2011). 345
33. Z. R. Tian, W. Tong, J. Y. Wang, N. G. Duan, V. V. Krishnan, and S. L. Suib, *Science*, 346
276, 926 (1997). 347
34. Y. Rao and D. M. Antonelli, *J. Mater. Chem.*, **19**, 1937 (2009). 348
35. M. Cabo, E. Pellicer, E. Rossinyol, M. Estrader, A. Lopez-Ortega, J. Nogues, 349
O. E. Castell, S. Surinach, and M. D. Baro, *J. Mater. Chem.*, **20**, 7021 350
(2010). 351
36. M. Z. Dai, L. Y. Song, J. T. LaBelle, and B. D. Vogt, *Chem. Mater.*, **23**, 2869 352
(2011). 353
37. H. T. Cui, M. Zayat, and D. Levy, *J. Sol-Gel Sci. Techn.*, **35**, 175 (2005). 354
38. R. N. Singh, J. F. Koenig, G. Poillerat, and P. Chartier, *J. Electrochem. Soc.*, **137**, 355
1408 (1990). 356
39. R. N. Singh, M. Hamdani, J. F. Koenig, G. Poillerat, J. L. Gautier, and P. Chartier, 357
J. Appl. Electrochem., **20**, 442 (1990). 358
40. C. C. Hu, W. C. Chen, and K. H. Chang, *J. Electrochem. Soc.*, **151**, A281 (2004). 359

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