Journal of New Materials for Electrochemical Systems 13, 295-299 (2010)
© J. New Mat. Electrochem. Systems

Li Promoted Sodium Zirconates as High Temperature Absorbent

V. Guzman Velderrain, D. Barraza Jimenez, D. Lardizabal Gutierrez, D. Delgado Vigil,
J. Salinas Gutierrez, A. Lopez Ortiz[†] and V. Collins-Martinez[*]

Departamento de Química de Materiales, Centro de Investigación en Materiales Avanzados, S. C.
Miguel de Cervantes 120, Chihuahua, Chih., México 31109.

Received: November 27, 2009, Accepted: February 10, 2010

Abstract: *Previous studies reported that Na_2ZrO_3 exhibited better high temperature CO_2 capture features than other Li-base materials towards its use in hydrogen production. This work is aimed to increase Na_2ZrO_3 absorption capacity by the addition of Li. Na_2ZrO_3 was synthesized by solid-state reaction and impregnated with $LiNO_3$ at different Li/Na molar ratios: 0, 0.03, 0.05, 0.1 and 0.25. Characterization consisted in XRD and SEM. Absorbents were evaluated by TGA at 600 °C, 80 % CO_2/Ar (absorption) and 800 °C, air (regeneration). XRD results found the Na_2ZrO_3 structure in all samples. However, Li promoted samples presented substitution of Na by Li in the Na_2ZrO_3 structure. According to TGA, absorption/regeneration kinetics was not modified by the effect of Li. Instead, CO_2 capture capacity increased with Li content up to a limit between 10 to 25 % mol. This was attributed to formation of Na_4ZrO_4 type structures, which can be responsible of the increase in capture capacity.*

Keywords: Li promoted Na_2ZrO_3, High temperature CO_2 absorption

1. INTRODUCTION

Hydrogen is an important raw material for today chemical and petroleum industry and can be considered a convenient and clean energy carrier, because energy produced from this gas generates water vapor as the only byproduct. Hydrogen can be produced from traditional fossil fuel sources such as petroleum, natural gas and coal as well as from renewable sources such as solar, wind, biomass and solid wastes [1].

Recently, high temperature CO_2 capture is playing an important role in converting conventional hydrogen production from fossil fuels into high efficient processes [2]. One example is the methane steam reforming (SMR) combined with CO_2 absorption (SER, sorption enhanced reforming), where high temperature CO_2 capture (600 ºC) generated important energy savings (≈ 23 %) with respect to the conventional SMR process [3].

CO_2 capture not only makes hydrogen production processes more efficient, but also helps to reduce the release of this greenhouse gas to the atmosphere, thus diminishing environmental problems such as global warming.

A crucial feature within the hydrogen production through this concept resides in the CO_2 solid absorbent, which must possess adequate absorption capacity and fast absorption-regeneration kinetics. Several researches have concentrated in the study of the effects of pressure, temperature and gas reactant composition on absorbents based on calcium oxide (CaO) using the thermogravimetric (TGA) experimental technique [4, 5]. However, sintering of these materials reduce their efficiency after several absorption-regeneration cycles. Calcined dolomite (CaO*MgO) have been proved to be a superior absorbent compared to CaO in multicycle tests [5]. Unfortunately, this absorbent of mineral origin requires high regeneration temperatures (T ≥ 950 °C) that cause degradation of the material after more than 10 absorption-regeneration cycles. Bandi et al. [6] proposed the use of the mineral huntite ($Mg_3Ca(CO_3)_4$) exhibiting good regeneration features. However, this absorbent has several disadvantages such as: a high regeneration temperature and low CO_2 capacity. Also of mineral origin the $Mg_6Al_2(CO_3)(OH)_{16}*4H_2O$ hydrotalcite was proposed by Hufton et al. [7] and Ding and Alpay [8], which was used as CO_2 adsorbent at moderate temperatures (400-500 °C) resulting in a low adsorption capacity.

To whom correspondence should be addressed:
*virginia.collins@cimav.edu.mx
†alejandro.lopez@cimav.edu.mx
Tel.: +52-614-439-1129, Tel.: +52-614-439-4815; fax: +52-614-439-1130

Recently, a new generation of synthetic solid absorbents was initially developed by Ohashi et al. [9], who proposed a novel CO_2 separation technique employing lithium zirconate (Li_2ZrO_3) as a regenerable solid CO_2 absorbent in a temperature range of 450-700 °C. Main advantages of this material were: low regeneration temperature (810 °C) and a high thermal stability compared to the mineral origin absorbents (which present sintering when exposed to high temperatures). These new materials hold their absorption capacity even after having performed more than 50 absorption-regeneration cycles. However, Li_2ZrO_3 absorption kinetics has been reported to be extremely slow [9]. Kato et al. [10] proposed other absorbents based on Li such as: lithium ferrite ($LiFeO_3$), lithium titanate (Li_2TiO_3), lithium metasilicate (Li_2SiO_3) and lithium orthosilicate (Li_4SiO_4) used at several temperatures. Among all of these, it was found that Li_4SiO_4 exhibited the highest CO_2 absorption capacity. They exposed Li_4SiO_4 to 50 absorption-regeneration cycles without losing its initial absorption capacity. However, the weight change (TGA tests) was only 82 % of its maximum theoretical capacity [10].

Even though this new generation of high temperature synthetic absorbent materials (such as Li_2ZrO_3 and Li_4SiO_4) has an adequate absorption capacity, fast regeneration kinetics and an exceptional thermal stability, are based on mixtures of Li oxides as their main component. This fact represents a disadvantage because Li and their compounds are relatively scarce in nature and consequently more expensive compared to other alkaline metals such as sodium and potassium. Some mixtures of metal oxides based on Na has been synthesized in our laboratory and studied as CO_2 absorbent materials [11]. It has been reported that sodium zirconate (Na_2ZrO_3) presents equal or even superior absorption features to those materials based on Li [2, 12]. The absorption mechanism was based on the following reaction [11]:

$$Na_2ZrO_3 + CO_2 \leftrightarrow Na_2CO_3 + ZrO_2 \qquad (1)$$

where Na_2ZrO_3 reacts reversibly with CO_2 forming sodium carbonate (Na_2CO_3) and zirconium oxide (ZrO_2) presenting a regeneration temperature of 780 °C. In this study it was found that Na_2ZrO_3 exhibited superior absorption kinetics compared to those absorbents based on Li (Li_2ZrO_3 and Li_4SiO_4) [13]. However, it was also found that Na_2ZrO_3 main disadvantage with respect to its synthetic counterparts is its lower CO_2 absorption capacity.

1.1. The use of Alkaline Metals as Promoters in CO_2 Absorbents

Nakagawa and Ohashi [14] reported the use of potassium carbonate (20 % W K_2CO_3) as promoter to increase Li_2ZrO_3 absorption reaction kinetics. Ida and Lin [12] and Ohashi et al. [9] explained with TGA-DSC data and the use of a reaction model how the mixture of Li_2CO_3 and K_2CO_3 form and eutectic around 500 °C, resulting in an enhancement of the Li_2ZrO_3 absorption reaction rate, which exhibited around 40 times faster absorption times than un-promoted Li_2ZrO_3. However, the absorption kinetics of this promoted material is restricted by the formation of the eutectic mixture Li_2CO_3-K_2CO_3 at 500 °C. Additionally, they used other alkaline carbonates as promoters (from 5 to 30 % mol) aiming to improve the Li_4SiO_4 absorption kinetics [10]. Some examples of promoters used by Ohashi et al. [9] were: sodium carbonate (Na_2CO_3), potassium carbonate (Ka_2CO_3), magnesium carbonate ($MgCO_3$) and calcium carbonate ($CaCO_3$). In all cases the use of these promoters increased the absorption kinetics to approximately 30 times with respect to the un-promoted absorbent. However, absorption temperatures were restricted to T ≥ 500 °C (in the case of K) where the eutectic region formed between Li_2CO_3 and K_2CO_3 is available. Yttrium has been also considered as a promoter as reported by Ida et al. [12].

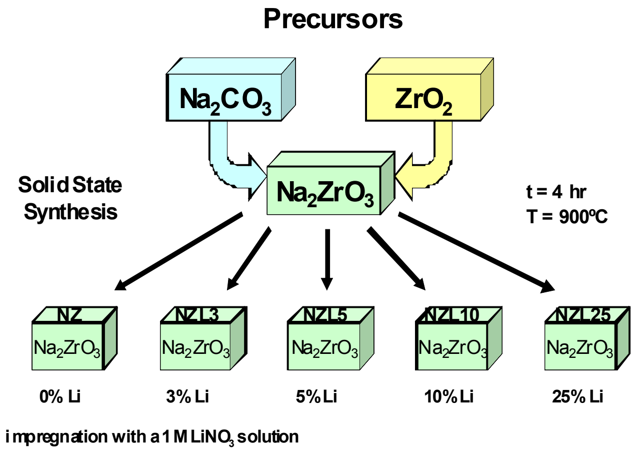

Figure1. Na_2ZrO_3 promoted with Li synthesis method

In all the previous research, in which alkaline promoters were used to improve the CO_2 absorption and/or regeneration features of those materials, resulted in the increase of the absorption kinetics, thermal stability and CO_2 capture capacity. Therefore, the present research is aimed to study the effect of Li as a promoter in Na_2ZrO_3 to increase the CO_2 absorption capacity at high temperature without significantly affecting the absorption and/or regeneration kinetics of this material. All of this in order to generate an adequate material to be used in a high efficient hydrogen production process.

2. EXPERIMENTAL

Na_2ZrO_3 was synthesized by solid state reaction following the procedure described by Lopez-Ortiz et al. [11] using a Na/Zr = 1 molar ratio. An equimolar mixture of Na_2CO_3 (J.T. Baker) and ZrO_2 (Spectrum Co.) were mixed and calcined at 900 °C for 4 hours to later be divided in five equal portions of 2g each one. These portions were separated to later be impregnated with a 1M aqueous solution of $LiNO_3$ (Sigma Aldrich) at different Li/Na molar ratios: 0, 0.03, 0.05, 0.1 and 0.25 and samples were named after NZ, NZL3, NZL5, NZL10 and NZL25, respectively according to the description of Figure 1. After impregnation the samples were calcined again at 900 °C for 1 hour. Characterization consisted in x-ray diffraction (XRD, Phillips XPERT-MPD with CuKα) and scanning electron microscopy (SEM, JEOL JSM 5800LV). Evaluation of the absorbents was carried out by thermogravimetric analysis (TGA, System-Pyris-1 Perkin Elmer) at 600 °C, 80 % CO_2 (absorption) and 800 °C, air (regeneration) at a flowrate of 100 cm^3/min.

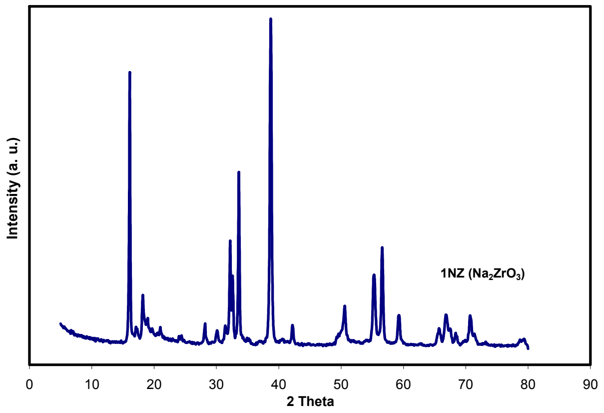

Figure 2. XRD pattern from sample NZ (Na_2ZrO_3)

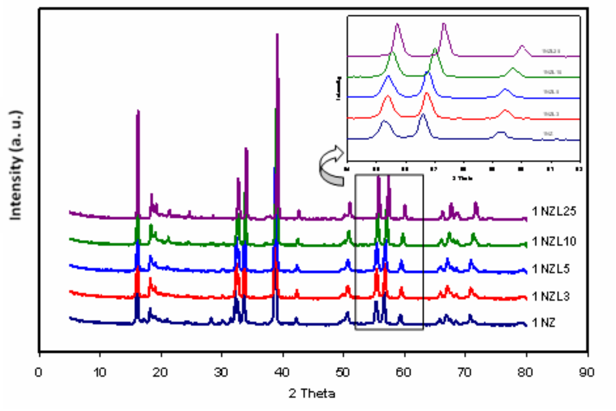

Figure 3. XRD results of Li promoted Na_2ZrO_3 samples

3. RESULTS AND DISCUSSION

3.1. X-Ray Diffraction

Na_2ZrO_3 diffraction pattern from sample NZ (Na_2ZrO_3) is shown in Figure 2. Analysis of the XRD pattern signal intensity ratios of this sample indicates the presence of a mixture of hexagonal and monoclinic Na_2ZrO_3 crystalline structures, which agrees with studies performed by Zhao et al. [15] who found similar ratios indicating the presence of these crystalline structures when the precursors were treated under an air atmosphere at 800 °C. It can be suggested that these synthesis conditions favor some portion of the monoclinic structure to be transformed into the hexagonal phase. XRD results of all Li promoted Na_2ZrO_3 samples only exhibited the sodium zirconate crystalline structure as observed in Figure 3.

In Figure 3, it can be observed that the absence of any other solid phase different from the Na_2ZrO_3 phase is evident in all the Li promoted samples. Moreover, powder diffractograms demonstrate the existence of Li atoms dissolution into the crystalline structure of Na_2ZrO_3, through the clear and continuous shift towards higher 2 θ angles when the lithium mole fraction increases with respect to the un-promoted material (NZ). This behavior is the result of the Na_2ZrO_3 unit cell distortion and shrinkage caused by the substitution of some sodium (ionic radius, 102 pm) by lithium atoms (ionic radius, 76 pm), which can be attributed to the decrease in interplanar distance in the Na_2ZrO_3 crystalline structure assuming the substitution of larger size (Na) by smaller ones (Li) [16]. This substitution is a consequence of the Li solubilizing capacity by the Na_2ZrO_3 structure that has been reported to be a maximum of 0.6 [17]. Leading to structures of the type $Na_xLi_yZrO_3$ that are reflected in the shift behavior observed in Figure 3. This shift is observed in all Li promoted samples because the highest Li content materials (NZL25) with a Li/Na = 0.25 wouldn't reach the maximum solubility limit as is reported by Pfeiffer et al. [17].

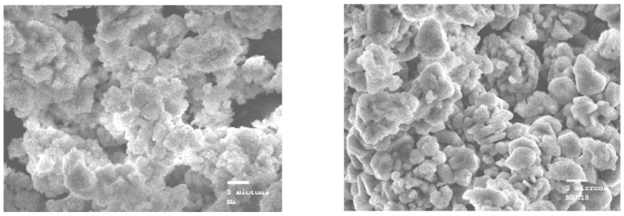

Figure 4. SEM images of un-doped NZ (left) and NZL10 (right) samples

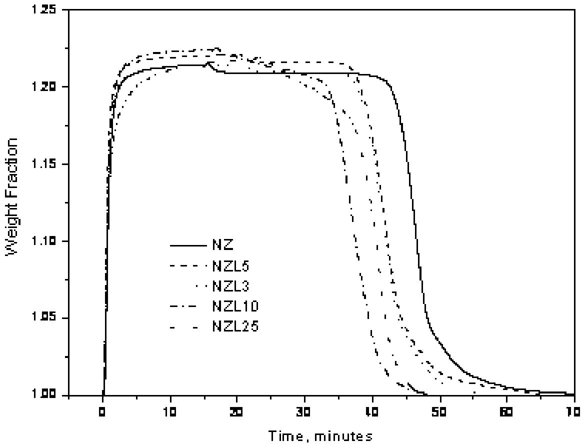

Figure 5. Absorption and regeneration TGA results of Na_2ZrO_3 samples

Figure 4 presents SEM images from samples NZ and NZL10. Sample NZ (un-promoted) exhibited morphology of agglomerates formed by spherical particles of 2-3 µm in size, which agrees with results reported by Zhao et al. [15] under similar synthesis conditions as in the present work.

On the other hand, morphology of sample NZL10 showed agglomerates composed of larger particles (2-5 µm). This can be explained by the fact that Li promoted samples were exposed to an additional calcination step (1h at 900 °C) after been impregnated with $LiNO_3$. All other Li promoted samples resulted in similar morphologies as the one observed in Figure 4 for sample NZL10.

Figure 5 presents results of TGA absorption-regeneration tests, where the absorbed weight fraction is plotted against reaction time for pure Na_2ZrO_3 and promoted samples. In this Figure it can be seen that the amount of Li within the Na_2ZrO_3 structure was not enough to significantly modify neither the absorption nor the regeneration kinetics. However, it can be observed that as the amount of Li was increased in Na_2ZrO_3 (at least up to 10 %) a rise in the amount of absorbed CO_2 was also achieved. For example, after 5 minutes of absorption the order, from small to large, in the amount of CO_2 absorbed was as follows: NZL25 < NZ < NZL3 < NZL5 < NZL10. As a consequence this would lead to a greater amount of carbonated material (Me_2CO_3, Me = Li and Na) that would reach up to a limit that can be found between 10 and 25 % mol Li, because according to results presented in Figure 5 sample NZL25 exhibited a small CO_2 capture capacity compared to sample NZ (un-promoted). The behavior of sample NZL25 can be attributed to a decrease in the CO_2 absorption kinetics, which was produced by the presence of a greater amount of the $Na_xLi_yZrO_3$ crystalline structure. This $Na_xLi_yZrO_3$ phase presumably exhibited a similar slow kinetic behavior characteristic of the Li_2ZrO_3 absorbent.

The increase in CO_2 capacity being proportional to the Li content in Na_2ZrO_3 can be explained in terms of the promoted absorbent, which has a greater amount of metal readily available to be carbonated and less amount of ZrO_2, that is inert to the absorption reaction, thus producing a more efficient absorbent. When substitution of Li with Na atoms takes place within the Na_2ZrO_3 structure the formation of a $Na_xLi_yZrO_3$ type phase is generated, thus leaving free Na atoms capable to form another structure like Na_4ZrO_4. It is reported in the literature [18] that zirconium oxide (ZrO_2) reacts with sodium carbonate (Na_2CO_3) through the reverse equation (1) to form Na_2ZrO_3. However, if the Na is found in excess, it is likely to form the Na_4ZrO_4 structure, which also can be predicted from phase diagrams based on thermodynamic data [19].

The fact that a Li content close to 25 % is traduced in a decrease in the absorption kinetics is directly related with a greater formation of the $Na_xLi_yZrO_3$ intermediate phase that presumably presents a slow kinetic behavior similar to Li_2ZrO_3 [11]. This behavior agrees with studies reported by Pfeiffer et al. [17] and Gamboa Hernández et al. [20].

A general inspection of the kinetic behavior during regeneration (Figure 5) of the CO_2 absorbed samples indicates that for practical purposes there are no changes of the promoted samples with respect to pure Na_2ZrO_3 (NZ). However, samples NZL10 and NZL25 presented a different behavior when these were exposed to low CO_2 concentrations (beginning of regeneration). This behavior can be associated to the formation of a greater amount of $Na_xLi_yZrO_3$ phase, which agrees with results reported by Gamboa Hernández et al. [20] that attributed such results to this phase being more susceptible to changes in the CO_2 partial pressure.

Table 1 reports absorbent conversions of synthesized materials evaluated by TGA in the present work at different absorption times. It is important to note that in order to determine the conversion; each of the absorbents was compared with its corresponding maximum theoretical CO_2 capacity, taking into account that this was different for every single sample.

In this Table it can be seen that NZ was the absorbent that exhibited greater conversions, followed by NZL5, NZL3, NZL10 and finally by NZL25. However, differences in conversions were not that significant, with the exception of sample NZL25, which reached a decrease of approximately 5 % with respect to NZ (2.5 min). These TGA results indicate that the addition of Li to Na_2ZrO_3 has a positive effect in generating an increase in the CO_2 absorption capacity without modifying the absorption and/or regeneration kinetics of the material.

Table 1. TGA results of CO_2 absorption conversions at different times

Sample Time (min)	Conversion (%)				
	NZ *(23.7 %)	NZL3 *(24.4 %)	NZL5 *(24.8 %)	NZL10 *(25.7 %)	NZL25 *(28.8 %)
2.5	97	97	97	96	92
4	98	97	97	97	93
6	98	97	98	97	93
8	98	97	98	97	94
12	98	98	98	97	94

*(theoretical CO_2 capacity)

4. CONCLUSIONS

According to TGA results, neither absorption nor regeneration kinetics were modified by the addition of Li to Na_2ZrO_3 (up to 25 %). Instead, the CO_2 capture capacity increased proportionally to the Li content up to a limit that can be found between 10 to 25 % mol Li. This behavior can be attributed to the fact that the promoted material contains a greater amount of available metal to be carbonated accompanied with a lower quantity of ZrO_2, which is inert to the absorption reaction, thus generating a more efficient absorbent. The order from small to large CO_2 absorption was as follows: NZL25 < NZ < NZL3 < NZL5 < NZL10. The decrease in the absorption kinetics that sample NZL25 exhibited can be explained from a existence of a greater amount of the $Na_xLi_yZrO_3$ type structure that presumably presents a similar slow absorption kinetic behavior as Li_2ZrO_3.

5. ACKNOWLEDGEMENTS

The authors gratefully acknowledge MSc. Enrique Torres, for his support during the XRD studies in the present research. The authors desire to acknowledge specially to The National Nanotechnology Laboratory at CIMAV.

REFERENCES

[1] E. L. Draper, R. A. Becker, "Research and Development Needs for the Sequestration of Carbon Dioxide as Part of a Carbon Management Strategy", The National Coal Council: Washington, D. C. (2000).

[2] M. Kato, S. Yoshikawa, K. Esaki, K. Nakagawa, "Novel CO_2 Absorbents Using Lithium-containing Oxides", In Toshiba Corporation. INTERMAC, Japan Electric Measuring Instruments Manufacturers' Association, Joint Technical Conference, Paper ID: SE-3, 1021 (2001).

[3] A. Lopez-Ortiz, D. P. Harrison, Ind. Eng. Chem. Res., 40, 5102 (2001).

[4] A. Silaban, D. P. Harrison, Chem. Eng. Comm., 147, 149 (1996).

[5] C. Han, D. P. Harrison, Sep. Sci. Technol., 32, 681 (1997).

[6] A. Bandi, M. Specht, P. Sichler, N. Nicoloso, "In situ gas conditioning in fuel reforming for hydrogen generation", 5th International Symposium on Gas Cleaning at High Temperature, Morgantown West Virginia, (2002). http://www.zsw-bw.de/en/docs/research/REG/pdfs/REG_5th_ISGC_2002.pdf.

[7] J. R. Hufton, S. G. Mayorga, S. Sircar, AIChE J., 45, 248 (1999).

[8] Y. Ding, E. Alpay, Process Saf. Environ. Prot., 79, 45 (2001).

[9] T. Ohashi, K. Nakagawa "Effect of Potassium Carbonate Additive on CO_2 Absorption in Lithium Zirconate Powder" In Materials and Devices Research Laboratories, Research and Development Center, Toshiba Corporation, Kawasaki, Japan. Materials Research Society Symposium Proceedings, 547 Solid-State Chemistry of Inorganic Materials II, 249, (1999).

[10]M. Kato, S. Yoshikawa, K. Nakagawa, J. Mater. Sci. Lett., 21, 485 (2002).

[11]A. López Ortiz, N. G. Pérez Rivera, A. Reyes Rojas, D. Lardizábal Gutiérrez, Sep. Sci. Technol., 39, 3559 (2004).

[12]J. Ida, R. Xiong, Y. S. Lin, Separ. Purif. Tech., 36, 41 (2004).

[13]D. Barraza Jiménez, V. Collins-Martínez, A. Reyes Rojas, V. Guzmán-Velderraín, A. López-Ortiz, Proceedings of the 2004 AIChE Annual Meeting/ November 10th Austin, TX, Novel Developments in Adsorption 263 (2004).

[14]K. Nakagawa, T. J. Ohashi, J. Electrochem. Soc., 145, 1344 (1998)

[15]T. Zhao, E. Ochoa-Fernández, R. Magnus, C. De, Chem. Mater., 19, 3294 (2007).

[16]S. Y. Li, Y. M. Xiong, W. Q. Mo, R. Fan, C. H. Wang, X. G. Luo, Z. Sun, H. T. Zhang, L. Li, L. Z. Cao, X. H. Chen, Phys. C: Superconductivity, 363, 219 (2001).

[17]H. Pfeiffer, E. Lima, P. Bosch, Chem. Mater., 18, 2642 (2006).

[18]Encyclopedia Britannica Volume V28, 991 (1991). http://encyclopedia.jrank.org/YAK_ZYM/ZIRCONIUM.html

[19]D. D. Sood, R. Prasad, J. Nucl. Mater., 228, 83 (1996).

[20]L. O. Gamboa Hernández, D. Lardizábal Gutiérrez, V. Collins-Martínez, A. López Ortiz, J. New Mater. Electrochem. Syst., 11, 137 (2008).