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# Effect of the hydrothermal synthesis temperature on the capacitive performance of $\alpha$ -MnO<sub>2</sub> particles

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A hydrothermal method was used to synthesise  $\alpha$ -MnO<sub>2</sub> particles, with manganese sulfate as the metal precursor and potassium permanganate as the oxidising agent. The  $\alpha$ -MnO<sub>2</sub> samples synthesised by hydrothermal treatment at 120 °C ( $\alpha$ -120) and 140 °C ( $\alpha$ -140) for 2 h exhibited different sample morphologies. The sample morphology consisted of a mixture of rose-like microflower and needles, and X-ray diffraction (XRD), scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) characterisation and Fourier transform infrared spectroscopy (FT–IR) were carried out on both the  $\alpha$ -120 and  $\alpha$ -140 samples. The results show that the only MnO<sub>2</sub> phase obtained in the synthesis was  $\alpha$ -MnO<sub>2</sub>. The electrochemical properties of the samples were analysed by cyclic voltammetry (CV) using a 0.1 M Na<sub>2</sub>SO<sub>4</sub> electrolyte solution at scan rates ranging from 5 to 100 mV s<sup>-1</sup>. The specific capacitance of the system was calculated from the CV curves. The  $\alpha$ -120 and  $\alpha$ -140 samples had specific surface areas of 128 m<sup>2</sup> g<sup>-1</sup> and 95 m<sup>2</sup> g<sup>-1</sup>, respectively, and specific capacitance as the scan rate increased for both samples.

Keywords: α-MnO<sub>2</sub> particles, average surface area, specific capacitance behaviour

# **1. INTRODUCTION**

Manganese dioxide (MnO<sub>2</sub>) exhibits excellent electrochemical performance for practical and environmental pollution applications, such as wastewater treatment [1], photocatalysis of dye degradation [2], catalysis of the oxygen reduction reaction [3], electrocatalysis [4], electrochemical sensors [5] and energy storage applications [6]. In addition, MnO<sub>2</sub> has been increasingly used in the growing market of modern portable electronic devices [7]. The ability of MnO<sub>2</sub> to store energy enables to be used as a pseudocapacitive material [8]. All the aforementioned applications rely on the unique physical and chemical properties of MnO<sub>2</sub>, namely, its stability in neutral and alkaline media, high specific surface area, low synthesis cost [9] and tuneable structural properties [10].

The crystalline structure, morphology and size of  $MnO_2$  particles are directly related to the electrochemical properties. The manganese octahedron [MnO<sub>6</sub>] is the basic unit of manganese dioxides and can exist in two types of structures [11]: layered structures, such as birnessite ( $\delta$ -MnO<sub>2</sub>), and tunnel structures, such as todorokite ( $\alpha$ -MnO<sub>2</sub>), pyrolusite ( $\beta$ -MnO<sub>2</sub>), nsutite ( $\gamma$ -MnO<sub>2</sub>) and ramsdellite (R-MnO<sub>2</sub>). Todorokite has a 2x2 tunnel structure, in which the [MnO<sub>6</sub>] octahedral units are corner-connected, with 0.46 nm pores [12].

The capacitive performance of  $\alpha$ -MnO<sub>2</sub> depends on its morphology and crystalline structure [13]. MnO<sub>2</sub>-based materials exhibit interesting electrochemical behaviour because their structures contain a sufficient number of gaps to accommodate the protons or cations in  $\alpha$ -MnO<sub>2</sub> during intercalation/deintercalation [11]. Research studies on improving the electrochemical performance of MnO<sub>2</sub>-based materials have focused on tuning the crystalline structures and surface areas [14]. MnO<sub>2</sub> particles can be fabricated with a variety of morphologies, for example, rods/wires, flowers and spheres. These morphologies may facilitate the kinetics of interfacial reactions, enabling the efficient use of the electroactive area of the material.

Studies on the electrochemical properties of MnO<sub>2</sub> have mostly focused on the electrochemical performance of the particles, and there has been limited research on the influence of the synthesis temperature on the morphology [15], which affects the electrochemical behaviour of the MnO<sub>2</sub> particles. The effect of the temperature of the hydrothermal synthesis on the specific surface area and the specific capacitance of MnO<sub>2</sub> was investigated in this study. The morphology changes of MnO<sub>2</sub> particles due to temperature treatment were examined using XRD, SEM, BET and FT–IR. The electrochemical analysis of the prepared samples was carried out using cyclic voltammetry in an Na<sub>2</sub>SO<sub>4</sub> aqueous electrolyte at different scan rates.

## 2. MATERIALS AND EXPERIMENTAL METHODS

## 2.1 Synthesis

A wide variety of methods are commonly used to synthesise  $MnO_2$  particles, such as hydrothermal synthesis [16,17], ultrasonic synthesis [18,19], sonochemical synthesis [20], chemical precipitation [21] and even a simple solvent-free synthesis [22], resulting in different chemical phases and morphologies. In this study, the  $\alpha$ -MnO<sub>2</sub> phase was prepared by a very simple hydrothermal synthesis [23] with MnSO<sub>4</sub>•2H<sub>2</sub>O (98–100% Fermont) and KMnO<sub>4</sub> (95–100% Meyer) as the Mn precursor and oxidising agent, respectively.  $\alpha$ -MnO<sub>2</sub> particles were synthesised as follows: a homogeneous solution was obtained by dissolving 0.2 g of MnSO<sub>4</sub>•2H<sub>2</sub>O and 0.5 g of KMnO<sub>4</sub> in 50 mL of distilled water under magnetic stirring for 45 min at 25 °C. The resulting solution was poured into a 50-mL Teflon-lined stainless-steel autoclave, which was maintained at two temperatures (120 °C and 140 °C) for 2 h in an electric oven to form  $\alpha$ -MnO<sub>2</sub> particles with different surface areas. The system was cooled to room temperature, and the resulting precipitate was washed with distilled water and absolute ethanol. Then, the precipitate was heated at 80 °C for 24 h. The samples obtained at two synthesis temperatures were labelled  $\alpha$ -120 and  $\alpha$ -140.

## 2.2 Characterisation

FT–IR spectra were obtained at wavelengths between 4000-400 cm<sup>-1</sup> using and FTIR 2000 (Perkin-Elmer) and KBr pellet technique. X-ray diffraction patterns were obtained on a powder diffractometer (Bruker D8Advance) using Cu-K $\alpha$  radiation (1.5418 Å) and a fluorescence screen between 10°-90° using a 1.0 mm grid and a scan rate of 0.02° 2 $\theta$  s<sup>-1</sup>. The morphology of the  $\alpha$ -MnO<sub>2</sub> particles was observed using field emission scanning electron microscopy (JEOL-6701F) at 5 kV. Nitrogen adsorption-desorption isotherms were obtained using a Quantachrome Autosorb iQ<sub>2</sub> model at –196 °C.

## 2.3 Electrochemical measurements

The electrochemical properties of the samples were determined using an electrochemical device with a three-electrode cell. A catalyst ink supported on glassy carbon, a graphite bar and Ag/AgCl (3 M NaCl) was used as the working electrode (WE), counter electrode (CE) and reference electrode (RE), respectively. The electrolyte was a 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution at room temperature. Electrochemical measurements were made using cycling voltammetry (CV), and the specific capacitance (Cs) of the electrode was calculated from the CV curves using the following expression [24]:

$$C_s = \frac{1}{v \, m \, \Delta V} \, \int_{V_a}^{V_c} I(V) dV \tag{1}$$

where  $C_S$  is the specific capacitance (F g<sup>-1</sup>), *m* is the mass of MnO<sub>2</sub> (g),  $\Delta V$  is the potential range (V), *v* is the scan rate (V s<sup>-1</sup>) and *I*(*V*) is the current response.

The catalyst ink was prepared by adding 30 mg of  $MnO_2$  particles and 1.5 mg of Vulcan XC 72 carbon black to a mixed solution containing 160 µL of acetone and 80 and 100 µL of a Nafion solution; the ink was then added to the  $\alpha$ -120 and  $\alpha$ -140 samples, respectively. Then, 1.5 µL of the  $\alpha$ -120 ink and 2 µL of the  $\alpha$ -140 ink were pipetted onto glassy carbon electrodes to form the working electrodes.

# **3. RESULTS AND DISCUSSION**

## 3.1 Chemical structure of $\alpha$ -MnO<sub>2</sub>

The FT–IR spectra of both the  $\alpha$ -120 and  $\alpha$ -140 samples were analysed to identify the chemical bonds and species in the MnO<sub>2</sub> particles. Figure 1 shows an infrared band related to the O-H stretching vibration of distilled H<sub>2</sub>O at approximately 3420 cm<sup>-1</sup>, which indicates the hydrous nature of the  $\alpha$ -MnO<sub>2</sub> samples. The absorption bands at approximately 1630, 1411 and 1132 cm<sup>-1</sup> could be ascribed to the bending vibrations of -OH combined with Mn atoms [25]. The bands at 690, 535 and 471 cm<sup>-1</sup> can be attributed to the Mn-O vibrations in the MnO<sub>6</sub> octahedral units of the  $\alpha$ -MnO<sub>2</sub> phase [26]. All the aforementioned bands were smooth in the spectra of the samples prepared at synthesis temperatures of 120 °C and 140 °C which indicates a change in the morphology of the particles between these temperatures.



**Figure 1.** FT–IR spectra for  $\alpha$ -MnO<sub>2</sub> particles synthesized by the hydrothermal method at 120 °C and 140 °C for 2 h, corresponding to the  $\alpha$ -120 and  $\alpha$ -140 samples.

#### 3.2 Structural analysis of $\alpha$ -MnO<sub>2</sub>

The crystalline structure of  $\alpha$ -MnO<sub>2</sub> particles was analysed by XRD. Figure 2 shows the XRD patterns of the  $\alpha$ -120 and  $\alpha$ -140 samples. The observed diffraction peaks in these patterns were indexed according to the JCPDS 44-0141 card [3,27], which corresponded to a tetragonal phase for  $\alpha$ -MnO<sub>2</sub> with lattice constants a = 9.785 Å and c = 2.863 Å.  $\alpha$ -MnO<sub>2</sub> contained double chains of edge-sharing [MnO<sub>6</sub>] octahedra, which shared corners to form 1D (2 x 2) and (1 x 1) tunnels that extended in a direction parallel to the c axis of the tetragonal unit cell [28]. No species other than  $\alpha$ -MnO<sub>2</sub> were detected. Consequently, it was concluded that  $\alpha$ -MnO<sub>2</sub> was produced by a reaction between KMnO<sub>4</sub> and MnSO<sub>4</sub> [27,29] under the aforementioned hydrothermal conditions:

$$2KMnO_4 + 3MnSO_4 + 2H_2O \xrightarrow{A} 5MnO_2 \downarrow + K_2SO_4 + 2H_2SO_4$$
(2)

Therefore, the formation of  $MnO_2$  was attributed to redox reactions including the oxidation of  $Mn^{2+}$  ions (Eq. 3) and reduction of  $Mn^{7+}$  ions (Eq. 4):

$$Mn^{2+} \rightarrow Mn^{4+} + 2e^{-} \tag{3}$$

$$Mn^{7+} + 3e^{-} \rightarrow Mn^{4+} \tag{4}$$

The XRD results show no changes in the  $MnO_2$  structure between the samples synthesised at 120 °C and 140 °C.



**Figure 2.** XDR patterns for  $\alpha$ -MnO<sub>2</sub> particles hydrothermally treated at 120 °C and 140 °C for 2 h, corresponding to the  $\alpha$ -120 and  $\alpha$ -140 samples.

The crystallite sizes of the  $\alpha$ -120 and  $\alpha$ -140 samples calculated from the XRD patterns using Scherrer's equation were 22 and 18 nm, respectively.

# 3.3 Morphologic analysis of $\alpha$ -MnO<sub>2</sub>

The morphology of the  $\alpha$ -120 and  $\alpha$ -140 samples was analysed by SEM. Figure 3 shows the effect of the of the hydrothermal synthesis temperatures, 120 °C and 140 °C, on the shape of the  $\alpha$ -MnO<sub>2</sub> particles. Figure 3a shows that the morphology of the  $\alpha$ -120 sample was heterogeneous and consisted of a mixture of rose-like microflowers composed of nanosheets with a thickness of 15–30 nm and needles with diameters of 40–60 nm and lengths ranging from hundreds of nanometres to several micrometres.



**Figure 3.** SEM images of the  $\alpha$ -MnO<sub>2</sub> particles synthesized hydrothermally. (a)  $\alpha$ -120 and (b)  $\alpha$ -140.

Figure 3b shows a micrograph of the  $\alpha$ -140 sample, which contained needles [30]. This morphology was not completely homogeneous because some of the rose-like microflowers did not transform completely and formed clusters. This transformation in the morphology of the  $\alpha$ -120 sample and the  $\alpha$ -140 sample was previously reported by Asim et al. [9] and is associated with the Ostwald ripening process [31] and the growth of solid grains during sintering with a liquid phase [32]. The crystal morphology and size of the  $\alpha$ -120 sample result in a high surface area and short diffusion path during CV tests.

Figure 4 shows the surface areas of the  $\alpha$ -120 and  $\alpha$ -140 samples determined from N<sub>2</sub> absorptiondesorption isotherms which are both common type II isotherms [33] with a narrow hysteresis loop in the medium-pressure areas. These characteristics have also observed for mesoporous materials [29]. The BET–specific surface areas for the  $\alpha$ -120 and  $\alpha$ -140 samples were 128 m<sup>2</sup> g<sup>-1</sup> and 95 m<sup>2</sup> g<sup>-1</sup>, respectively. The effect of the synthesis temperature on the samples can be explained in terms of a nucleation and growth process.



**Figure 4.** Nitrogen adsorption-desorption isotherms of the  $\alpha$ -120 and  $\alpha$ -140 samples synthesised hydrothermally at 120 °C and 140 °C for 2h, respectively.

During the synthesis,  $MnO_2$  nuclei were formed from KMnO<sub>4</sub> and MnSO<sub>4</sub>. Lowering the temperature from 140 °C to 120 °C accelerated the formation of MnO<sub>2</sub>, thereby reducing the particle size and increasing the surface area of the system.

## 3.4 Electrochemical evaluation of $\alpha$ -MnO<sub>2</sub>

## 3.4.1 Cyclic voltammetry results

The electrochemical behaviour of the MnO<sub>2</sub> synthesised samples was determined by performing cyclic voltammetry in a 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution at room temperature. The potential window was from 0 to 0.9 V, and the scan rate was between 5 and 100 mV s<sup>-1</sup>. Figure 5 shows rectangular CV curves for the  $\alpha$ -120 sample obtained at low scan rates between 5 and 20 mV s<sup>-1</sup>, which are associated with ideal capacitive behaviour [34,35]. Increasing the scan rate from 50 to 100 mV s<sup>-1</sup> resulted in the rectangular

CV curves becoming quasi-rectangular, which may have been due to the polarisation effect of the electrode [23]. Figure 6 shows similar CV curves for the  $\alpha$ -140 sample at all scan rates.



**Figure 5.** CV curves for α–MnO<sub>2</sub> particles synthesised hydrothermally at 120 °C using a 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution at different scan rates from 0 to 0.9 V.



**Figure 6.** CV curves for α–MnO<sub>2</sub> particles synthesised hydrothermally at 140 °C using a 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution at different scan rates from 0 to 0.9 V.

An anodic peak ( $P_a$ ) was observed during the anodic sweep between 0.3 and 0.42 V vs. saturated calomel electrode (SCE), which is ascribed to de-insertion of the Na<sup>+</sup> ion, whereas a cathodic peak ( $P_c$ ) was observed in the reverse direction between 0.2 and 0.4 V vs. SCE, which is attributed to the insertion of the Na<sup>+</sup> ion, according to the following reaction [36]:

$$MnO_2 + Na^+ + e^- \rightleftarrows NaMnO_2$$
(5)

Figure 6 shows that increasing the scan rate shifted the anodic peak to the right to higher potentials values and the cathodic peak to the left to lower potentials, which could be attributed to diffusion-limited redox processes [13]. However, increasing the scan rate caused the intensity of the anodic and cathodic peaks to increase. With increasing scan rate, the CV curves exhibited an increase in the anodic area but retained the same shape.



Figure 7. CV curves obtained at a scan rate of 5 mV s<sup>-1</sup> for  $\alpha$ -MnO<sub>2</sub> particles synthesised at 120 °C and 140 °C.

Figure 7 shows the CV curves of the  $\alpha$ -MnO<sub>2</sub> synthesised materials,  $\alpha$ -120 and  $\alpha$ -140, obtained at the same scan rate (5 mV s<sup>-1</sup>). The CV curve of the  $\alpha$ -120 sample has a larger area than that of the  $\alpha$ -140 sample, resulting in higher specific capacitance values. The  $\alpha$ -120 sample has a higher specific surface area (128 cm<sup>2</sup> g<sup>-1</sup>) than the  $\alpha$ -140 sample and an average pore diameter of 42 nm. The higher specific capacitance of the  $\alpha$ -120 sample may be due to its open material structure and smaller interconnected tunnels, which promotes the diffusion of alkali cations and protons into the MnO<sub>2</sub> bulk.

## 3.4.2 Specific capacitance results

The specific capacitance of the system was estimated from the area of the CV curves and Eq. 1. Figure 8 shows that the specific capacitance depends on the scan rate which affects the diffusion of  $H^+$  and  $Na^+$  ions in  $\alpha$ -MnO<sub>2</sub>.



**Figure 8.** Specific capacitance as a function of the scan rate for the  $\alpha$ -120 and  $\alpha$ -140 samples.

At high scan rates, protons and cations only diffuse in the superficial layer of the electrode, resulting in a low specific capacitance for the material [24]. At lower scan rates, the ions from the electrolyte reach the pores of the electrode more easily, increasing the adsorption/desorption of electrolyte cations and, consequently, the specific capacitance [37]. The highest specific capacitance values obtained at a scan rate of 5 mV s<sup>-1</sup> for the  $\alpha$ -120 and  $\alpha$ -140 samples were 112.8 F g<sup>-1</sup> and 34.86 F g<sup>-1</sup>, respectively. Table 1 is a summary of the specific capacitance values at each scan rates ranging from 5 to 100 mV s<sup>-1</sup> calculated using Eq. 1.

Scan rate	Specific capacitance C <sub>s</sub> (F g <sup>-1</sup> )			
$(mV s^{-1})$	α-120	α-140		
5	112.80	34.86		
10	105.60	33.05		
20	97.50	31.34		
50	82.90	28.25		
100	67.45	23.21		

Table	1.	Average	specific	capacitance	for the	α-120	and	α-140	samples	calculated	from	CV	curves
	oł	otained at	scan rate	es ranging fro	om 5 to	100 m <sup>•</sup>	$Vs^{-1}$ .						

**Table 2.** Comparison of the morphology, surface area and average specific capacitance at 5 mV s<sup>-1</sup> of the  $\alpha$ -120 and  $\alpha$ -140 samples.

Sample	Morphology	Specific capacitance	Surface area		
		(F g <sup>-1</sup> )	$(\mathbf{m}^2 \mathbf{g}^{-1})$		
α-120	Rose-like micro flowers and	112.8	128		
	needles				
α-140	Needles with	34.86	95		
	residual rose-like micro flowers				

The specific capacitance of the  $\alpha$ -120 and  $\alpha$ -140 samples decreased with increasing scan rate. However, Table 1 shows that the specific capacitance increase noticeably for scan rates between 50 and 100 mV s<sup>-1</sup>. Table 2 is a comparison of the morphology, surface area and specific capacitance at 5 mV s<sup>-1</sup> of the  $\alpha$ -120 and  $\alpha$ -140 samples.

These results show that the  $\alpha$ -120 sample, with a morphology of rose-like microflowers and needles, possesses the higher average specific capacitance. This result could be attributed to the needle size and space between the flakes in which the clusters of rose-like microflowers formed. This structure effectively improves the transport properties of the electrolyte [16].

The electrode used for the  $\alpha$ -120 sample exhibited a higher specific capacitance of 112.8 F g<sup>-1</sup> than has been previously reported, except for that reported by Wang et al. [40] of 123 F g<sup>-1</sup> at 2 mV s<sup>-1</sup> scan rate. Table 3 is a comparison between the electrochemical performance of our materials and those reported in the literature.

Sample	Reference	Specific capacitance	Scan rate	
		( <b>F</b> g <sup>-1</sup> )	$(\mathbf{mV s^{-1}})$	
a-MnO2 (a-120)	This study	112.8	5	
a-MnO <sub>2</sub> (a-140)	This study	34.86	5	
a-MnO <sub>2</sub>	[38]	91.20	5	
a-MnO <sub>2</sub>	[39]	100.5	1	
a-MnO2	[40]	123	2	
a-MnO2	[41]	100	5	

**Table 3.** Comparison of the specific capacitance of the as-prepared electrodes and reported  $\alpha$ -MnO<sub>2</sub> samples.

The voltammetric charge density q (C g<sup>-1</sup>) was calculated from the specific capacitance, *Cs* (F g<sup>-1</sup>), and the potential window,  $\Delta V$  (V), using the following expression [42]:

 $q = Cs \, \Delta V \tag{6}$ 

The outer voltammetric charge density (*q*<sub>0</sub>), which corresponds to the outermost and most accessible active surface sites, can be estimated by extrapolating *q* from the *q* vs.  $v^{-l/2}$  plots to  $v = \infty$ .



Figure 9. Effect of the scan rate on the voltammetric charge density.

Figure 9 shows that  $q_0$  increases with  $v^{-1/2}$  (decreases with v) for the  $\alpha$ -120 and  $\alpha$ -140 samples. Thus, protons can diffuse more easily to the inner and less accessible surfaces at low scan rates than at high scan rates. The  $q_0$  values estimated from Figure 9 for the  $\alpha$ -120 and  $\alpha$ -140 samples were 56.9 and 20.5 C g<sup>-1</sup>, respectively. The higher  $q_0$  of the  $\alpha$ -MnO<sub>2</sub> of the  $\alpha$ -120 sample results from the higher specific surface area of MnO<sub>2</sub> of this sample compared to that of the  $\alpha$ -140 sample.

# **4. CONCLUSION**

 $\alpha$ -MnO<sub>2</sub> particles with morphologies of rose-like microflowers and needles were synthesised by adjusting the reaction temperature of the hydrothermal synthesis. Synthesis temperatures of 120 °C and 140 °C were used: only rose-like microflowers formed at the lower synthesis temperature, whereas needles formed at both temperatures. The highest specific capacitances of the  $\alpha$ -120 and  $\alpha$ -140 samples of 112.8 F g<sup>-1</sup> and 34.86 F g<sup>-1</sup>, respectively, were obtained at a scan rate of 5 mV s<sup>-1</sup>. The BET specific surface areas for the  $\alpha$ -120 and  $\alpha$ -140 samples were 128 m<sup>2</sup> g<sup>-1</sup> and 95 m<sup>2</sup> g<sup>-1</sup>, respectively. The outer voltammetric charge, corresponding to the outermost and most accessible active surface sites, was 56.9 and 20.5 C g<sup>-1</sup> for the  $\alpha$ -120 and  $\alpha$ -140 samples, respectively.

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## References

- S. Panimalar, S. Logambal, R. Thambidurai, C. Inmozhi, R. Uthrakumar, A. Muthukumaran, R. A. Rasheed, M. K. Ghatasheh, A. Raja, J. Kennedy and K. Kaviyarasu, *Environ. Res.*, 205 (2022) 112560.
- 2. M. Gayathri, M. Shanthi, E. Satheeshkumar, N. Jayaprakash and E. Sundaravadivel, *Mater. Today: Proceedings*, 42 (2021) 1506.
- 3. J. Yang, J. Wang, S. Ma, B. Ke, L. Yu, W. Zeng, Y. Li and J. Wang, *Physica E*, 109 (2019) 191.
- 4. Y. Chen, S. Yang, H. Liu, W. Zhang and R. Cao, Chin. J Catal., 42 (2021) 724.
- 5. A. Shoba, B. Kavitha, H. Aswathaman, H. Ganesan and N. Senthil Kumar, *Mater. Today: Proc.*, 48 (2022) 521.
- 6. M. Okutan, N. Doğan, M. Öztürk and O. Yalçın, J. Mol. Struct., 1241 (2021) 130516.
- 7. N. Tang, X. Tian, C. Yang, Z. Pi and Q. Han, J. Phys. Chem. Solids, 71 (2010) 258.
- 8. S. Sivakumar and L. Nelson Prabu, Mater. Today: Proc., 47 (2021) 52.
- 9. U. Asim, S. M. Husnain, N. Abbas, F. Shahzad, A. R. Khan and T. Ali, *J. Ind. Eng. Chem.*, 98 (2021) 375.
- 10. L. Zeng, G. Zhang, X. Huang, H. Wang, T. Zhou and H. Xie, Vacuum, 192 (2021) 110398.
- 11. Rusi and S. R. Majid, Solid State Ionics, 262 (2014) 220.
- 12. T. Lin, L. Yu, M. Sun, G. Cheng, B. Lan and Z. Fu, Chem. Eng. J., 286 (2016) 114.
- 13. X. Yang, Z. Qiao, F. Liu, S. Yang, L. Zhang and B. Cao, *Electrochim. Acta*, 280 (2018) 77.
- 14. G. Gupta, K. Selvakumar, N. Lakshminarasimhan, S. M. Senthil Kumar and M. Mamlouk, *J. Power Sources*, 461 (2020) 228131.
- 15. S. Zhao, T. Liu, D. Shi, Y. Zhang, W. Zeng, T. Li and B. Miao, Appl. Surf. Sci., 351 (2015) 862.
- 16. H. Wei, J. Wang, S. Yang, Y. Zhang, T. Li and S. Zhao, Physica E, 83 (2016) 41.

- 17. L. Wang, G. Duan, S. M. Chen and X. Liu, J. Alloys Compd., 752 (2018) 123.
- V. Balakumar, J. W. Ryu, H. Kim, R. Manivannan and Y.-A. Son, *Ultrason. Sonochem.*, 62 (2019) 104870.
- 19. J. S. Markovski, V. Đokić, M. Milosavljević, M. Mitrić, A. A. Perić-Grujić, A. E. Onjia and A. D. Marinković, *Ultrason. Sonochem.*, 21 (2014) 790.
- 20. Z. Razmara and M. Kubicki, J. Mol. Struct., 1234 (2021) 130143.
- 21. S. Sivakumar and L. N. Prabu, Mater Today: Proc., 47 (2021) 52.
- 22. M. H. Alfaruqi, S. Islam, J. Gim, J. Song, S. Kim, D. T. Pham, J. Jo, Z. Xiu, V. Mathew and J. Kim, *Chem. Phys. Lett.*, 650 (2016) 64.
- 23. X. Bai, X. Tong, Y. Gao, W. Zhu, C. Fu, J. Ma, T. Tan, C. Wang, Y. Luo and H. Sun, *Electrochim. Acta*, 281 (2018) 525.
- 24. Z. Fan, M. Xie, X. Jin, J. Yan and T. Wei, J. Electroanal. Chem., 659 (2011) 191.
- 25. M. Aghazadeh, M. Asadi, M. G. Maragheh, M. R. Ganjali, P. Norouzi and F. Faridbodc, *Appl. Surf. Sci.*, 364 (2016) 726.
- 26. D. P. Dubal, W. B. Kim and C. D. Lokhande, J. Alloy Compd., 509 (2011) 10050
- 27. M. R. Majidi, F. S. Farahani, M. Hosseini and I. Ahadzadeh, Bioelectrochemistry, 125 (2019) 38.
- 28. N. Li, X. Zhu, C. Zhang, L. Lai, R. Jiang and J. Zhu, J. Alloy Compd., 692 (2017) 26.
- 29. B. Kishore, V. Gopal and M. Nookala, J. Appl. Chem., 5, (2016) 738.
- 30. T. Cetinkaya, U. Toçoğlu, M. Uysal, M. O. Güler and H. Akbulut, *Microelectron. Eng.*, 126 (2014) 54.
- 31. B. Li, G. Rong, Y. Xie, L. Huang and C. Feng, Inorg. Chem., 45 (2006) 6404.
- 32. J. S. Moya, C. Baudín and P. Miranzo, *Encyclopedia of Physical Science and Technology (Third Edition)*, (2003) 865-878.
- 33. B. He, G. Cheng, S. Zhao, X. Zeng, Y. Li, R. Yang, M. Sun and L. Yu, J. Solid State Chem., 269 (2019) 305.
- 34. M. Kazazi, Ceram. Int., 44, (2018) 10863.
- 35. N. Kaabi, B. Chouchene, W. Mabrouk, F. Matoussi and E. Selmane B.H. Hmida, *Solid State Ionics*, 325, (2018) 74.
- 36. L. Bao, J. Zang and X. Li, Nano Lett., 11, (2011) 1215.
- 37. J Yan, T Wei, J. Chen, Z. Fan and M. Zhang, Mater. Res. Bull., 45 (2010) 210.
- 38. Q. Liu, S. Ji, J. Yang, H. Wang, B.G. Pollet and R. Wang, *Materials*, 10, (2017) 988.
- 39. N. Shimamura, R. Kanda, Y. Matsukubo, Y. Hirai, H. Abe, Y, Hirai, T. Yoshida, H. Kabu and A. Masuhara, *ACS Omega*, 4 (2019) 3827.
- 40. J-G Wang, Y. Yang, Z-H Huang and F. Kang, Mater. Chem. Phys., 140, (2013) 643.
- 41. P. Yu, X. Zhang, D. Wang, L. Wang and Y. Ma, Cryst. Growth Des., 9 (2009) 528.
- 42. J. Yan, Z. Fan, T. Wei, J. Cheng, B. Shao, K. Wang, L. Song and M. Zhang, *J. Power Sources*. 194, (2009) 1202.

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