American Journal of Analytical Chemistry, 2025, 16(8), 153-160
https://www.scirp.org/journal/ajac
ISSN Online: 2156-8278
ISSN Print: 2156-8251

Effect of Ball Milling and Annealing Temperature on Electrochemical Properties of Nsutite Materials

Manika Chaudhary[1], Michael Gammon[1], Lekan J. Oyelola[1], Noah Lee[1], Tess E. Masi[1], Vikhyat Sahi[2], Peter K. LeMaire[1], Rahul Singhal[1*]

[1]Department of Physics and Engineering Physics, Central Connecticut State University, New Britain, USA
[2]Rouse High School, Leander, USA
Email: *singhal@ccsu.edu

How to cite this paper: Chaudhary, M., Gammon, M., Oyelola, L.J., Lee, N., Masi, T.E., Sahi, V., LeMaire, P.K. and Singhal, R. (2025) Effect of Ball Milling and Annealing Temperature on Electrochemical Properties of Nsutite Materials. *American Journal of Analytical Chemistry*, **16**, 153-160.
https://doi.org/10.4236/ajac.2025.168009

Received: April 11, 2025
Accepted: August 3, 2025
Published: August 6, 2025

Abstract

In our previous study, we found that nsutite materials showed electrochemical properties and can be found suitable for supercapacitor applications. In this study, we ball milled and annealed the nsutite materials at different temperatures, based on the transition temperatures obtained from differential thermal analysis and thermogravimetric analysis (DSC/TGA). X-ray diffraction studies confirmed the gamma-MnO_2 phase of nsutite material, and electrochemical studies showed electrochemical behavior. The specific capacitance of ball milled nsutite material was 36 F/g at 0.5 A/g current density. The specific capacitance of the ball milled samples annealed at 350˚C and 580˚C was 18 F/g and 11.3 F/g, respectively at a current density of 0.5 A/g.

Keywords

Supercapacitor, Nsutite, Specific Capacitance, Energy Storage, XRD

1. Introduction

To meet current and future energy needs, scientists are looking for alternate renewable energy sources. Also, there is a need of reliable energy storage devices to store the energy produced by alternate renewable energy sources. Rechargeable batteries [1] [2] and supercapacitors [3] [4] are promising energy storage devices. Over the years, scientists have been looking for cheap, environmentally friendly, and high energy density supercapacitor materials [5]. Various transition metal oxides [6]-[8], sulfides [9] [10], and nitrides [11] materials have been found to be suitable for supercapacitor applications. Among these materials, MnO_2 [12] are considered and promising material for supercapacitor applications because of its good electrochemical properties, environmental friendliness, abundance in nature and low cost. Li and coworkers synthesized MnO_2 by one pot method and reported its specific capacitance as 124.9 F/g at 1 A/g [13]. Naturally MnO_2 can be obtained from nsutite, an ore found in a town called Nsuta in Ghana. Nsutite has the composition $Mn_{1-x}^{4+}Mn_x^{2+}O_{2-2x}(OH)_{2x}$ where x = 0.06 - 0.07 [14]. It was reported that naturally occurring MnO_2 can be used for supercapacitor applications [15]. In our previous article, we found that pure nsutite materials showed the electrochemical behavior and the specific capacitance of pure nsutite material was found as 14.65 F/g at a current density of 1 A/g [16]. In order to further improve the electrochemical properties of the nsutite materials we ball milled and then annealed the materials. The effect of the annealing temperature on electrochemical behavior of nsutite was studied and reported in this paper.

2. Materials and Characterizations

Nsutite samples were obtained from Ghana Manganese Company, Nsuta, Ghana, where nsutite was first discovered. Sodium sulfate was received from Alfa Aesar, USA and used as received. Nsutite samples were crushed into small pieces and then ball milled using Planetary Ball Mill [ACROSS International USA, Model PQ-N04]. The nsutite samples were ball milled using 8 silica ball of 6 mm and at the rate of 300 rpm for 15 minutes and then paused for 15 min and the cycle was repeated 32 times. The counter cylinder had equal weight of sand and 8 silica balls.

The ball milled sample was characterized using DSC/TGA and then annealed at 350˚C and 580˚C based on the transitions seen from DSC/TGA thermogram [16]. X-ray diffraction studies of ball milled and annealed ball milled samples were carried out using Rigaku Miniflex-II x-ray diffractometer employing Cu K_α radiation with a wavelength of 1.5406 Å at a scan rate of 3˚ min^{-1}.

The slurry of the nsutite materials were prepared by mixing 80% of the nsutite material, 10% carbon black, and 10% PVDF binder using n-NMP as a solvent in a pastel mortar. The slurry was then coated onto Ni foil and dried overnight. The mass of the active materials on the electrodes was between 3.0 mg - 5.0 mg. The electrochemical studies were performed using a Squidstat plus potentiostat (Admiral Instruments, USA). The electrochemical characterization was carried out in a three-electrode cell configuration using prepared nsutite electrodes, Pt. foil, and Ag/AgCl as working, counter, and reference electrode, respectively. 1 M sodium sulfate aqueous solution was used as electrolyte.

3. Results and Discussions

Figure 1. shows the X-ray diffraction pattern of pure and annealed ball milled nsutite. Pure ball milled sample has peaks at 2θ/(d-spacing, Å) 22.46˚/3.96 Å, 26.8/3.33 Å, 28.76˚/3.10 Å, 37.3˚/2.41 Å, 38.42˚/2.34 Å, 42.6˚/2.12 Å, 56.24˚/1.64 Å, 65.18˚/1.43 Å, 69.28˚/1.36 Å, and 71.8˚/1.31 Å. The results indicates that the ball milled samples correspond to 1.64 type nsutite, containing 90.57% manganese, which was further determined as gamma MnO_2 [17]. Upon heating the ma-

terials some peaks disappear and at 580˚C MnO_2 converted to Mn_2O_3, which is in agreement with the literature [18].

Figure 2 represents the cyclic voltammogram of various nsutite samples. The cyclic voltammetric studies were performed in air atmosphere at room temperature

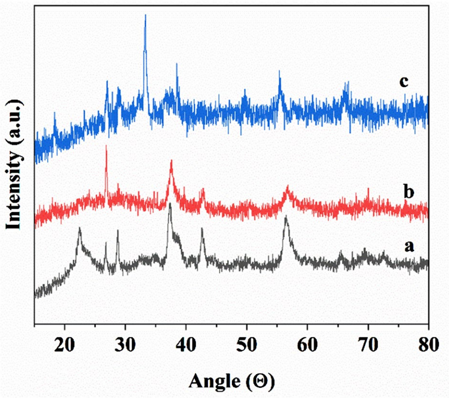

Figure 1. X-ray diffraction studies of (a) pure ball milled nsutite, (b) ball milled sample annealed at 350˚C, and (c) ball milled sample annealed at 580˚C.

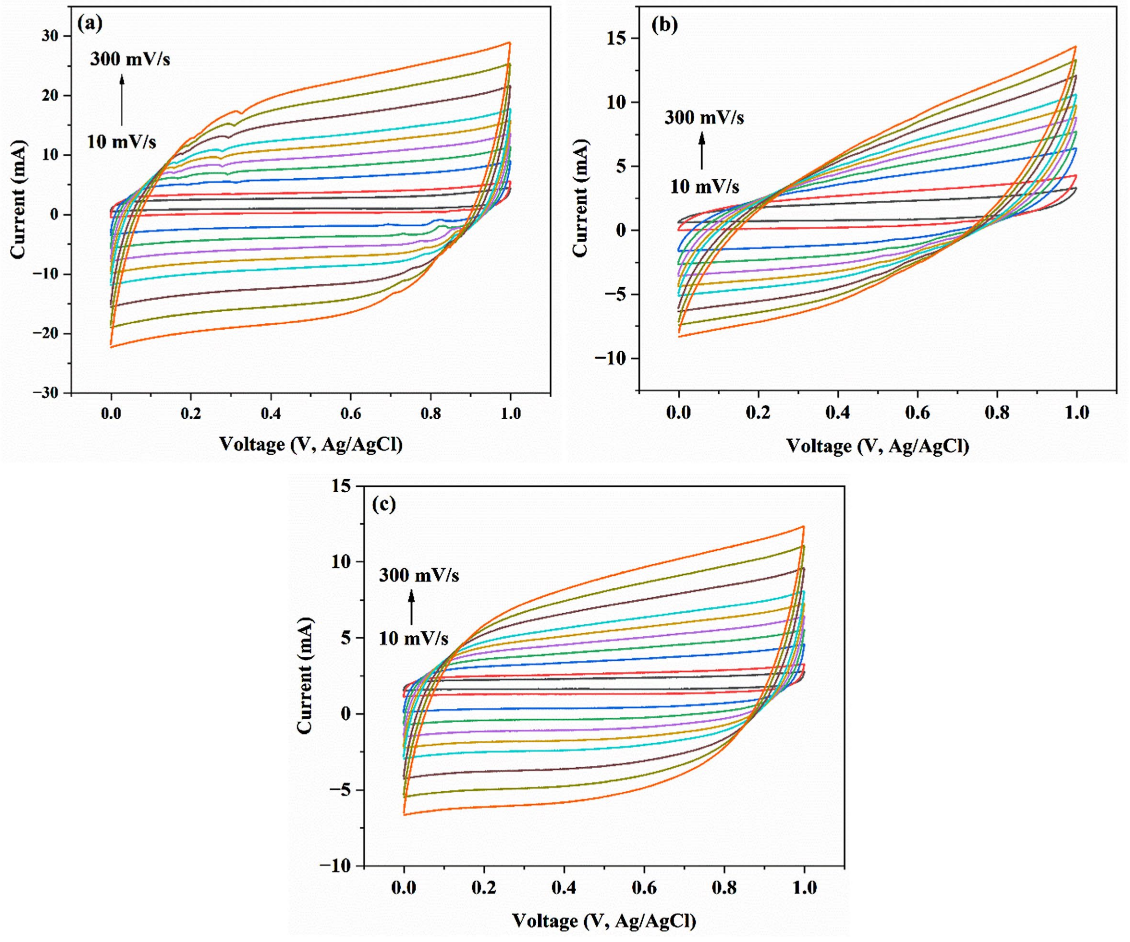

Figure 2. Cyclic voltammetric studies of (a) pure ball milled nsutite, (b) ball milled sample annealed at 350˚C, and (c) ball milled sample annealed at 580˚C.

between 0 V - 1 V at various scan rates such as 10 mV/s, 20 mV/s, 50 mV/s, 75 mV/s, 100 mV/s, 125 mV/s, 150 mV/s, 200 mV/s, 250 mV/s, and 300 mV/s. The specific capacitance from cyclic voltammetric studies was calculated using the formula,

$$C_{sp} = \left(\int I \cdot dV \right) \Big/ \left(\Delta V \times \vartheta \times m \right) \quad (1)$$

where, I is the current, ΔV is the potential range (V), ϑ represents the scan rate (mV/s) and m (*gram*) is the mass of the samples.

It can be seen from Figure 2 that the shapes of the cyclic voltammogram are almost rectangular, which indicate that the electrodes have charge-discharge capacity. Also, it can be seen from Figure 2 that the electrodes are stable even at a higher scan rate of 300 mV/s. Table 1 shows the specific capacitance of various nsutite samples, obtained from cyclic voltammetric studies. It can be seen from Table 1 that the maximum specific capacitance of 63.61 F/g was obtained for pure ball milled sample at a scan rate of 10 mV/s. At a scan rate of 100 mV/s, the specific capacitance for pure ball milled, ball milled samples annealed at 350˚C, and 580˚C was obtained as 49.29 F/g, 11.44 F/g, and 17.53 F/g, respectively.

Table 1. Specific capacitance of various nsutite materials obtained from cyclic voltammetric studies.

Material	Ball Milled Pure	Ball Milled 350˚C	Ball Milled 580˚C
Scan rate (mV/s)	Specific capacitance (F/g)	Specific capacitance (F/g)	Specific capacitance (F/g)
10	63.61	23.81	23.07
20	60.27	21.83	21.69
50	54.69	15.76	19.53
75	51.65	13.16	18.42
100	49.29	11.44	17.53
125	47.45	10.18	16.83
150	45.70	9.21	16.16
200	42.58	7.70	15.03
250	40.00	6.65	14.06
300	37.76	5.86	13.23

Figure 3 represents the charge-discharge studies of ball milled, ball milled samples annealed at 350˚C, and 580˚C. All charge-discharge studies were performed in air atmosphere and at room temperature in the voltage range of 0 V - 1 V and at current densities of 0.5 A/g, 1 A/g, and 2 A/g. The specific capacitance was calculated from the formula,

$$C_s = \left(I * \Delta t \right) \Big/ \left(m * \Delta V \right) \quad (2)$$

where, I is the current (A), t is the discharge time (*s*), m is the mass of the active material (*gram*), and ΔV is the voltage range (*V*). Table 2 summarizes specific capacitance of various nsutite samples. It can be seen from Figure 3 and Table 2 that the maximum specific capacitance was obtained for pure ball milled samples. The specific capacitance of pure ball milled sample was obtained as 36 F/g, 34 F/g, and 34 F/g at a current density of 0.5 A/g, 1 A/g, and 2 A/g, respectively. Upon annealing the ball milled nsutite at 350˚C, and 580˚C the specific capacitance was 18 F/g, and 11.3 F/g at current density of 0.5 A/g. In our previous studies it was reported that raw nsutite samples showed a specific capacitance of 13.05 F/g at 0.5 A/g current density [14]. In this study the ball milled nsutite samples showed significant improvement of capacitance, compared to our previous published results (14.65 F/g at 1 A/g) of pure nsutite materials [16]. This may be due to the reduced particle size, which results in increased surface area of the nsutite samples after milling.

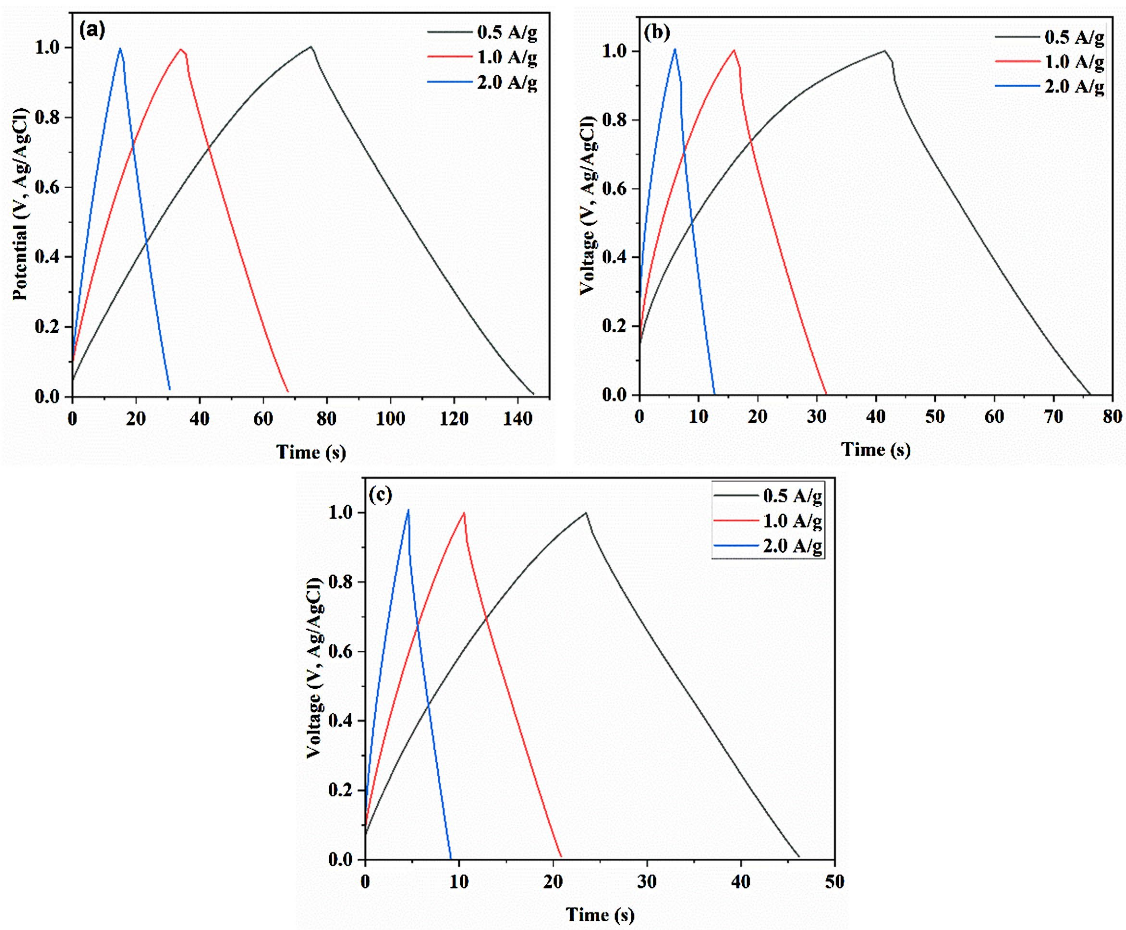

Figure 3. Charge-discharge studies of (a) pure ball milled nsutite, (b) ball milled sample annealed at 350˚C, and (c) ball milled sample annealed at 580˚C.

Table 2. Specific capacitance of various nsutite materials obtained from charge-discharge studies.

Material	Current Density (A/g)	Specific capacitance (F/g)
Ball Milled pure	0.5	36
	1	34
	2	34

Continued

Ball Milled 350˚C	0.5	18
	1	16
	2	14
Ball Milled 580˚C	0.5	11.3
	1	10.3
	2	9.2

4. Conclusion

It can be seen that ball milled nsutite materials can be used for supercapacitor applications. The specific capacitance of ball milled, ball milled samples annealed at 350˚C, and 580˚C was found to be as 34 F/g, 16 F/g, and 10.3 F/g at a current density of 1 A/g. On the other hand, cyclic voltammetric studies confirm the electrochemical behavior of nsutite materials and stabilities of the electrodes at a higher scan rate of 300 mV/s. More investigation is required to improve the electrochemical properties of nsutite materials to obtain inexpensive, environmentally friendly, and abundant supercapacitor materials.

Data Availability Statement

Data sets generated during the current study are available from the corresponding author on reasonable request.

CRediT Authorship Contribution Statement

Rahul Singhal: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Resources, Software, Supervision, Writing—original draft, Writing—review & editing, **Michael Gammon:** Data curation, Formal Analysis, Investigation, Writing—original draft, **Lekan J. Oyelola:** Data curation, Formal Analysis, Investigation, **Noah Lee:** Data curation, Formal Analysis, **Tess E. Masi:** Data curation, Formal Analysis, **Manika Chaudhary:** Data curation, Formal Analysis, Writing-Original draft, **Vikhyat Sahi:** Formal Analysis, writing—review & editing, **Peter K. LeMaire:** Conceptualization, Resources, Writing—review & editing.

Funding

CSCU AAUP Faculty Research Grant.

Acknowledgements

The authors acknowledge 2023 CSCU AAUP Faculty Research Grant received in support of this project.

Conflicts of Interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

References

[1] Wu, J., Wu, Y., Wang, L., Ye, H., Lu, J. and Li, Y. (2024) Challenges and Advances in Rechargeable Batteries for Extreme-Condition Applications. *Advanced Materials*, **36**, Article 2308193. https://doi.org/10.1002/adma.202308193

[2] Chen, T., Banda, H., Wang, J., Oppenheim, J.J., Franceschi, A. and Dincă, M. (2024) A Layered Organic Cathode for High-Energy, Fast-Charging, and Long-Lasting Li-Ion Batteries. *ACS Central Science*, **10**, 569-578. https://doi.org/10.1021/acscentsci.3c01478

[3] Wiston, B.R., Tewatia, S. and Ashok, M. (2023) Insights into Coprecipitated Cerium Oxide/Hydroxide-Nickel Hydroxide Composite for High Efficacy Supercapacitors. *Materials Today Sustainability*, **21**, Article 100291. https://doi.org/10.1016/j.mtsust.2022.100291

[4] Shi, C., Cao, H., Li, S., Guo, L., Wang, Y. and Yang, J. (2022) Flexible Nickel Cobalt Metal-Organic Frameworks/Reduced Graphene Oxide Hybrid Film for High-Performance Supercapacitors. *Journal of Energy Storage*, **54**, Article 105270. https://doi.org/10.1016/j.est.2022.105270

[5] Singhal, R., Chaudhary, M., Tyagi, S., Tyagi, D., Bhardwaj, V. and Singh, B.P. (2022) Recent Developments in Transition Metal-Based Nanomaterials for Supercapacitor Applications. *Journal of Materials Research*, **37**, 2124-2149.

[6] Xia, P., Wang, Q., Wang, Y., Quan, W., Jiang, D. and Chen, M. (2019) Hierarchical $NiCO_2O_4$@$Ni(OH)_2$ Core-Shell Nanoarrays as Advanced Electrodes for Asymmetric Supercapacitors with High Energy Density. *Journal of Alloys and Compounds*, **771**, 784-792. https://doi.org/10.1016/j.jallcom.2018.08.163

[7] Babu, I.M., William, J.J. and Muralidharan, G. (2019) Ordered Mesoporous CO_3O_4/CMC Nanoflakes for Superior Cyclic Life and Ultra High Energy Density Supercapacitor. *Applied Surface Science*, **480**, 371-383. https://doi.org/10.1016/j.apsusc.2019.02.215

[8] Li, S., Xie, Y., Zhou, J., Wang, L., Wang, M., Wang, L., *et al.* (2023) Morphologically Controlled Synthesis of $MnCO_2O_4$ Arrays on ACF as Binder-Free Electrode for Asymmetric Supercapacitor. *Materials Research Bulletin*, **167**, Article 112441. https://doi.org/10.1016/j.materresbull.2023.112441

[9] Cai, W., Lai, T., Lai, J., Xie, H., Ouyang, L., Ye, J., *et al.* (2016) Transition Metal Sulfides Grown on Graphene Fibers for Wearable Asymmetric Supercapacitors with High Volumetric Capacitance and High Energy Density. *Scientific Reports*, **6**, Article No. 26890. https://doi.org/10.1038/srep26890

[10] Kumar, Y.A., Rao, S.S., Punnoose, D., Tulasivarma, C.V., Gopi, C.V.V.M., *et al.* (2017) Influence of Solvents in the Preparation of Cobalt Sulfide for Supercapacitors. *Royal Society Open Science*, **4**, Article 170427. https://doi.org/10.1098/rsos.170427

[11] Adalati, R., Sharma, M., Sharma, S., Kumar, A., Malik, G., Boukherroub, R., *et al.* (2022) Metal Nitrides as Efficient Electrode Material for Supercapacitors: A Review. *Journal of Energy Storage*, **56**, Article 105912. https://doi.org/10.1016/j.est.2022.105912

[12] Singhal, R., Sadowski, T., Chaudhary, M., Tucci, R.V., Scanley, J., Patel, R., *et al.* (2024) Optimization of Manganese Dioxide-Multiwall Carbon Nanotube Composite Electrodes for Supercapacitor Applications. *Materials Science for Energy Technologies*, **7**, 228-236. https://doi.org/10.1016/j.mset.2023.12.001

[13] Li, L., Hu, Z.A., An, N., Yang, Y.Y., Li, Z.M. and Wu, H.Y. (2014) Facile Synthesis of MnO_2/CNTs Composite for Supercapacitor Electrodes with Long Cycle Stability. *The Journal of Physical Chemistry C*, **118**, 22865-22872. https://doi.org/10.1021/jp505744p

[14] Post, J.E. (1999) Manganese Oxide Minerals: Crystal Structures and Economic and Environmental Significance. *Proceedings of the National Academy of Sciences*, **96**, 3447-3454. https://doi.org/10.1073/pnas.96.7.3447

[15] Soulamidis, G., Stouraiti, C., Kourmousi, M., Tzevelekidis, P., Charalampous, E. and Mitsopoulou, C.A. (2023) Structural and Electrochemical Characterization of Natural Manganese Oxides for Energy Storage Applications. *Materials Proceedings*, **15**, Article 64. https://doi.org/10.3390/materproc2023015064

[16] Singhal, R., Lembeck, J., LeMaire, P.C.K., Pereira, D. and LeMaire, P.K. (2021) Physical and Electrochemical Characterization of Nsutite. *American Journal of Analytical Chemistry*, **12**, 440-445. https://doi.org/10.4236/ajac.2021.1211027

[17] Zwicker, W.K., Groeneveld Meijer W.O.J. and Jaffe, H.W. (1962) Nsutite—A Widespread Manganese Oxide Mineral. *American Mineralogist*, **47**, 246-266.

[18] Faulring, G.M. (1965) Unit Cell Determination and Thermal Transformation of Nsutite. *The American Mineralogist*, **50**, 170-179.