

Electrochemical impedance and dielectric spectroscopy study of TiO₂-nanofilled PEO/PVP/NaIO₄ ionic polymer electrolytes

Y. G. Marinov^{1*}, G. B. Hadjichristov¹, T. E. Vlachov¹, H. K. Koduru^{2,3}, N. Scaramuzza³

¹Georgi Nadjakov Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee Blvd., BG-1784 Sofia, Bulgaria

²Department of Physics, Madanapalle Institute of Technology & Science (MITS), Madanapalle, Andhra Pradesh, IN-517325, India

³Dipartimento di Fisica, Università degli Studi della Calabria, Via P. Bucci, Cubo 33B, Rende (CS), IT-87036, Italy

Received November 08, 2019; Accepted January 03, 2020

We have experimentally investigated the ion-conducting and dielectric properties of nanocomposite ion-conductive polymer electrolytes based on two-polymer blend of poly(ethylene oxide) (PEO) and polyvinyl pyrrolidone (PVP), with added sodium metaperiodate (NaIO₄) at concentration of 10 wt%. The polymer-ion complexes PEO/PVP/NaIO₄ are doped with small amount (up to 3 wt%) TiO₂ nanoparticles of average size ~ 10 nm. Chemically-stable free-standing thin films (150 μm) of the synthesized PEO/PVP/NaIO₄/TiO₂ solid-state polymer electrolyte material are formed by using conventional solution-cast technique. The electrical and dielectric properties of these nanocomposites are studied by complex electrical impedance and dielectric spectroscopy over the frequency range 1 Hz – 1 MHz. The ionic conductivity of TiO₂-nanofilled PEO/PVP/NaIO₄/TiO₂ is determined as dependent on the concentration of the included TiO₂ nanoparticles. The obtained results indicate that both the Na⁺-ion conductivity and the dielectric function of PEO/PVP/NaIO₄/TiO₂ nanocomposite electrolytes are enhanced upon addition of TiO₂ nanoparticles. Thus, the produced NaIO₄ salt-complexed TiO₂-nanofilled ionic polymer electrolytes are attractive for use in sodium ion secondary batteries, electrochemical applications, as well as in organic electronics.

Keywords: conductivity; electrical impedance spectroscopy; dielectric spectroscopy.

INTRODUCTION

In view of the outstanding technological achievements in the multidisciplinary scientific & industrial fields, the polymer nanocomposite electrolytes (NCPEs) have been gaining vital significance owing to their unique useful properties [1]. Various nano-size inorganic fillers (such as zinc oxide, alumina, titania, silica, graphene oxide, MgO, MgAl₂O₄, γ-LiAlO₂) have been employed to fabricate NCPEs having improved properties [2–10]. Thus, one can even obtain multifunctional nanocomposite materials having versatile applications. Generally, the incorporation of proper nanoparticles (NPs) into suitable polymer matrix may substantially improve the electrical performance of the resultant polymer-based nanocomposite without sacrificing the mechanical strength of the material. In fact, this effect in polymer nanocomposites occurs due to specific interfacial interactions between the included NPs and polymer chains. In polymer nanocomposites the role of the interface is related to a fundamental length-scale in the order of the radius of gyration of the polymer chains. As a result, synergistic interactions arise in the ‘nanoscopically confined interfacial nanocomposite matrix’ and contribute to

the enhancement of the segmental mobility, electrical and mechanical properties. The same effect of interfacial interactions in nanometer ranges between polymer chains and inorganic nanofillers with high surface area takes place in NCPEs. The nanofiller-polymer interactions and possible conformational changes in the host polymer lead to increased mobility of mobile ions in amorphous phase regions in the polymer matrix of NCPEs [1,6,10–12].

Solid polymer electrolytes based on poly(ethylene oxide) (PEO) and complexed with various alkali metal salts have been recognized as permissible systems to be employed in solid state rechargeable batteries and polymer electronics [13,14]. Substantial research efforts are currently in progress to enhance the properties of the Na-ion-conducting polymer electrolytes and to search of novel Na-ion-conductor materials in order to satisfy the requirements for efficient electrolyte function and for other advanced applications. Various Na salt-complexed PEO-based polymer electrolytes intended to be used for Na⁺ battery and other applications have been reported [15–18]. Also, there are numerous investigations on Na⁺-ion-conducting polymer electrolyte systems based on blends of PEO with the high-amorphous polymer polyvinyl pyrrolidone (PVP), as complexed with

* To whom all correspondence should be sent.
E-mail: ymarinov@issp.bas.bg

various sodium salts [19–23]. The blending of PEO with PVP reduces the degree of crystallinity of polymer matrix, thus enhancing the ionic conductivity. Thus, PEO/PVP complexed with the ionic compound sodium metaperiodate (NaIO₄) showed ion-electrolytic properties attractive for electrochemical and other applications [22,23].

The next step is the reinforcement of these polymer electrolyte systems by doping with nano-sized material in order to properly modify their properties and further enhance their ion conductivity. In the present work, our investigations are focused on PEO/PVP blend based electrolyte system complexed with the ionic compound NaIO₄ and doped with nano-sized TiO₂. In particular, TiO₂ NPs were incorporated at concentration of 1, 2 and 3 wt% in PEO(70 wt%)/PVP(30 wt%) polymer blend complexed with 10 wt% NaIO₄. The effect of the inclusion of TiO₂ NPs in the PEO/PVP/NaIO₄ on the ion (Na⁺) conductivity and dielectric properties of the resulting NCPEs was studied by means of electrochemical impedance spectroscopy (EIS) and dielectric spectroscopy.

EXPERIMENTAL

PEO and PVP of molecular weights of 5×10^6 and 3.6×10^5 , respectively, were procured from Aldrich and employed without any further purification to prepare the polymer blend electrolytes. The molecular structures of both polymers are shown in Fig. 1. The salt Sodium metaperiodate (NaIO₄) and Titanium dioxide (TiO₂ nanopowder), both from Sigma Aldrich, were used as additives. The mean size of TiO₂ NPs was ca. 10 nm (given from manufacturer).

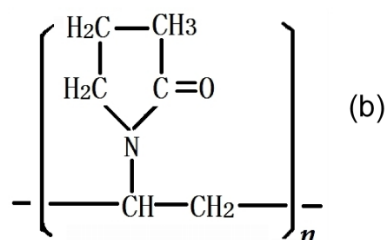
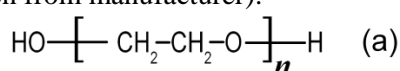


Fig. 1 Molecular structure of: (a) poly(ethylene oxide) (PEO); (b) polyvinyl pyrrolidone (PVP)

All substances were dissolved in methanol with high purity from Aldrich. First, PEO and PVP polymers were individually dissolved in methanol, then appropriate amounts of PEO and PVP solutions (w/w ratio 70% : 30% in present experiments) were mixed (Fig. 2a), followed by mechanical stirring at room temperature for 15

hours to obtain uniform mixture. In the meanwhile, 10 wt% of NaIO₄ salt was separately dissolved in methanol and this solution was added to the prepared viscous PEO/PVP polymer solution in order to be produced PEO/PVP/NaIO₄ polymer complex [22]. Separately, the powder of nano-sized TiO₂ was homogeneously dispersed in methanol. This solution was sonicated for 30 minutes and then added to PEO/PVP/NaIO₄ solution to prepare PEO/PVP/NaIO₄/TiO₂ - nanocomposite polymer blend solution with complexed salt ions and incorporated TiO₂ nanofillers (Fig. 2b). Technologically, this was done by drop-by-drop method. The concentration of the salt NaIO₄ in the PEO/PVP/NaIO₄/TiO₂ nano-composite blend solutions was kept at 10 wt%, whereas the TiO₂ NPs were included in the polymer blend at three concentrations: 1, 2 and 3 wt%.

Chemically-stable free-standing thin films (150 μm) of the synthesized PEO/PVP/NaIO₄/TiO₂ salt-complexed polymer blend material with excellent dimensional stability are formed by using solution casting of nanocomposite blend solution. The as-prepared viscous nanocomposite blend solutions were poured into polypropylene dishes and the solvent (methanol) was allowed to evaporate slowly at room temperature to obtain free-standing polymer electrolyte films of thickness of 150 μm. The final products of polymer blend electrolyte films were dried at 45°C under vacuum at 10⁻³ mbar pressure to remove traces of methanol solvent. Then the films were kept in desiccators filled with silica gel desiccants for several hours before being characterized, to avoid any traces of moisture.

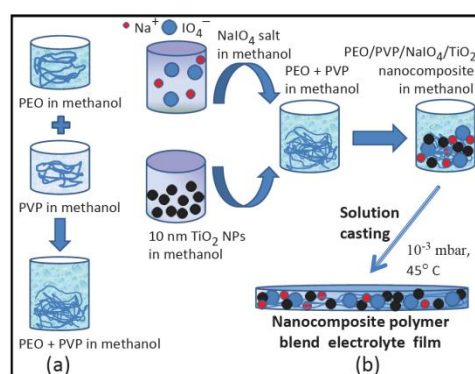


Fig. 2. A scheme showing the preparation of PEO/PVP/NaIO₄/TiO₂ solid-state nanocomposite polymer electrolytes.

Methods

For ionic conductivity measurements, the produced solid polymer electrolyte films were sandwiched between two copper electrodes with diameter 1 cm. The conductivity studies were

carried out at room temperature by EIS. Frequency spectra of complex electrical impedance were taken in the range 1 Hz – 1 MHz using potentiostat /galvanostat/ impedance-meter BioLogic SP-200. During these measurements, the voltage amplitude applied to the polymer electrolyte films was fixed at 0.5 V_{RMS}.

The ionic conductivity (σ) of the samples was calculated according to the relation

$$\sigma = t/(A \cdot R_B), \quad (1)$$

where t and A are the thickness of the sample and the area of the electrodes (i.e., the electrically-active area of the electrolyte film), respectively. R_B is the bulk resistance of the samples. This quantity is determined through impedance spectra.

Dielectric spectra of NCPEs PEO/PVP/NaIO₄/TiO₂ were obtained from the real (Z') and imaginary (Z'') parts of complex electrical impedance. In alternating-current electric field, the relative permittivity is a complex function and is defined by $\epsilon^* = \epsilon' - j \epsilon''$. Real (ϵ') and imaginary (ϵ'') parts of dielectric permittivity were calculated using the relations [24]:

$$\epsilon' = -\frac{Z''}{\omega C_0 (Z'^2 + Z''^2)} \quad (2)$$

and

$$\epsilon'' = \frac{Z'}{\omega C_0 (Z'^2 + Z''^2)}, \quad (3)$$

where C_0 is the vacuum capacitance ($C_0 = \epsilon_0 A/t$; $\epsilon_0 = 8.85 \times 10^{-12}$ F/m is the permittivity of free space). The angular frequency is given as $\omega = 2\pi f$, where f is the frequency of applied electric field.

RESULTS AND DISCUSSION

Fig. 3 shows the complex impedance plane diagrams, the Nyquist plots (Z' vs Z'') for the studied PEO/PVP/NaIO₄/TiO₂ NCPEs, as obtained from their frequency spectra of complex electrical impedance measured by EIS. For all our samples, the Nyquist plots demonstrate a well-defined semicircle at intermediate frequencies, which can be explained by parallel combination of bulk resistance and bulk capacitance [25].

The ionic conductivity (σ) of the PEO/PVP/NaIO₄/TiO₂ was calculated by Eq. (1). The bulk resistance R_B was obtained from the intercept of the semicircle with the real axis (Z'). The room-temperature σ estimated by this way for PEO/PVP/NaIO₄(10 wt%) electrolyte film was 1.57×10^{-7} S/cm [22]. As a result of the inclusion of 1 wt% of TiO₂ NPs, the value of σ of Na⁺-conducting NCPE becomes about three times higher than σ of the undoped PEO/PVP/NaIO₄ electrolyte (Fig. 4).

By increasing concentration of TiO₂ nanofillers, R_B is decreased (Fig. 3). Accordingly, at 2 wt% TiO₂ the increase in σ of TiO₂-doped PEO/PVP/NaIO₄ is about six times, and at 3 wt% TiO₂ – more than 12 times (Fig. 4).

The enhancement of conductivity as a result of inclusion of TiO₂ NPs is relevant to reduction in crystallinity of the polymer chains in blend polymer electrolyte. Certainly, this improves the sodium ion transport and hence improves the ionic conductivity of the polymer electrolyte [26,27].

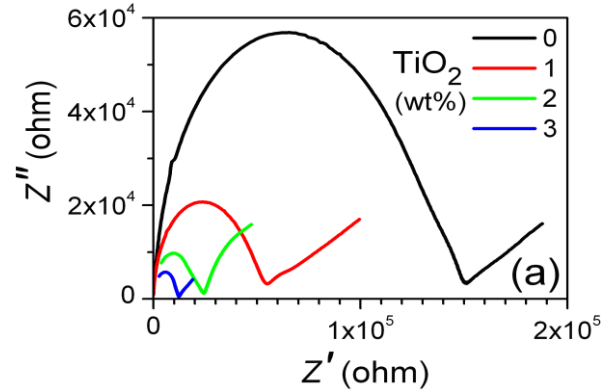


Fig. 3. Nyquist complex impedance plots for PEO/PVP/NaIO₄/TiO₂ NCPE system composed with TiO₂ NPs at concentrations 1, 2 and 3 wt%.

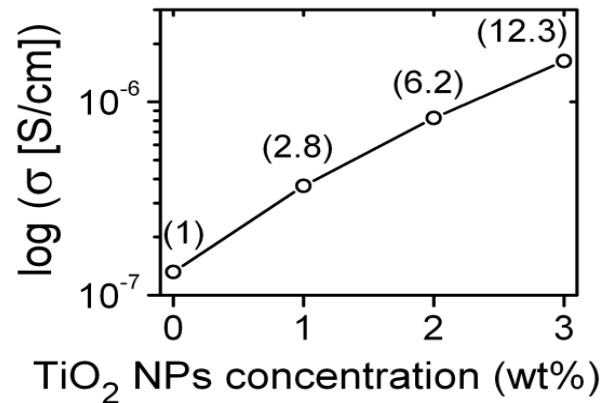


Fig. 4. Room-temperature ionic conductivity (σ) of the studied PEO/PVP/NaIO₄/TiO₂ NCPEs vs the concentration of TiO₂ NPs. The numbers in parentheses indicate the conductivity enhancement factors due to TiO₂ inclusion.

This effect occurs due to high interfacial interactions between the organic moieties of both polymers and TiO₂ NPs [1]. Such interactions of doping NPs with the polymer chains lead to improvement in the amorphicity and flexibility of the polymer matrix [28] that leads to a further increase in segmental motion of the polymer chains in the amorphous domain, which supports the mobility enhancement of the charge carriers in flexible solid-like amorphous-rich polymer electrolytes, thus increasing their ionic conductivity

[1,6,29,30]. Note that because the TiO₂ NPs are inert additives, they do not provide and conduct ions by themselves. Such inactive (passive) NPs do not participate in the ionic conduction process (are not involved in the Na⁺ transport process). But the size and the characteristics of the TiO₂ nanofillers predetermine in a large extent the electrochemical properties of the PEO/PVP/NaIO₄/TiO₂ NCPE system.

Besides the ionic conductivity, the dielectric properties of the considered NCPE are also of interest because they determine the ability of this dielectric material to store electrical energy. The real part of complex dielectric permittivity ϵ' has the same significance as that of the ordinary dielectric constant of the material. This physical quantity is directly related to the energy that can be stored in the material during each charging cycle and returned to the electric field at the end of the cycle. Fig. 5 presents the dielectric behavior (the frequency spectra of the real and imaginary parts of dielectric function) of the studied electrolyte systems, as calculated by Eqs. (2) and (3). As seen from Fig. 5, the TiO₂-doped PEO/PVP/NaIO₄ exhibits an enhanced dielectric response in comparison to undoped electrolyte PEO/PVP/NaIO₄. Moreover, the dielectric permittivity of PEO/PVP/NaIO₄/TiO₂ NCPE is increased by increasing concentration of the TiO₂ nanofillers. It should be noted that this trend does not hold at higher frequencies (> 1 kHz). The explanation of such effect requires to perform various complementary measurements and additional analyses that is out of scope of the present work, such as, for example, the calculation of ion mobility in these systems as the percentage concentration of TiO₂ varies.

The observed increase in ϵ (Fig. 5) can be explained by the capability of TiO₂ NPs to do a dissociation of undissociated salt/ion aggregates into free ions (anions) in the polymer matrix of the considered solid polymer electrolyte [31,32]. This feature is related to the conductivity processes and it evidences that the conduction in polymer electrolytes takes place through charge migration of ions between coordinated sites of the polymer along with the segmental relaxation of polymer [33].

CONCLUSIONS

By inclusion of TiO₂ NPs with a size of ~ 10 nm, the ion-conducting and dielectric properties of PEO/PVP blend solid polymer electrolytes complexed with NaIO₄ salt are considerably changed. As a result from high interfacial interactions between polymer chains and the surface of TiO₂ nanoparticles, the TiO₂ nanofillers

lead to increase of Na⁺-ion conductivity of PEO/PVP/NaIO₄/TiO₂ NCPE system, as compared to undoped electrolyte PEO/PVP/NaIO₄.

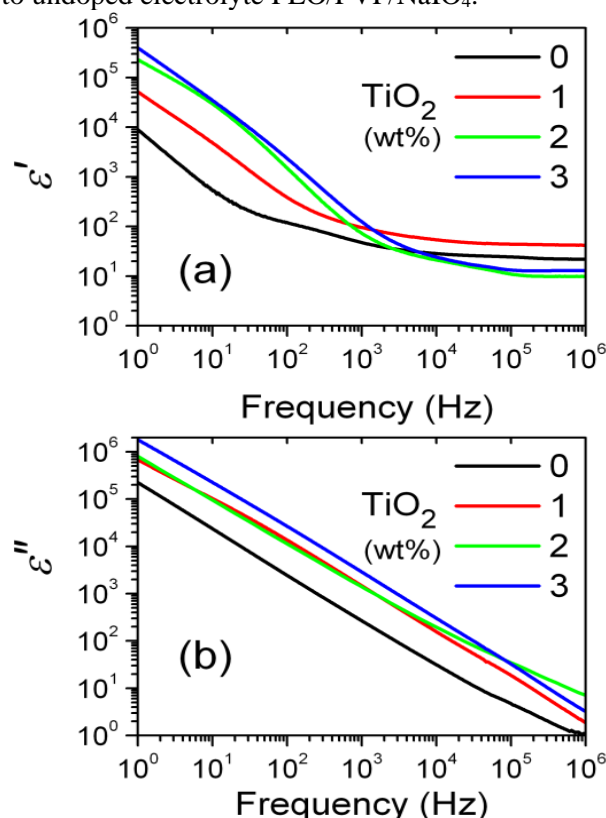


Fig. 5. (a) Frequency-dependent real (a) and imaginary (b) parts of dielectric function of PEO/PVP/NaIO₄/TiO₂ NCPEs containing 1, 2 or 3 wt% TiO₂ nanofillers. For the sake of comparison, data obtained for dielectric function of undoped PEO/PVP/NaIO₄ solid polymer electrolyte are also given.

It is demonstrated that the Na⁺-ion conductivity of PEO/PVP/NaIO₄/TiO₂ NCPEs is strongly (exponentially) enhanced with the addition of TiO₂ nanofillers when the concentration of these nanodopants is up to a level of 3 wt%. Further, in comparison to PEO/PVP/NaIO₄ electrolyte, the TiO₂-doped NCPE PEO/PVP/NaIO₄ considered here demonstrated enhanced dielectric permittivity due to increase of dissociated ions in the polymer blend matrix upon addition of TiO₂ nanofillers. Such modifications of electrical and dielectric properties characterize the PEO/PVP/NaIO₄/TiO₂ NCPE system as a promising ionic conductor, feasible to be applied in ionic devices including Na batteries, in electrochemical cells and in organic electronics. These results are encouraging to further investigate other interesting aspects regarding the electrical and dielectric properties of the produced NaIO₄ salt-complexed TiO₂-nanofilled ionic polymer electrolytes (work in progress).

Acknowledgements: Work supported by the European Regional Development Fund within OP

Y. Marinov et al.: Electrochemical impedance and dielectric spectroscopy study of TiO₂-nanofilled....
 “Science and Education for Smart Growth 2014-2020”, Project CoE “National Center of Mechatronics and Clean Technologies”, BG05M2OP001-1.001-0008-C01. This study was partially supported by the Bulgarian Ministry of Education and Science under the National Research Programme “Young scientists and postdoctoral students” approved by DCM # 577 / 17.08.2018

REFERENCES

1. S. A. Suthanthiraraj, M. Johnsi, *Ionics*, **23**, 1 (2016).
2. M. R. Johan, O. H. Shy, S. Ibrahim, S. M. M. Yassin, T. Y. Hui, *Solid State Ionics*, **196**, 41 (2011).
3. M. Yuan, J. Erdman, C. Tang, H. Ardebili, *RSC Adv.*, **4**, 59637 (2014).
4. J. H. Lee, C. H. Park, J. P. Jung, J. H. Kim, *J. Power Sources*, **298**, 14 (2015).
5. Y. Deng, C. Fang, G. Chen, *J. Power Sources*, **304**, 81 (2016).
6. H. K. Koduru, F. Scarpelli, Y. G. Marinov, G. B. Hadjichristov, P. M. Rafailov, I. K. Miloushev, A. G. Petrov, N. Godbert, L. Bruno, N. Scaramuzza, *Ionics*, **24** 3459 (2018).
7. M. S. Johnsi, S. A. Suthanthiraraj, *Macromolec. Research*, **26**, 100 (2018).
8. X. Zhang, X. Wang, S. Liu, Z. Tao, J. Chen, *Nano Research*, **11**, 6244(2018).
9. J. Sharma, S. Hashmi, *J. Polym. Compos.*, **40**, 1295 (2019).
10. H. K. Koduru, L. Bruno, Y. G. Marinov, G. B. Hadjichristov, N. Scaramuzza, *J. Solid State Electrochem.*, **23**, 2707 (2019).
11. F. Bertasi, K. Vezzu, G. A. Giffin, T. Nosach, P. Sidens, S. Greenbaumd, M. Vittadello, V. D. Noto, *Int. J. Hydrog. Energy*, **39**, 2884 (2014).
12. K. N. Kumar, K. Saijyothi, M. Kang, Y. C. Ratnakaram, K. H. Krishna, D. Jin, Y. M. Lee, *Appl. Phys. A*, **122**, art. 698 (2016).
13. J. M. Tarascon, M. Armand, *Nature*, **414**, 359 (2001).
14. S. K. Kim, D. G. Kim, A. Lee, H. S. John, J. J. Wie, N. A. Nguyen, M. E. Mackay, J. C. Lee, *Macromolecules*, **45**, 9347(2012).
15. A. M. Stephan, K. S. Nahm, *Polymer*, **47**, 5952 (2006).
16. S. Mohapatra, A. Thakur, R. N. P. Choudhary, *Ionics*, **14**, 255 (2008).
17. M. Patel, K. G. Chandrappa, A. J. Bhattacharyya, *Solid State Ionics*, **181**, 844 (2010).
18. K. Vignarooban, R. Kushagra, A. Elango, P. Badami, B. E. Mellander, X. Xu, T. G. Tucker, C. Nam, A. M. Kannan, *Int. J. Hydrogen Energy*, **41**, 2829 (2016).
19. K. K. Kumar, M. Ravi, Y. Pavani, S. Bhavani, V. V. R. N. Rao, *Physica B: Condens. Matter*, **406**, 1706 (2011).
20. K. K. Kumar, M. Ravi, Y. Pavani, S. Bhavani, V. V. R. N. Rao, *J. Non-Crystalline Solids*, **358**, 3205 (2012).
21. K. K. Kumar, M. Ravi, Y. Pavani, S. Bhavani, A. K. Sharma, V. V. R. N. Rao, *J. Membr. Sci.*, **454**, 200 (2014).
22. H. K. Koduru, L. Marino, F. Scarpelli, A. G. Petrov, Y. G. Marinov, G. B. Hadjichristov, M. T. Iliev, N. Scaramuzza, *Curr. Appl. Phys.*, **17**, 1518 (2017).
23. G. B. Hadjichristov, Tz. E. Ivanov, Y. G. Marinov, H. K. Koduru, N. Scaramuzza, *Physica Status Solidi (A): Appl. Mater. Sci.*, **216**, 1800739 (2019).
24. K. Deshmukh, S. Sankaran, B. Ahamed, K. K. Sadasivuni, K. S. K. Pasha, D. Ponnamma, P. S. R. Sreekanth, K. Chidambaram, in: Spectroscopic Methods for Nanomaterials Characterization, S. Thomas, R. Thomas, A. K. Zachariah, R. K. Mishra (eds), vol. 2, Elsevier, Amsterdam, 2017, p. 248.
25. E. Barsoukov, J. R. Macdonald (eds), Impedance Spectroscopy: Theory, Experiment, and Applications, Wiley Intescience, Hoboken, New Jersey, 2005.
26. D. Carlier, J. H. Cheng, R. Berthelot, M. Guignard, M. Yoncheva, R. Stoyanova, B. J. Hwang, C. Delmas, *Dalton Transactions*, **40**, 9306 (2011).
27. Y. C. Lin, J. H. Cheng, M. Venkateswarlu, F. M. Wang, R. Santhanam, B. J. Hwang, *J. Chin. Chem. Soc.*, **59**, 1250 (2012).
28. C. W. Lin, C. L. Hung, M. Venkateswarlu, B. J. Hwang, *J. Power Sources*, **146**, 397 (2005).
29. H. K. Koduru, M. T. Iliev, K. Kondamareddy, D. Karashanova, T. Vlachov, X. Z. Zhao, and N. Scaramuzza, *J. Phys. Conf. Ser.*, **764**, 012006 (2016).
30. H. K. Koduru, K. K. Kondamareddy, M. T. Iliev, Y. G. Marinov, G. B. Hadjichristov, D. Karashanova, N. Scaramuzza, *J. Phys. Conf. Ser.*, **780**, 012006 (2017).
31. D. Kumar, S. A. Hashmi, *Solid State Ionics*, **181**, 416 (2010).
32. A. Bhide, K Hariharan, *Polym. Int.*, **57**, 523 (2008).
33. M. A. L. Nobre, S. Langfredi, *J. Phys. Chem. Solids*, **62**, 1999 (2001).