

Dielectric studies of composite paper reinforced with polypyrrole coated pulp fibers from wasted egg holders

Aamir Razaq,¹ Muhammad Idrees,¹ Adeel Malik,¹ Nafeesa Mushtaq,² Muhammad Nadeem,³ Irshad Hussain,⁴ Muhammad Yar²

¹Department of Physics, COMSATS Institute of Information Technology, Lahore 54000, Pakistan

²Interdisciplinary Research Centre in Biomedical Materials, COMSATS Institute of Information Technology, Lahore 54000, Pakistan

³EMMG, Physics Division, PINSTECH, P. O. Nilore, Islamabad, Pakistan

⁴Department of Chemistry, SBA School of Science and Engineering (SSE), Lahore University of Management Sciences (LUMS), DHA, Lahore Cantt 54792, Pakistan

Correspondence to: A. Razaq (E-mail: aamirrazaq@ciitlahore.edu.pk)

ABSTRACT: Development of thin, flexible, light-weight, renewable, low-cost, and environmentally friendly electrode materials are highly feasible in era of modern disposable electronic technology. This article presents the synthesis and dielectric studies of polypyrrole (PPy) coated pulp fibers, directly collected from wasted egg holder's tray. PPy coated pulp fibers converted into compact sheet for the development of potential renewable and low-cost electrode materials. The morphology, chemical structure, and thermal stability of naked and PPy coated pulp fibril sheets were investigated by scanning electron microscopy (SEM), Fourier transform infrared (FTIR) and thermogravimetric analysis (TGA), respectively. PPy coated pulp fibers revealed better thermal stability and compactness of sheet morphology. Impedance measurements showed a high value of dielectric constant of 1.15×10^6 at 0.5 Hz and conductivity of 7.45×10^{-4} S/cm at room temperature for PPy coated pulp fibril sheet. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42422.

KEYWORDS: biopolymers & renewable polymers; cellulose and other wood products; coatings; conducting polymers; dielectric properties

Received 10 February 2015; accepted 27 April 2015

DOI: 10.1002/app.42422

INTRODUCTION

Conducting polymers (CPs) coated on light-weight, low-cost, environment friendly, and flexible substrates are in high demand for disposable electronics and energy storage devices. First conducting polymer (CP), was investigated in mid-19th century by Henry Letheby *et al.*¹ Subsequently Heeger, MacDiarmid, and Shirakawa reported high conductivity in oxidized iodine-doped polyacetylene² and was awarded Nobel Prize (Chemistry) in 2000 for development of CPs. This magical discovery led to extensive research for the use of CPs in several versatile applications including molecular electronics,³ biomedical sensors,⁴ chemical sensors,⁵ thin film transistors,⁶ electrochromic devices,⁷ light emitting diodes (LEDs),⁸ electromagnetic shielding,⁹ and energy storage devices.^{10–15}

Among CPs family, polypyrrole (PPy) has wide applications due to its efficient redox switching potential, easier synthesis and relatively high electric conductivity. In general, chemical synthesis of PPy is preferred over electrochemical method for bulk

production. Several insulating and electrically conducting substrates are used for coating of PPy, e.g., stainless steel,¹⁶ gold-coated PVDF membrane,¹⁷ carbon paper,¹⁸ V₂O₅ nanoribbons,¹⁹ graphene,²⁰ and CNT.^{21–26} Natural fibrous polymers are also attractive candidates as suitable substrates for PPy coating due to their organic nature and compatibility, light-weight, mechanical flexibility, and environmental friendly characteristics. Consequently several natural fiber based substrates have been investigated for PPy coating, e.g., daily used nylon Lycra fabric,²⁷ common printing paper,²⁸ cellulose nanocrystals extracted from cotton,²⁹ cladophora nanocellulose,³⁰ and nanocellulose from wood.³¹ Recently, the use of waste materials is being highly encouraged because it leads to clean and green environment. In this regard, waste pulp fibers could be ideal candidate for PPy coating to prepare cost-effective, conductive and electroactive paper composites for high-tech applications.

Pulp (most abundant raw material) consists of lignocellulose fibers and is obtained by separating from wood, waste paper,

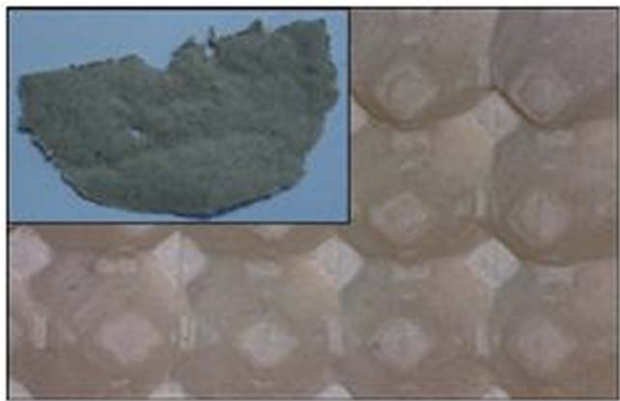


Figure 1. Optical image of raw waste paper pulp with an inset image of bleached pulp sheet. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and many other fibril sources. Commonly chemical pulping,³² mechanical pulping,³³ thermo-mechanical pulping,³⁴ and chemithermomechanical pulping³⁵ methods are used to prepare pulp from wood, whereas deinked pulping method³⁶ is quite commonly applied to isolate pulp from used papers. Recycled pulp is utilized in the production of papers, boards, textile, and cellulose derivatives.

The determination of the physical parameters such as electrical resistance and capacitance of microstructural phases play a pivotal role in understanding the macroscopic properties of the materials.³⁷ This study presents the synthesis of conductive composite paper (pulp/PPy) reinforced by coating of PPy on pulp fibers obtained from wasted egg holders. Impedance spectroscopy is particularly employed to investigate the dielectric behavior of different phases in synthesized composition. According to our literature survey, present work is the first attempt to coat the PPy on directly collected pulp fibers from wasted egg holders, and its impedance investigations.

MATERIALS AND METHODS

Chemicals and Reagents

Raw waste paper pulp (as shown in Figure 1) was obtained from wasted egg tray holders. Pyrrole, sodium hypochlorite (NaOCl), iron (III) chloride, and hydrochloric acid were used as supplied by Merck.

Synthesis of Paper Sheets

Preparation of Bleached Pulp Sheet. Grounded raw cellulose (1.5 g) was dispersed in 20% NaOCl solution (200 mL) for 2 h at room temperature. The bleached pulp was filtered, partially dried under vacuum and compressed for overnight.

Preparation of Pulp/PPy Sheet. Bleached pulp fibers (1 g) were dispersed in 50 mL distilled water at room temperature. Pyrrole solution was prepared by dissolving pyrrole (0.022 mol, 1.5 mL) and one drop of tween 80 in 0.5M HCl (50 mL). Then pulp slurry was mixed with pyrrole solution and stirred for 5 min at RT. Subsequently, FeCl₃ solution prepared by dissolving FeCl₃ (0.048 mol, 12.857 g) in 100 mL of 0.5M HCl, was gradually added to the pulp-pyrrole solution and kept under stirring for 40 min at RT to complete the polymerization reaction. The

pulp-polyrrole slurry was filtered, washed with HCl solution (0.5M, 2.5L), and compressed overnight to achieve surface smoothness of sheets.

Characterization

Surface characterization of bleached sheet and PPy coated pulp sheet was performed by field emission scanning electron microscope (FESEM, JSM 7500F by JEOL) using secondary electron detector without further conductive coating on either of these sheets.

The chemical structure and intermolecular interactions between composites of raw pulp, bleached pulp, and PPy coated pulp sheets were investigated by Fourier transform infrared (FTIR) spectroscopy. FTIR spectra of samples were recorded with Thermo Scientific Nicolet 8700 FTIR spectrometer at 8 cm⁻¹ resolution in averaging of 256 scans. The spectra were collected over 4000–400 cm⁻¹ range.

Simultaneous thermogravimetric (TG) of all sheets were carried out from ambient temperature to 800°C at a heating rate of 10°C/min under nitrogen atmosphere using SDT Q600 TG/DTA thermogravimetric analyzer. Dried empty platinum pan was used as a reference material, and platinum sample holder was employed for taking curves. In order to ensure the uniformity of temperature of the sample and good reproducibility, small amounts (1–3 mg) were taken.

The ac electrical properties in a wide frequency range (0.5–10 MHz) were measured at room temperature using Alpha N Impedance analyzer (Novo control, Germany). The contacts were made on opposite sides of sheet using silver paste, and subsequently cured under a tungsten lamp for 3 h. Leads were carefully checked to ensure the absence of any irrelevant resistive or capacitive coupling in the measured frequency range.

RESULTS AND DISCUSSION

Figure 2 shows the SEM images of (a) bleached pulp (b) and PPy coated pulp fibril sheets. Interlocking fibril morphology of bleached pulp sheet, can be seen in Figure 2(a) within diameter range of 50–100 μm. Figure 2(b) revealed the cauliflower like structure of PPy coated pulp fibers. It can observe from Figure 2(b) that fibers retained their structure after coating with PPy. The inset in Figure 2(b) displays the compact sheet morphology of pulp/PPy composite sheet.

The functional groups present in the wasted paper pulp were identified by FTIR as shown in Figure 3. The FTIR spectrum of raw pulp shows a band at 1052 cm⁻¹, which is attributed to C–O ring stretching. The second absorption at 1680 cm⁻¹ corresponds to amide I band. The absorption peak at 2930 cm⁻¹ is due to C–H stretching vibrations peaks. The strong absorption peak at 3390 cm⁻¹ is due to O–H/N–H stretching vibration of alcohols and amines/amides, respectively. These peaks suggested the presence of cellulose materials and some amount of proteins.³⁸ In observation, no significant difference appeared between FTIR spectrum of raw pulp and bleached pulp sheets which actually indicates no effect on chemical nature of raw pulp. The FTIR spectrum of PPy coated material shows the absorption pattern which is characteristic of PPy.³⁹ For example,

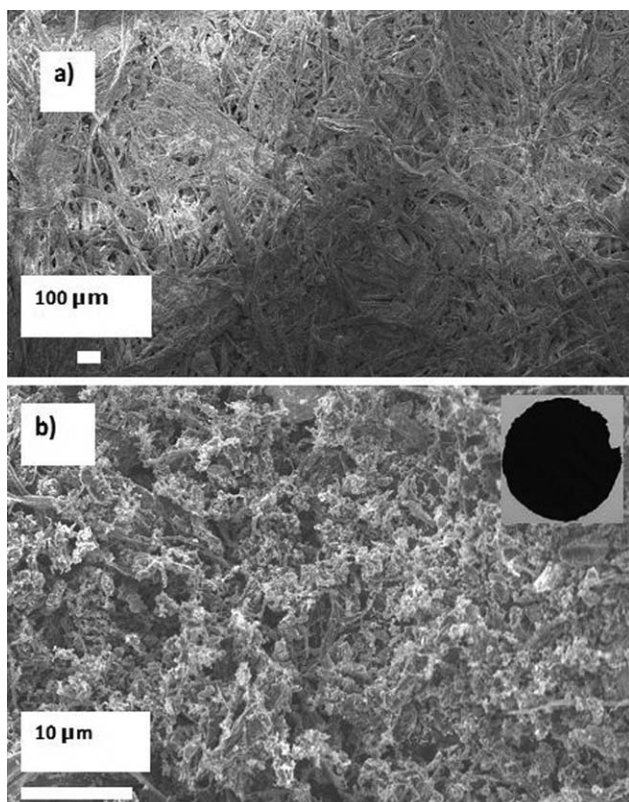


Figure 2. SEM images of (a) bleached sheet (b) PPy coated pulp sheet. Embedded image in **b** shows the bulk view of PPy coated pulp sheet.

889 cm^{-1} is $=\text{C}-\text{H}$ out of plane vibration peak, 1043 cm^{-1} is due to $=\text{C}-\text{H}$ in plane vibration, 1165 cm^{-1} is due to $\text{N}-\text{C}$ stretch bending and 1415 cm^{-1} band is due to pyrrole ring vibration.

Figure 4 shows the thermal stability of raw, bleached and coated pulp sheets, analyzed by thermogravimetric analysis (TGA). Figure 4 shows that thermal stability of raw pulp is better than

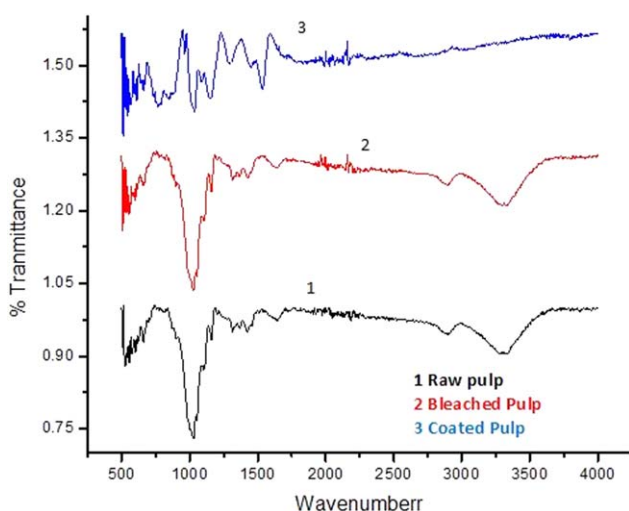


Figure 3. FTIR spectrum of raw (1) pulp, (2) bleached pulp, and (3) PPy coated pulp. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

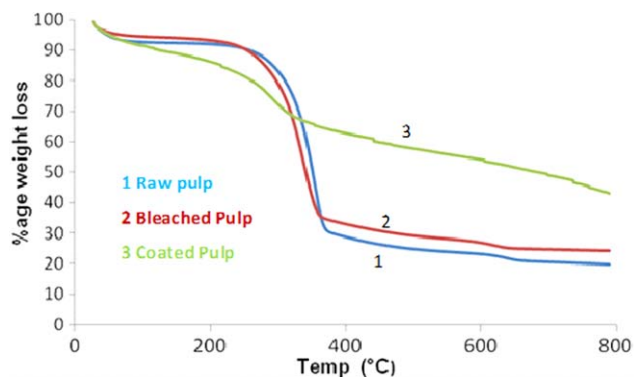


Figure 4. TGA of (1) raw pulp, (2) bleached pulp, and (3) PPy coated pulp. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that of bleached one which is reduced by almost 3% due to the removal of pigments. Raw and bleached pulps displayed decomposition at 275, 220°C and lost almost 70% weight until 370°C as shown in Figure 4. Pulp/PPy coated sheet showed greater thermal stability than control pulp, although gradual decomposition started at lower temperature but only 50% weight loss was observed, whereas raw and naked pulp fibers showed around 80% weight loss.

Figure 5 shows the plot between the real part against imaginary part of the impedance as a parametric function of frequency (impedance plane plot) at room temperature for the synthesized pulp/PPy composite. The inset shows the magnified image of the low frequency part of the plane plot. The frequency increases from right to left. The solid squares are the experimental data and the solid lines are the theoretical fit to the experimental data. Existence of two relaxation effects is obvious from Figure 5 and inset. The first and prominent relaxation appears at higher frequencies as a semicircular arc. Moreover, it is obvious that the semicircular arc is depressed below the real axis, i.e., the radius of the arc along the imaginary axis (Z''_{max}) is smaller along the real axis ($Z'_{\text{max}}/2$). This depression of the arc may be due to the presence of more than one relaxation effects with their relaxation frequencies differing less than 1.4 order of magnitude.³⁷ The second highly depressed arc at low frequency region (inset) is a relaxation effect with relatively higher capacitance and can be viewed as nearly a line parallel to the real axis. Hence, the impedance data was modeled by an equivalent circuit (R_1Q_1) (R_2Q_2). 'Q' is the constant phase element included to account for the depression of the arcs such that $C=R^{(1-n)/n}Q^{1/n}$.³⁷ The superscript 'n' ($0 \leq n \leq 1$) is a measure of depression of the arcs. It is found by the fitting analysis that the low frequency effect has an associated resistance of 3197 Ω . Owing to the highly depressed nature, the capacitance associated with this arc cannot be estimated reasonably. The resistance and capacitance associated with the high frequency arc are found to be 24,354 Ω and 1.45 nF. The low frequency arc having smaller resistance is due to the conductive PPy coating whereas the relaxation effect at higher frequencies is due to the pulp fibers. The depression ($n=0.8$, depression angle = 20°) of the arc associated with raw pulp may be due to its different phases such as lignin and hemicellulose with relatively different resistivity.

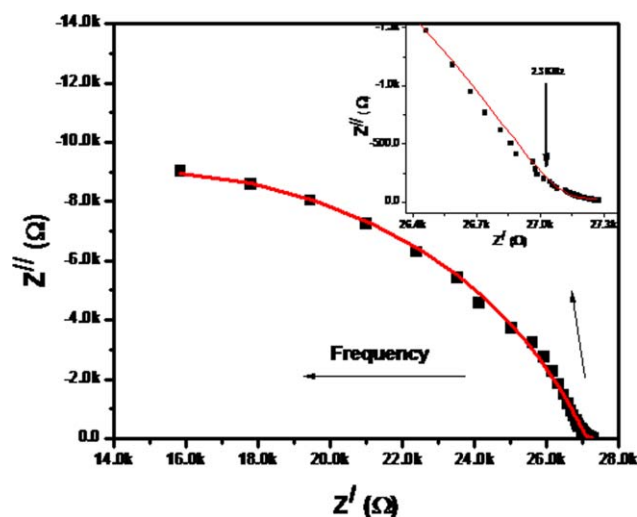


Figure 5. Impedance plane plot of PPY coated sheet at room temperature. Solid squares are the experimental data. Solid line is the fitted data. Frequency increases in the direction of the arrow from left to right. Inset shows the magnified image of the low frequency region. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6 shows the frequency dependence of the real permittivity (dielectric constant) of the synthesized PPY coated sample at log-log scale. The curve is divided into two parts with different slopes below and above 2.3 KHz. These results are in accordance to above mentioned results of impedance plane plot in Figure 5 where the presence of two relaxation effects were observed. The high value of the dielectric constant at low frequencies is due to the presence of all types of polarizations from communal phases such as PPY and pulp fibers. However, as the frequency increases, the electric dipoles become less and less mobile enough to follow the variations in the ac electric field. As a consequence the dielectric constant decreases at higher frequencies. The observed value of the dielectric constant is 1.15×10^6 at 0.5 Hz which further decreased to 2×10^4 at 100 Hz. Saafan

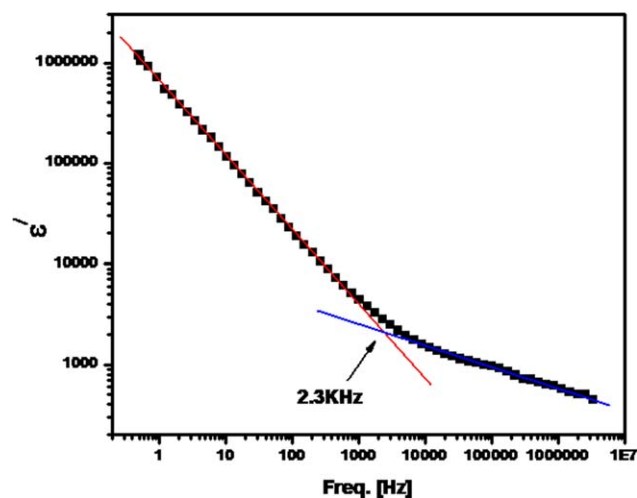


Figure 6. Real part of the complex permittivity at room temperature plotted against frequency for PPY coated sheet. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

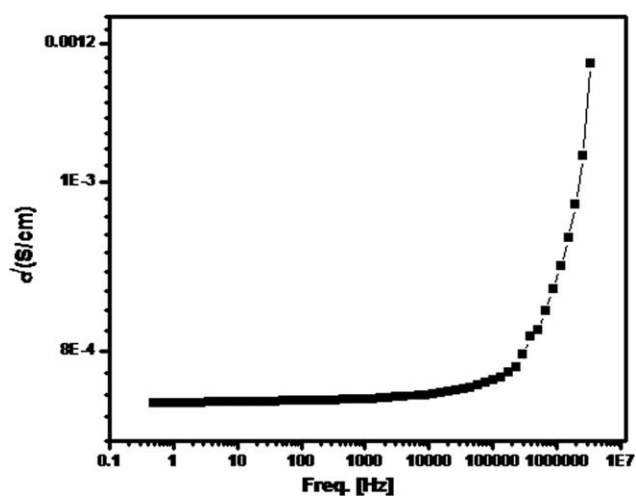


Figure 7. Real part of the ac conductivity (σ') of PPY coated sheet at room temperature as a function of frequency for the synthesized composite at log-log scale.

et al. reported the dependence of dielectric constant (10^6 – 10^4 at 0.1 Hz) of PPY on the synthesis route and showed similar decrease in the dielectric constant with an increase in frequency.⁴⁰ The relatively higher values of the dielectric constant in our case may also be attributed to the combined contribution from both PPY and pulp.

Figure 7 shows the frequency dependence of ac conductivity of pulp/PPY at room temperature in the investigated frequency range. Like other conducting polymers and their composites, the ac conductivity at lower frequencies is independent of the applied frequency whereas dependence appeared with further increase in the frequency, which match with the observation of literature.⁴⁰ However, the observed value of the conductivity in the frequency independent region (7.45×10^{-4} S/cm) is higher in comparison with pure PPY⁴⁰ which can attribute to compactness of pulp/PPY sheet. This is interesting because the pulp is highly insulating and increase in conductivity of pulp/PPY composite can be interpreted on the basis of increase in the degree of compactness which is obvious from the SEM images. It is also shown in literature that conductivity of clay/PPY and Y_2O_3/PPY composites are higher than that of the pure PPY which is attributed to an increase in degree of compactness.^{41,42}

CONCLUSION

In this study, the raw pulp was obtained from wasted egg holder trays and used as substrate for the synthesis of conductive composite paper sheets. The raw pulp fibers were bleached and coated with polypyrrole *via* chemically oxidative polymerization. SEM images revealed the fibril structure of pulp and unwavering integrity after coating with PPY. FTIR spectroscopic data confirmed the coating of PPY on bleached pulp and TGA data displayed the better thermal stability of PPY coated fibers. Dielectric properties of presented pulp/PPY composite were investigated by impedance analyzer. PPY coated pulp fibril sheet showed the dielectric constant of 1.15×10^6 at 0.5 Hz which was further decreased to 2×10^4 at 100 Hz. The ac conductivity of the coated sheet was 7.45×10^{-4} S/cm. The observed

value of the conductivity in the frequency independent region (7.45×10^{-4} S/cm) is higher in comparison with that of pure PPy which can be attributed to compactness of pulp/PPy sheet. The synthesized pulp/PPy sheets are potential candidates for environment friendly and low-cost electrode materials particularly for disposable electronics and energy storage devices.

ACKNOWLEDGMENTS

The financial support from CRGP CIIT (16-46/CRGP/CIIT/LHR13) and HEC Pakistan startup research grant (No. PD/IPFP/HRD/HEC/2013/1922) are greatly acknowledged.

REFERENCES

- Inzelt, G. In *Conducting Polymers: A New Era in Electrochemistry*; Scholz, F., Ed.; Monographs in Electrochemistry; Springer: New York, **2008**; Chapter 8, p 265.
- Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G.; Chiang, C. K.; Heeger, A. J. *J. Chem. Soc. Chem. Commun.* **1977**, 16, 578.
- Bradley, D. D. C. *Chem. Br.* **1991**, 27, 719.
- Nambiar, S.; Yeow, J. T. *Biosens. Bioelectron.* **2011**, 26, 1825.
- Janata, J.; Josowicz, M. *Nat. Mater.* **2003**, 2, 19.
- Ong, B. S.; Wu, Y.; Liu, P.; Gardner, S. *J. Am. Chem. Soc.* **2004**, 126, 3378.
- Mastragostino, M.; Arbizzani, C.; Bongini, A.; Barbarella, G.; Zambianchi, M. *Electrochim. Acta* **1993**, 38, 135.
- Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem. Int. Ed. Engl.* **1998**, 37, 402.
- Joo, J.; Lee, C. Y. *J. Appl. Phys.* **2000**, 88, 513.
- Burke, A. *J. Power Sources* **2000**, 91, 37.
- Nyholm, L.; Nyström, G.; Mihranyan, A.; Strømme, M. *Adv. Mater.* **2011**, 23, 3751.
- Snook, G. A.; Kao, P.; Best, A. S. *J. Power Sources* **2011**, 196, 1.
- Rudge, A.; Davey, J.; Raistrick, I.; Gottesfeld, S.; Ferraris, J. P. *J. Power Sources* **1994**, 47, 89.
- Mastragostino, M.; Arbizzani, C.; Soavi, F. *Solid State Ionics* **2002**, 148, 493.
- Laforgue, A.; Simon, P.; Sarrazin, C.; Fauvarque, J. F. *J. Power Sources* **1999**, 80, 142.
- Zhang, J.; Kong, L. B.; Li, H.; Luo, Y. C.; Kang, L. *J. Mater. Sci.* **2010**, 45, 1947.
- Kim, B. C.; Too, C. O.; Kwon, J. S.; Ko, J. M.; Wallace, G. G. *Synth. Met.* **2011**, 161, 1130.
- White, A.; Slade, R. *Macromol. Symp.* **2004**, 212, 275.
- Qu, Q.; Zhu, Y.; Gao, X.; Wu, Y. *Adv. Energy Mater.* **2012**, 2, 950.
- Davies, A.; Audette, P.; Farrow, B.; Hassan, F.; Chen, Z.; Choi, J. Y.; Yu, A. *J. Phys. Chem. C* **2011**, 115, 17612.
- Jurewicz, K.; Delpoux, S.; Bertagna, V.; Beguin, F.; Frackowiak, E. *Chem. Phys. Lett.* **2001**, 347, 36.
- Fang, Y.; Liu, J.; Yu, D. J.; Wicksted, J. P.; Kalkan, K.; Topal, C. O.; Flanders, B. N.; Wu, J.; Li, J. *J. Power Sources* **2010**, 195, 674.
- An, K. H.; Jeon, K. K.; Heo, J. K.; Lim, S. C.; Bae, D. J.; Lee, Y. H. *J. Electrochem. Soc.* **2002**, 149, A1058.
- Sahoo, N. G.; Jung, Y. C.; So, H. H.; Cho, J. W. *Synth. Met.* **2007**, 157, 374.
- Hu, Y.; Zhao, Y.; Li, Y.; Li, H.; Shao, H.; Qu, L. *Electrochim. Acta* **2012**, 66, 279.
- Frackowiak, E.; Jurewicz, K.; Szostak, K.; Delpoux, S.; Beguin, F. *Fuel Process. Technol.* **2002**, 77, 213.
- Yue, B.; Wang, C.; Ding, X.; Wallace, G. G. *Electrochim. Acta* **2012**, 68, 18.
- Yuan, L.; Yao, B.; Hu, B.; Huo, K.; Chen, W.; Zhou, J. *Energy Environ. Sci.* **2013**, 6, 470.
- Liew, S. Y.; Thielemans, W.; Walsh, D. A. *J. Phys. Chem. C* **2010**, 114, 17926.
- Razaq, A.; Nyholm, L.; Sjödin, M.; Strømme, M.; Mihranyan, A. *Adv. Energy Mater.* **2012**, 2, 445.
- Nystroöm, G.; Mihranyan, A.; Razaq, A.; Lindstroöm, T.; Nyholm, L.; Strømme, M. *J. Phys. Chem. B* **2010**, 114, 4178.
- Richter, G. A. U.S. Patent No. 2,065,396; Washington, DC: U.S. Patent and Trademark Office, **1936**.
- McDonald, D.; Miles, K.; Amiri, R. *Pulp Paper Can.* **2004**, 105, 27.
- Myers, G. C. *Wood Fiber Sci.* **2002**, 34, 108.
- Prusas, Z. C. U.S. Patent No. 4,486,267; U.S. Patent and Trademark Office: Washington, DC.
- Krofta, M. U.S. Patent No. 5,242,585; U.S. Patent and Trademark Office: Washington, DC, **1993**.
- Barsoukov, E.; Macdonald, J. R. In *Impedance Spectroscopy: Theory, Experiment, and Applications*; Wiley: New York, **2005**, Vol. 2, p 1.
- Castro, L.; Blazquez, M. L.; González, F.; Muñoz, J. A.; Ballester, A. *Chem. Eng. J.* **2010**, 164, 92.
- Chougule, M. A.; Pawar, S. G.; Godse, P. R.; Mulik, R. N.; Sen, S.; Patil, V. *Soft Nanosci. Lett.* **2011**, 1, 6.
- Saafan, S. A.; El-Nimr, M. K.; El-Ghazzawy, E. H. *J. Appl. Polym. Sci.* **2006**, 99, 3370.
- Seyfullah, M.; Emrah, C.; MemetVezir, K.; Kadir, E. *Chem. Pap.* **2013**, 67, 1048.
- Vishnuvardhan, K.; Kulkarni, V. R.; Basavaraja, C.; Raghavendra, S. C. *Bull. Mater. Sci.* **2006**, 29, 77.