Malaysian Journal of Analytical Sciences (MJAS)
Published by Malaysian Analytical Sciences Society
ANALIS Persatuan Sains Analisis Malaysia

STRUCTURAL AND CONDUCTIVITY STUDIES OF CHOLINE CHLORIDE-BASED DEEP EUTECTIC SOLVENT AS A POTENTIAL ELECTROLYTE IN LITHIUM-ION BATTERIES

(Kajian Struktur dan Kekonduksian Pelarut Eutektik Dalam Berasaskan Kolina Klorida yang Berpotensi sebagai Elektrolit dalam Bateri Ion Litium)

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Received: 14 February 2022; Accepted: 18 August 2022 ; Published: 30 October 2022

Abstract

Utilizing volatile and flammable electrolytes in lithium-ion batteries has become a primary concern worldwide. Consequently, a safer high-performance electrolytes approach is required to solve the issue. In this circumstance, deep eutectic solvent (DES) might be the best option to substitute the harmful conventional liquid electrolytes. The present study explores the potential of ternary DES, which comprises choline chloride (ChCl), 1,4-butanediol (1,4-BD), and lithium triflate (LiTf), as an electrolyte in lithium-ion batteries. The structural and conductivity of ChCl/1,4-BD at 1:1, 1:2; and 1:3 mole ratios and ChCl/1,4-BD/LiTf at 2.5, 5, and 10 wt.% LiTf systems were investigated. The ChCl/1,4-BD at 1:1 ratio (DES1:1) recorded the highest ionic conductivity of 2.41 mS cm^{-1}, which resulted from the least amount of hydrogen bonds between ChCl and 1,4-BD. Subsequently, the DES1:1 was doped with different percentages of LiTf. The highest ionic conductivity, 2.56 mS cm^{-1}, was obtained from the ChCl/1,4-BD/2.5 wt.% LiTf system. The elevated ionic conductivity was attributable to the high amount of mobile lithium ions available due to fewer hydrogen bonds formed between the ChCl/1,4-BD and LiTf. Conclusively, the highly conducting ChCl/1,4-BD/2.5 wt.% LiTf demonstrated the best potential for application in lithium-ion batteries.

Keywords: deep eutectic solvents, liquid electrolytes, lithium salts, ionic conductivity

Abstrak

Penggunaan elektrolit yang mudah meruap dan terbakar dalam bateri ion litium merupakan isu utama di seluruh dunia. Oleh itu, elektrolit yang berprestasi tinggi dengan pendekatan yang lebih selamat diperlukan bagi menyelesaikan isu ini. Dalam keadaan ini, pelarut eutektik dalam (DES) dilihat sebagai alternatif terbaik untuk menggantikan cecair elektrolit konvensional yang berbahaya. Kajian ini meneroka potensi DES ternari yang terdiri daripada kolina klorida (ChCl), 1,4-butanadiol (1,4-BD) dan litium triflat (LiTf) sebagai elektrolit hijau dalam bateri ion litium. Struktur dan kekonduksian bagi sistem dengan 1:1, 1:2; dan 1:3 nisbah mol ChCl/1,4-BD dan ChCl/1,4-BD/LiTf dengan 2.5, 5, 10 wt.% LiTf telah dikaji. Sistem ChCl/1,4-BD dengan 1:1 nisbah mol (DES1:1) telah menunjukkan kekonduksian ionik paling tinggi, iaitu 2.41 mS cm^{-1}, yang terhasil daripada interaksi ikatan hidrogen yang rendah antara ChCl dengan 1,4-BD. Seterusnya, DES1:1 telah ditambah dengan LiTf pada peratusan yang berbeza.

Kekonduksian ionik yang tertinggi, iaitu 2.56 mS cm^{-1}, telah diperoleh sistem ChCl/1,4-BD/2.5 wt.% LiTf. Kekonduksian yang tinggi ini disumbangkan oleh kehadiran ion litium bebas yang tinggi hasil daripada kurang interaksi ikatan hidrogen antara ChCl/1,4-BD dengan LiTf. Kesimpulannya, ChCl/1,4-BD/2.5 wt.% LiTf dengan kekonduksian yang tinggi menunjukkan potensi terbaik untuk digunakan dalam bateri ion litium.

Kata kunci: pelarut eutektik dalam, cecair elektrolit, garam litium, kekonduksian ionik

Introduction

The rapid increase in the world population and economic power has escalated energy demand. Accordingly, exceptionally efficient, stable, and ecologically benign energy storage systems are highly desired. Lithium-ion batteries are one of the most widely studied devices for energy storage as they possess great energy density and thermal stability and are less expensive than other types of batteries [1, 2]. Moreover, the application of lithium-ion batteries is not limited to mobile phones, they are also employed in medical and aerospace instruments [3]. Nevertheless, the conventional liquid electrolytes of lithium-ion batteries comprise flammable and volatile organic solvents [4] that result in issues such as leakages, corrosion, and even explosions.

The utilization of ionic liquids (IL)-based liquid electrolytes has been extensively investigated [4, 5]. The IL provides superior safety attributes to liquid electrolytes as it possesses distinctive physical properties, such as non-flammable, low melting point and volatility, and high thermal stability [6]. Nonetheless, deep eutectic solvents (DES) have been reported to exhibit more desirable properties, including cost-effectiveness, high biodegradability, and very low toxicity, despite sharing similar physicochemical properties with IL (non-flammable, low volatility, high thermal stability) [4, 7].

The DES is obtainable from the self-association of hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD) via a simple heating technique [8]. Consequently, its biodegradability is contributed by their natural HBA (choline chloride (ChCl), phosphonium salts) and HBD (carboxylic acid, urea, renewable polyols, amines, amides, carbohydrates) contents. The DES consisted of N-methylacetamide (MAc) and different lithium salts (lithium bis[(trifluoromethyl)sulfonyl]) imide (LiTFSI) and lithium hexafluorophosphate ($LiPF_6$) has been reported as potential electrolytes for lithium-ion batteries. Nevertheless, liquid-state-electrolytes were not obtainable when the Li molar fraction was over 0.35, hence limiting the ionic conductivity to only 1 mS cm^{-1} [9]. The finding led to the development of ternary DES, such as ChCl/ethylene glycol/$LiPF_6$, that remains in a liquid state even at a 0.5 Li molar fraction, hence bearing higher ionic conductivity of 7.95 mS cm^{-1}. Nonetheless, the $LiPF_6$ exhibited low thermal decomposition temperature [10,11], thus deteriorating when subjected to high temperatures.

The lithium triflate (LiTf) has been demonstrated to possess higher thermal stability than $LiPF_6$ [11]. Consequently, the current study investigated a DES ternary system comprising a choline chloride (ChCl), 1,4-butanediol (1,4-BD), and LiTf mixture. The most optimum ChCl to1,4-BD mole ratio (1:1, 1:2; or 1:3) as the solvent for LiTf was first investigated. The study then doped the ChCl/1,4-BD with different weight percentages of LiTf (2.5, 5, and 10 wt.%). The structural and conductivity assessments of the systems were conducted with Fourier Transform Infrared Spectroscopy (FTIR) and conductivity meter, respectively.

Materials and Methods

Preparation of DES

The chemical components DES, 99% ChCl (Acros Organic), > 99% 1,4-butanediol (Sigma), and 99% LiTf (Sigma) were employed in the present study without further purification. Three ChCl/1,4-BD mixtures at 1:1, 1:2, and 1:3 mole ratios, labelled as DES1:1, DES1:2, and DES1:3, respectively, were mixed and heated at 80℃ while stirring until dissolution. Subsequently, LiTf with different weight percentages, 2.5, 5, and 10 wt.%, were dissolved in the highest conducting ChCl/1,4-BD while stirring and were designated as LE2.5, LE5, and

LE10, respectively. All the samples were kept in a desiccator before being characterized.

Fourier Transform Infrared Spectroscopy

The FTIR spectra of the samples evaluated in this study were recorded with a Perkin Elmer spectroscope at room temperature. First, the samples were dropped directly onto the crystal before measurements were obtained under the transmittance mode over the 4000-600 cm^{-1} frequency range with 4 cm^{-1} resolutions and 16 scans. Peak deconvolution was carried out with the Origin 8.1 software, in which the Gaussian function was employed to resolve overlapping bands. Prior to the deconvolution process, baseline corrections were conducted.

Conductivity meter

A conductivity meter (HANNA Instruments) was utilized to measure the ionic conductivities of the samples in the current study. The samples were placed in 50 ml beakers and the conductivity meter was dipped into each solution. The assessment was performed at room temperature and the ionic conductivities were recorded three times for each sample.

Result and Discussion

Preparation of the ChCl/1,4-BD mixture

The present study successfully obtained the homogenous liquid mixtures of ChCl/1,4-BD at varying mole ratios. Furthermore, the mixtures remained in their liquid conditions even at room temperature.

Structural analyses of the ChCl/1,4-BD

Figure 1 displays the FTIR spectra for the ChCl, 1,4-BD and the ChCl/1,4-BD mixtures at different mole ratios. The FTIR peaks representing ChCl were observed at 3222, 1480, and 1349 cm^{-1} due to OH stretching and CH_2 and CH_3 bending, respectively [12]. The FTIR spectra of the 1,4-BD appeared at 3292, 1169, and 1428 cm^{-1}, which denoted the O-H and C-O stretching and CH_2 bending, respectively [13]. The O-H stretching peak of the 1,4-BD also shifted to a higher wavenumber, from 3292 to 3297, 3298, and 3293 cm^{-1}, in the DES1:1, DES1:2 and DES1:3 samples, respectively. The observations confirmed the hydrogen bonding interactions between ChCl and 1,4-BD in the binary DES obtained. The peak intensities of the solutions were also reduced.

The decrease in the peak intensity of O-H stretching with the increasing amount of 1,4-BD indicated the diminished free O-H stretching in the system. The phenomenon might be due to the formation of hydrogen bonding interactions between the O-H···O-H and O-H···Cl in the ChCl/1,4-BD mixtures, as illustrated in Figure 2. The interaction between ChCl and 1,4-BD could also be further confirmed by the upshift in the CH_2 bending of 1,4-BD from 1428 to 1441, 1442, and 1448 cm^{-1} in the DES1:1, DES1:2, and DES1:3, respectively. The trends observed in this study agreed with a previous investigation on the formation of citric acid monohydrate-ChCl based DES [12].

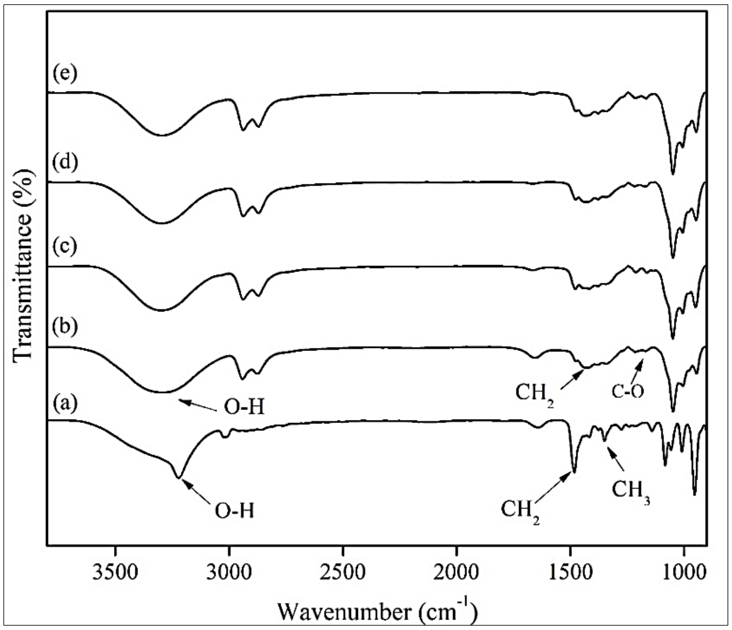

Figure 1. The FTIR spectra of (a) ChCl, (b) 1,4-BD, (c) DES1:1, (d) DES1:2, and (e) DES1:3

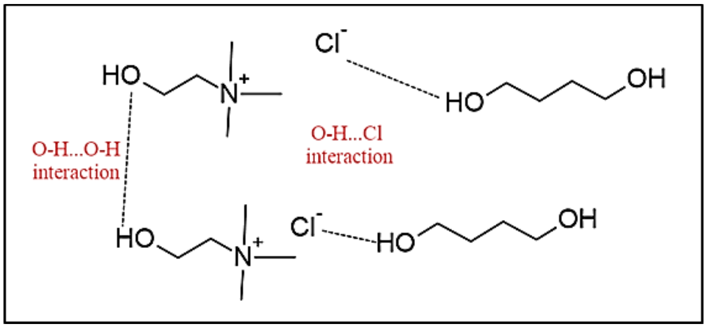

Figure 2. The possible hydrogen bonding interactions in ChCl/1,4-BD

Wang and co-workers [14] reported that the amount of hydrogen bonding interactions in ChCl-polyol DES could be further confirmed by the deconvolution and band-fitting of the broad O-H stretching peak between the 3700–3100 cm^{-1} region. Accordingly, the deconvolution and band fitting of DES1:1, DES1:2, and DES1:3 samples were conducted and is illustrated in Figure 3. Three types of O-H peaks were present at ~3400, ~3300, and ~3200 cm^{-1}, which corresponded to the free O-H stretching and inter- and intramolecular O-H···O-H and O-H···Cl stretching, respectively. As the amount of 1,4-BD increased, the amount of free O-H stretching decreased. The observations were due to the elevated inter- and intramolecular O-H···O-H and O-H···Cl interactions in the ChCl/1,4-BD mixtures.

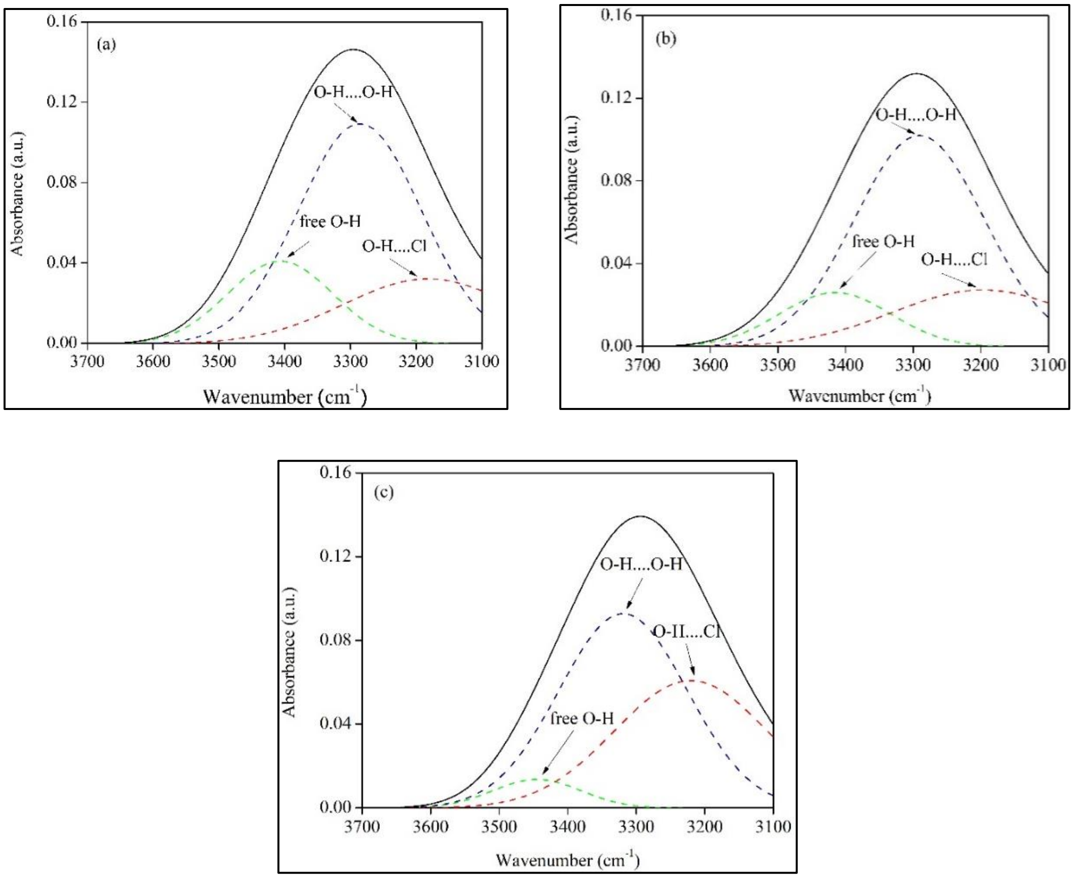

Figure 3. The deconvolution and band fitting of the FTIR spectra from 3700–3100 cm^{-1} of the (a) DES1:1, (b) DES1:2, and (c) DES1:3 samples

Conductivity assessments of the ChCl/1,4-BD

Table 1 lists the ionic conductivity values of the varying mole ratios of ChCl/1,4BD produced in the current study. The highest ionic conductivity, 2.41 mS cm^{-1}, was recorded by the DES1:1, however, the value decreased with higher 1,4-BD in the DES1:2 and DES1:3 systems. The observations resulted from elevated hydrogen bonds confirmed in the FTIR analysis. Furthermore, the presence of an excessive amount of 1,4-BD alkyl chain in the ChCl/1,4-BD mixture might also contribute to the diminished ionic conductivity of the samples.

The HBD alkyl chain structure has been reported to affect the ionic conductivity of DES [6]. As the amount of 1,4-BD was increased, an excessive amount of alkyl chain was produced in the ChCl/1,4-BD system, resulting in higher van der Waals interactions within the ChCl/1,4-BD. Consequently, the mobility of the ions was lowered, hence decreasing the ionic conductivity of the system. Similar observations were reported by Zhang and co-workers [5].

The ionic conductivity values of the DES1:1 was slightly higher if compared to other DES systems such as ChCl/EG (1.79 mS cm^{-1}) [15] and TBABr/EG (0.53 mS cm^{-1}) [6]. The findings were attributable to the non-excessive hydrogen bonds formed between HBA and HBD, which would ease the movement of lithium ions. Hence, the ChCl/1,4-BD at a 1:1 mole ratio was the optimal solvent selection for dissolving LiTf in the present study.

Table 1. The ionic conductivities of the ChCl/1,4BD systems

System	Ionic conductivity (Mean ± SD, mS cm^{-1})
DES1:1	2.41 ± 0.27
DES1:2	1.34 ± 0.44
DES1:3	0.92 ± 0.12

Preparation of the ChCl/1,4-BD/LiTf

In the current study, homogenous liquid mixtures of ChCl/1,4-BD/LiTf with different LiTf weight percentages were successfully obtained. Furthermore, the mixtures remained as liquids even at room temperature.

Structural evaluations of the ChCl/1,4-BD/LiTf

Figure 4 demonstrates the FTIR spectra for the DES1:1 with LiTf LE2.5, LE5, and LE10. The SO_3 and CF_3 stretching peaks were recorded at 1265 and 1182 cm^{-1}, respectively, for pure LiTf. Upon incorporation of LiTf into the ChCl/1,4-BD system, the SO_3 and CF_3 stretching peaks of LiTf were observed, hence confirming the miscibility of LiTf in ChCl/1,4-BD [16]. The O-H stretching peaks of the DES1:1 shifted to higher wavenumbers, from 3297 to 3303, 3301, and 3335 cm^{-1}, respectively, in the LE2.5, LE5, and LE10 systems. Moreover, the peak intensities were diminished.

Meanwhile, the peak intensities of the SO_3 and CF_3 stretching of LiTf were recorded to increase with higher amounts of LiTf. The findings indicated that interactions between the LiTf anions and the hydrogen from the DES hydroxyl groups occurred, as demonstrated in Figure 5. Furthermore, the decreased peak intensity of the OH stretching in the samples indicated that more hydrogen bonding between the LiTf and ChCl/I,4-BD transpired as the percentage of the LiTf added was increased. Dhingra and co-workers also reported similar results in the study of ChCl/urea/lithium chloride DES [4].

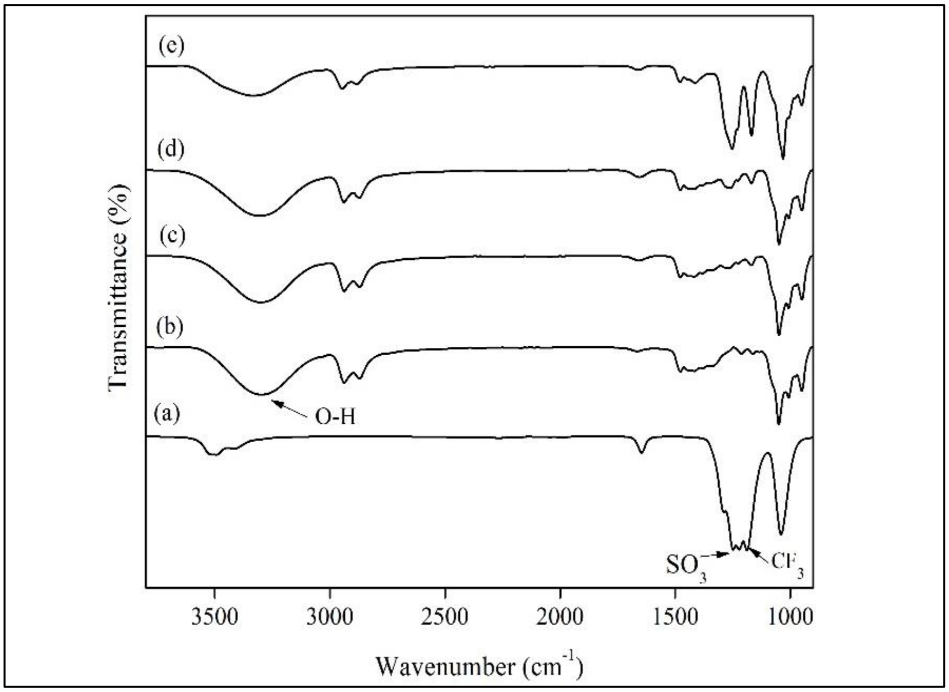

Figure 4. The FTIR spectra of the (a) LiTf, (b) DES1:1, (c) LE2.5, (d) LE5, and (e) LE10

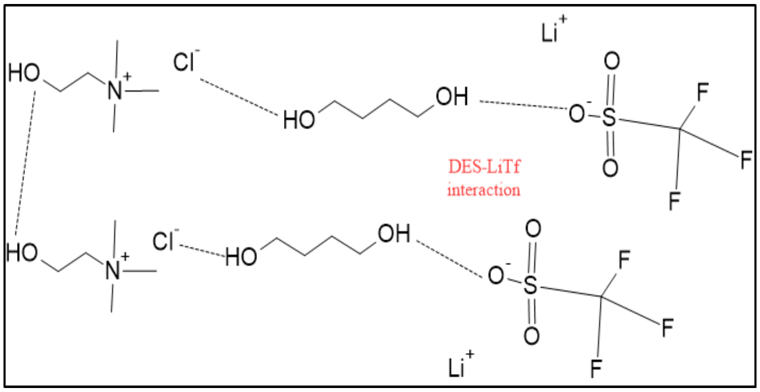

Figure 5. Possible hydrogen bonding interactions in the ChCl/1,4-BD/LiTf samples

Conductivity studies of the ChCl/1,4-BD/LiTf

Table 2 lists the ionic conductivity of the ChCl/1,4-BD/LiTf systems manufactured in the present study. The conductivity of the system increased from 2.41 to 2.56 mS cm^{-1} as 2.5 wt.% of LiTf was added into the ChCl/1,4-BD. The ionic conductivity increment was attributable to the free mobility of the lithium ions in the DES mixtures, which resulted from the formation of hydrogen bonds between the anions in the salt and DES that was confirmed with FTIR.

The amount of mobile lithium ions has been demonstrated to affect the ionic conductivity of DES systems [16]. Nevertheless, as the addition of LiTf in the current study was increased to 5 and 10 wt.%, the conductivity reduced to 1.84 mS cm^{-1} and 0.65 mS cm^{-1}, respectively. The observations might be due to the formation of more hydrogen bonds that eventually prevented lithium ions from moving freely. Nonetheless, the highest conductivity value obtained in the present study was comparable to other ternary DES systems comprising EG/ChCl/ LiPF$_6$ (7.95 mS cm^{-1}) [7].

Table 2. Ionic Conductivity for ChCl/1,4-BD/LiTf System

System	**Ionic conductivity (Mean ± SD, mS cm^{-1})**
LE2.5	2.56 ± 0.12
LE5	1.84 ± 0.26
LE10	0.65 ± 0.17

Conclusion

An increased 1,4-BD amount would lead to more hydrogen bonding formation, hence reducing the free mobility of ions and conductivity of ChCl/1,4BD systems. In the present study, the optimal ChCl/1,4-BD to dissolve LiTf was recorded at a 1:1 mole ratio as the solution contained non-excessive hydrogen bonds, thus easing lithium-ion movements. Moreover, adding 2.5 wt.% of LiTf to the ChCl/1,4-BD mixture resulted in the highest number of mobile ions, contributing to its conductivity, 2.56 mS cm^{-1}, which was the highest. Conclusively, ternary DES consisting of a 1:1 mole ratio of ChCl/1,4-BD and 2.5% LiTf exhibited the optimal potential of being applied in lithium-ion batteries.

Acknowledgement

The authors would like to acknowledge Faculty of Applied Sciences, UiTM Perlis branch for supporting this research. Financial support by Dana Pembudayaan Penyelidikan Dalaman (DPPD) (600-TNCPI 5/3/DDN (09) (018/2020)) is highly acknowledged.

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