

Ionic Conductivity and Dielectric Study of Sodium Iodide-Sodium Dicyanamide Solid Electrolyte

Mohd Khairul Hazwan Yusof¹ and *Azizah Hanom Ahmad^{1,2}

Abstract—Sodium solid electrolyte based on sodium dicyanamide, $\text{NaN}(\text{CN})_2$ doped with sodium iodide, NaI was prepared by ultra-fined grinding using planetary milling and pelletised with pellet press. Electrical conductivity and dielectric permittivity study were carried out by Electrochemical impedance spectroscopy (EIS) at frequency range between 50 Hz to 5.00×10^6 Hz. Highest conducting sample at room temperature condition managed to achieved by optimizing the doped sodium salt content with weight composition of 10NaI–90NaN(CN)₂ with ionic conductivity value of $(5.67 \pm 1.26) \times 10^{-4}$ S cm⁻¹ at ambient temperature condition. The findings are further supported with 10 wt.% NaI in solid electrolyte system sample possessed highest dielectric constant and dielectric loss values at lower frequency region that showed non-Debye behavior for charge storage. Transference number measurement were performed and obtained a value of 0.96 that confirmed the sodium solid electrolyte sample is ionic conductor in nature.

Index Terms—sodium iodide, sodium dicyanamide, impedance spectroscopy, ionic conductivity, sodium solid electrolyte.

I. INTRODUCTION

The currently depletion of fossil fuels and concern over carbon emission have brought researchers to find alternative sources of energy such as using renewables from wind and solar for industrial and household consumption. Despite the promising of renewables, still the challenges that need to be address are the intermittent issues and storage of those unlimited energy during time it is needed especially at night where the sun does not shine and during days where there is no wind [1].

Sodium based solid electrolyte that may counter several known liquid electrolyte issues such as flammable, leakage and long-term electrode degradation has become attractive to be used in solid state batteries for renewable energy storage. This is due to its natural abundant and economically viable for large-scale applications [2]. One of the commercially available sodium solid electrolyte is the Na-β"-Alumina used in Na/S batteries. However, it only showed good conductivity performance at very high temperature of ~300°C thus requires high maintenance, strict procedures and prone to some hazard [3].

Although some authors have successfully synthesised some glassy-ceramic sodium based solid electrolyte such as

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$\text{Na}_{1.5}\text{Y}_{0.3}\text{Ga}_{0.2}\text{Ge}_{1.5}(\text{PO}_4)_3$ [4] and $\text{Na}_5\text{DySi}_4\text{O}_{12}$ [5] they also exhibited great conductivity values at well above room temperature. This limits its applications for household consumers that favours ambient temperature environment. Thus researchers are constantly finding new material combinations to develop sodium solid electrolyte that gives better room temperature conductivity performance.

Iodide-based alkali metal was said to exhibit high ionic conductivity values in range of $\sim 10^{-3}$ S cm⁻¹ as it is referred to be superionic conductors [6]–[9]. One example of this material that had gain some interest among several researchers [10], [11] is NaI. The Na⁺ cation that possessed smaller ionic radius size (second smallest ionic radius just after Li⁺) compared to I⁻ anion is said has the ability to become main charge carriers thus facilitate in rapid ionic conduction. While another sodium-based material which is sodium dicyanamide, $\text{NaN}(\text{CN})_2$ is an inorganic compound with anionic bridging ligand structure feature that could form versatile supramolecule has some interesting electronic properties that are worthy to further explore [12], [13] This dicyanamide based material may act as the conducting pathway for fast Na⁺ ions movement thus give rise to ionic conductivity.

This study had taken a bold step to determine maximum room temperature conductivity value by preparing new sodium solid state electrolyte binary system consists of NaI–NaN(CN)₂ with various composition thru ball milling method. The samples were then characterised with Electrochemical impedance spectroscopy (EIS) in temperature range of 303–373 K to carried out ionic conductivity and dielectric permittivity study.

II. EXPERIMENTAL

Materials in this study are sodium iodide, NaI (500 gram pack size, ReagentPlus[®], ≥99%, 217638 Sigma-Aldrich) and sodium dicyanamide, $\text{NaN}(\text{CN})_2$ (25 gram pack size, 96%, 178322 Sigma-Aldrich) were used as-received. Both powder were weighed by different weight percentage of NaI from 5-70% to find optimum composition that gives highest room temperature conductivity value. Once it was weighed accordingly, the powder was grind with mortar and pastel for approximately two minutes. Then the mixture was mechanically milled with Retsch PM200 planetary ball mill for two hours with 200RPM speed and ball-to-powder ratio of 2:1. Each milling vial filled with 2.0 gram mixture powder. The main purpose of this ball milling technique is to ensure the final sample completely homogenised and introducing some crystal defects within the materials [14], [15] Upon milling, the mixture was pelletised using ENERPAC 10

tonne pellet press (Max 1000 psi/700 bar) with actual applied pressure of 200 bar before it was sent for characterisation.

Room temperature ionic conductivity of the prepared pellet samples were measured using HIOKI 3532-50 LCR HI Tester in frequency range from 50 Hz to 5.00×10^6 Hz. While for temperature dependence conductivity, the impedance spectroscopy instrument was connected to Espec SH-241 Temperature and Humidity Benchtop Chamber. The Cole-cole plot was obtained at different temperature from 303–373 K where the readings were taken at 10 K interval each.

A plot of imaginary part, Z_i against real part, Z_r was obtained from the complex impedance spectrum. Through that, the bulk resistance, R_b was obtained for conductivity measurement by using the below equation:

$$\sigma = \frac{L}{AR} \quad (1)$$

σ is noted by the electrical conductivity ($S\ cm^{-1}$), “ L ” is thickness of pellet sample (cm), “ A ” is the surface area (cm^2) of sample pellet that touches the stainless-blocking electrodes while “ R_b ” is the bulk resistance.

Total transference number measurement were conducted using Wagner’s polarisation technique whereby the optimum composition of binary system solid electrolyte was sandwiched between two stainless-steel blocking electrodes. Ionic transference number was calculated based on below equation:

$$t_i = \frac{I_i - I_f}{I_i} \quad (2)$$

“ I_i ” is the total initial current applied across the solid electrolyte and “ I_f ” is final residual electronic current. All these values were determined from the polarisation current versus time plot. The sample was applied with fixed dc potential until the current became constant.

III. RESULT & DISCUSSION

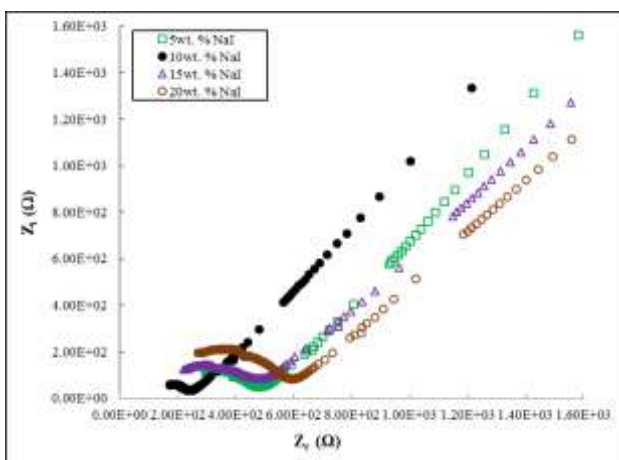


Fig. 1. Room temperature Cole-cole plots of NaI-NaN(CN)₂ solid electrolyte at various composition

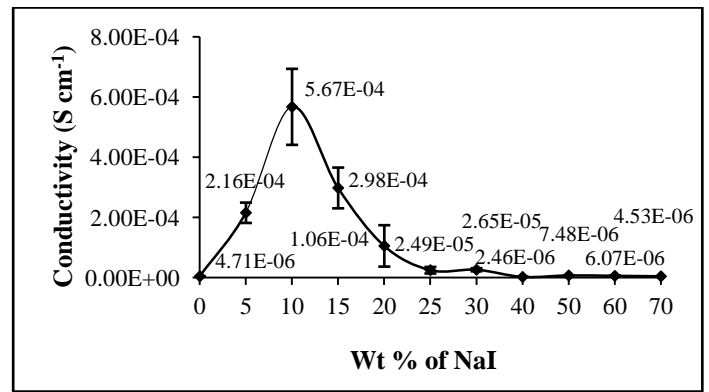


Fig. 2. Room temperature conductivity values of NaI-NaN(CN)₂ solid electrolyte for different weight percentage of doped NaI salt

Fig. 1 shows plots of complex impedance spectra for various weight percentage of sodium salt concentration from 5% to 70% in the binary system solid electrolyte. Bulk resistance, R_b could be seen at the lower frequency region which is the intercept at x-axis by the semicircle formed. The significant spikes at higher frequency region of the Cole-cole plot is assigned as the grain boundary of the solid electrolyte system [16]. As stated in Eq. 1, conductivity values is inversely proportional to the bulk resistance, R_b of each sample due to the fact that a higher R_b values limits the overall fast movement of Na^+ ions inside the bulk binary system material. Smallest bulk resistance value was obtained from 10% by weight percent of NaI compared to other composition combinations as fewer grain boundary restriction need to overcome by the Na^+ charge carriers thus maximizing its ionic conduction ability. Thus the 10% NaI sample has highest conductivity value. For 5%, 15% and 20% of NaI content, majority of mobile sodium cation is enclosed within the bulk material consequently depressing the chances to overcome grain boundary effect.

Variation of charge carriers Na^+ ions concentration against the conductivity values are demonstrated as in Fig. 2. At low concentration of 5 wt.% NaI, conductivity started to slightly increased and higher compared to pure NaN(CN)₂ sample. This is due to dissociation of Na^+ ions which is the main charge carriers from NaI started to take place. Introducing NaI has assisted in sodium ionic conduction. Nonetheless, at this low content of NaI, still the conductivity is yet to achieve the optimum level. Another possible reason for this lower conductivity is that many void still present within the lattice that resulted less efficient ionic conduction [10]

Once the sodium ion concentration reached 10% by weight, a maximum ionic conductivity value of $(5.67 \pm 1.26) \times 10^{-4} S\ cm^{-1}$ was obtained before it further decreases upon addition of more NaI. 10NaI–90NaN(CN)₂ is the optimum composition for highest conducting sample as at this rate, the number of available freely moving Na^+ ions is equally present with the availability of conducting pathway provided by the dicyanamide ligand leading to an efficient solid electrolyte system.

A decrease trend in ionic conductivity was observed after addition of more than 10 wt.% NaI. There is an immense amount of mobile ions that are not enough for the conducting pathway to occupy thus leading to collisions between the free ions. This in turn lead to the so called blocking effect phenomenon [17] Overall resistance has increased hence

resulted lower ionic conductivity.

The temperature dependence findings are illustrated as in Fig. 3. It is observed that conductivity increases as a function of temperature. Higher temperature had promoted more rapid movement of mobile ions across the solid in the form of 'hopping' [18]. This hopping of ions to nearest vacant sites is dominated by activation energy, E_a which defined as the minimum energy barrier requirement for each ion to hop around freely to neighboring sites that give rise to conductivity [19]. The activation energy, E_a could be quantified by this following Arrhenius Expression:

$$\sigma = \sigma_0 \exp \left[\frac{-E_a}{kT} \right] \quad (3)$$

σ is ionic conductivity at given temperature of T (in Kelvin), k is noted by the Boltzmann's constant, E_a is the activation energy while σ_0 is pre-exponential factor which are all the remaining factors other than activation that may affects the activation energy, E_a . This expression may easily further deduced to calculate the E_a by plotting $\log \sigma$ versus $1000/T$ graph whereby E_a was determined from the gradient of the plot. As seen in Fig. 3, the highest conducting sample has regression value, R^2 towards unity and the calculated activation energy, E_a of 0.133 eV which is the lowest compared to other samples. Samples that contains 5%, 15% and 20% weight of NaI has higher E_a values which are 0.144 eV, 0.181 eV and 0.256 eV respectively. Values of activation energy according based on different composition of binary system were also summarised in Table 1. This is proven that mobile sodium ions in 10NaI–90NaN(CN)₂ system needs the smallest energy to migrate from one sites to another leading a much higher conductivity value hence it obeys Arrhenius rule. The correlation of this low activation energy, high conductivity is in agreement with other findings [4], [20]–[22].

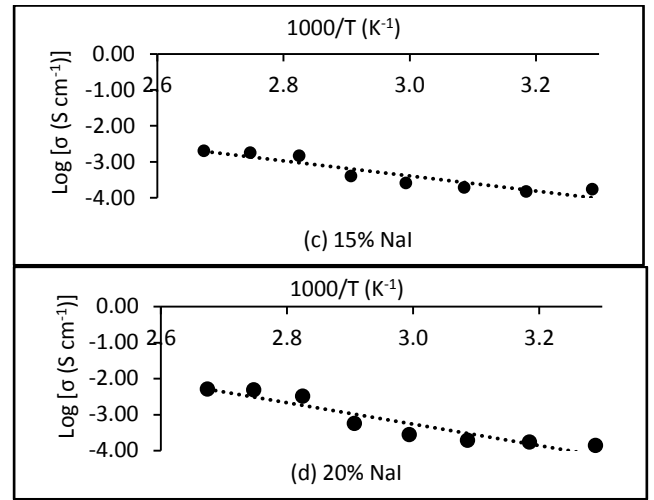
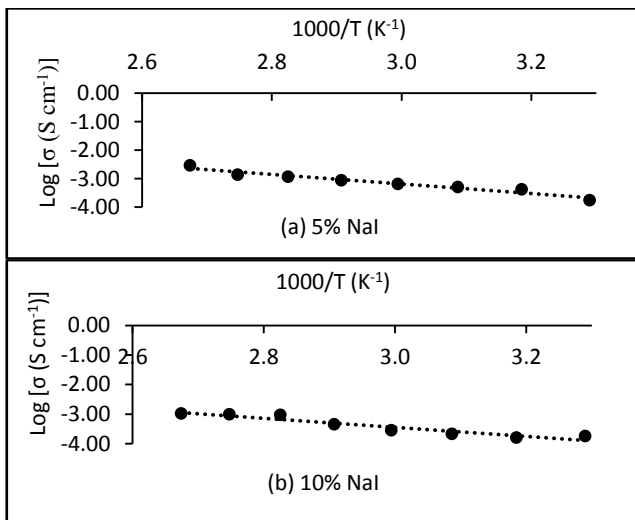


Fig. 3: Logarithm conductivity temperature dependence of various composition NaI-NaN(CN)₂ solid electrolyte with (a) 5% NaI, (b) 10% NaI, (c) 15% NaI and (d) 20% NaI

Binary sodium solid electrolyte	Ionic conductivity (S cm ⁻¹)	Activation energy, E_a (eV)	Regression value, R^2
5NaI–95NaN(CN) ₂	$(2.16 \pm 0.34) \times 10^{-4}$	0.144	0.9517
10NaI–90NaN(CN) ₂	$(5.67 \pm 1.26) \times 10^{-4}$	0.133	0.9111
15NaI–85NaN(CN) ₂	$(2.98 \pm 0.68) \times 10^{-4}$	0.181	0.8709
20NaI–80NaN(CN) ₂	$(1.06 \pm 0.69) \times 10^{-4}$	0.256	0.8831

Table 1: Ionic conductivity and activation energy values of different NaI-NaN(CN)₂ binary solid electrolyte composition by weight percent

Impedance data were further examined to obtained insight regarding the polarisation of binary system solid electrolyte thru dielectric behaviour study. In this study, two parameters are taken into consideration. The first one is dielectric constant, ϵ_r which is the measurement of charge stored in the solid electrolyte while the second is dielectric loss, ϵ_i represents energy loss due to rapid collision of charge carriers. Both parameters could be calculated by the below equations:

$$\epsilon_r = \frac{Z_i}{\omega C_0 (Z_r^2 + Z_i^2)} \quad (4)$$

$$\epsilon_i = \frac{Z_r}{\omega C_0 (Z_r^2 + Z_i^2)} \quad (5)$$

Z_i and Z_r are the imaginary and real impedance which obtained from the Cole-cole plot; ω represented by angular frequency where it is easily calculate by the formula $2\pi f$, f is frequency in Hz; C_0 is noted by permittivity in free space which equal to $\epsilon_0 A/t$, ϵ_0 is the Permittivity constant 8.85×10^{-12} F m⁻¹, A is sample's surface area while t is thickness of sample.

Interdependent relationship between dielectric permittivity and frequency are displayed in Fig. 4 and Fig. 5. It could be deduced that both dielectric constant, ϵ_r and dielectric loss, ϵ_i

decreased monotonically as the frequency increases. High values of dielectric constant and dielectric loss at lower frequency region are accounted to mobile charges at the electrode and electrolyte interface had accumulated [17], [23] since space charge polarisation process had occurred [24] leading to high capacitance. The binary system solid electrolyte is confirmed to exhibit non-Debye in nature as in agreement with some authors [25].

values at low frequency region. This further supports the fact that the system contains optimum mobile ions that increases the amount of stored charges thus facilitated in fast Na⁺ ions migrations. Samples containing higher concentration of NaI salt have lower dielectrics values as re-association of ions have occurred and also due to fewer polarisation compared to 10 wt.% of NaI sample.

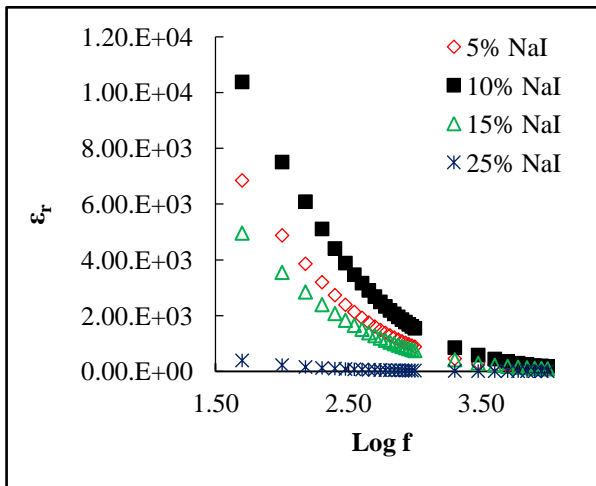


Fig. 4. Dielectric constant of NaI-NaN(CN)₂ binary system solid electrolyte at various NaI salt content

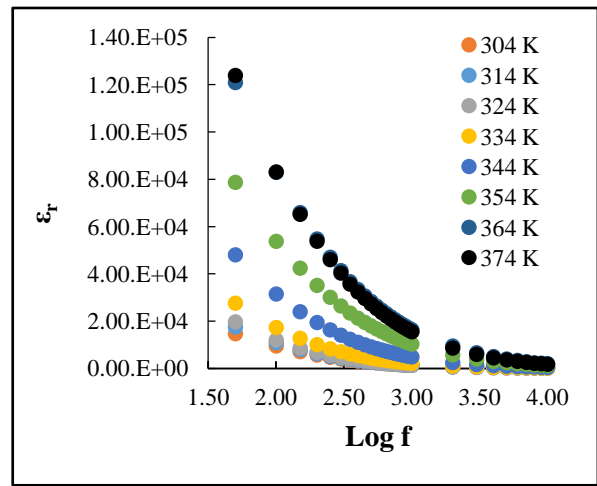


Fig. 6. Dielectric constant of 10NaI-90NaN(CN)₂ solid electrolyte at different temperature

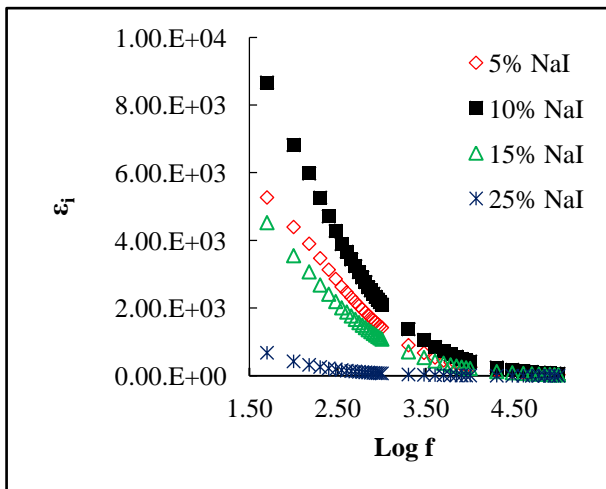


Fig. 5: Dielectric loss of NaI-NaN(CN)₂ binary system solid electrolyte at various NaI salt content

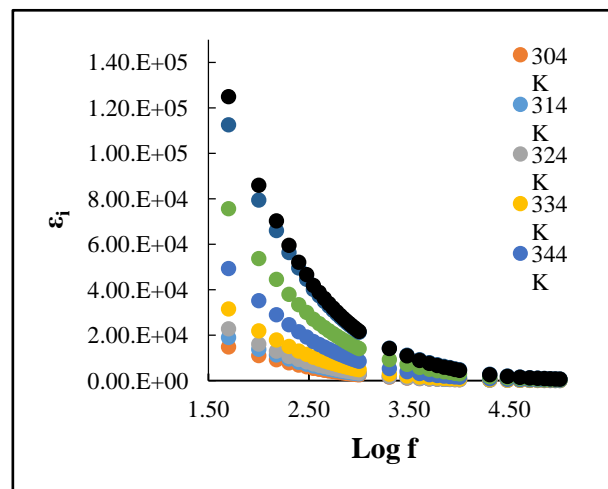


Fig. 7. Dielectric loss of 10NaI-90NaN(CN)₂ solid electrolyte at different temperature

Dielectric constant and dielectric loss continues to further decrease exponentially until reaching higher frequency region at 10 kHz and 100 kHz respectively. A declined in dielectric constant at the higher frequency range is attributed to high periodic reversal [23] of electric field within the interface. This causes decreased in contribution of charge carriers towards dielectrics thus also decreasing the polarisability of mobile ions.

Significant dispersion shift in dielectrics may be seen from Fig. 6 and Fig. 7 at higher frequency region as the temperature varied. Both dielectric constant and dielectric loss for 10NaI-90NaN(CN)₂ system follows the trend of directly proportional increase as temperature increases that are in consistent with Fig. 3 (b). The increase in dielectric constant is due to conductivity enhancement of the material as temperature elevated [17].

Apart from that, Fig. 4 and Fig. 5 also depicted the optimum composition binary system 10NaI-90NaN(CN)₂ shows the highest dielectric constant and dielectric loss

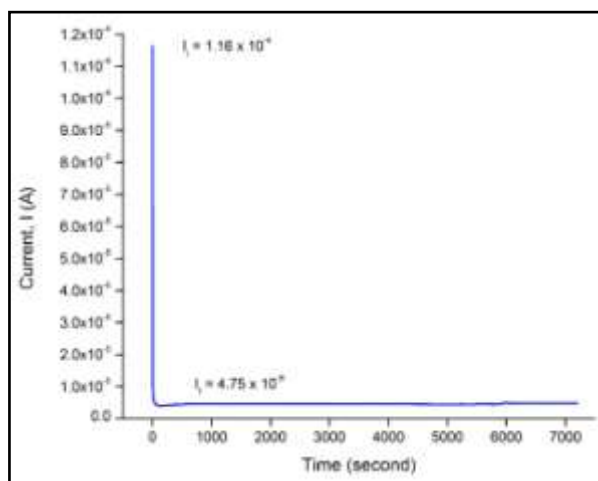


Fig. 8. Normalised current versus time of 10NaI-90NaN(CN)₂ solid electrolyte

Fig. 8 shows the plot of polarisation current against time for the highest conducting sodium solid electrolyte sample. It is seen that the current saturated at 4.75×10^{-6} A after 2 hours of applied normalised current. The resulting residual current upon saturation is due to electronic current. Based on Eq. 2, the value of ionic transference number (t_{ion}) is 0.96 which proven that the charge transport in the solid electrolyte is predominantly due to ions not electrons.

IV. CONCLUSION

This study has proven experimentally the possibility of dicyanamide sodium-based inorganic compound doped with sodium iodide to be used as solid electrolyte. Pelletised samples were successfully prepared by all solid-state reaction thru ball milling technique for two hours and milling speed of 200 rotation per minute. Highest ambient temperature ionic conductivity of $(5.67 \pm 1.26) \times 10^{-4}$ S cm⁻¹ was achieved with binary system composition of 10%NaI-90%NaN(CN)₂. A direct proportional relationship of ionic conductivity with increasing temperature from 304 K to 374 K also showed that the system obeys Arrhenius rule with smallest activation energy of 0.133 eV obtained. Both dielectric constant and dielectric loss were higher at the lower frequency region. Optimum composition of binary system solid electrolyte had highest dielectric values was assigned to the contribution of main charge carries. Overall conductivity in the sodium solid electrolyte was proven successfully due to ions from ionic transference number calculation.

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