

Effect of Choline Proline Ionic Liquid Additives on Hydrogen Evolution in Alkaline Water Electrolysis

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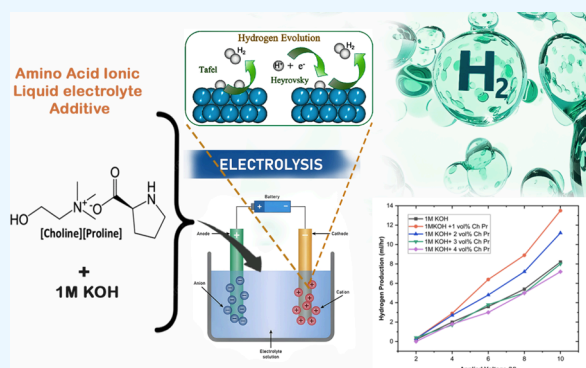
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ABSTRACT: Conventional hydrogen generation mostly depends on steam methane reforming (SMR), thereby contributing to greenhouse gas emissions. Alkaline water electrolysis using KOH is a promising method for green hydrogen production, but faces significant technical challenges such as high energy consumption and lower hydrogen production. Despite extensive research on various electrolyte modifications, a significant gap exists in the application of biodegradable and biocompatible amino acid-based ionic liquids as electrolyte additives. This study used a modified Hofman cell reaction setup for performing water electrolysis experiments. The selected ionic liquid (IL) was synthesized, and its chemical structure and purity were characterized by FT-IR and ¹H NMR spectroscopy. Subsequently, comprehensive electrochemical analyses, including linear sweep voltammetry, electrochemical impedance spectroscopy, Tafel analysis, and chronoamperometry, were conducted to investigate the electrochemical behavior of the system. The electrochemical analyses were conducted using a three-electrode setup in a 1 M KOH solution with 0 to 4 vol % choline proline [Cho][Pro] as an additive. Consequently, the decrease in charge transfer resistance (R_{ct}) was observed from 36.1 to 20.5 k Ω during electrochemical impedance spectroscopy. Moreover, the incorporation of [Cho][Pro] increases hydrogen production by 1.6-fold and reduces power consumption by 1.3-fold compared to pure 1 M KOH. The findings demonstrate that amino acid-based ionic liquids can significantly enhance the efficiency and sustainability of alkaline water electrolysis, thereby promoting the transition to sustainable energy systems and reducing dependence on fossil fuels.



1. INTRODUCTION

The increasing worldwide energy demand and the drive for sustainability are causing a paradigm shift in energy. One potential path is toward a hydrogen economy, and water electrolysis is unquestionably the cleanest means of producing green hydrogen.^{1–3} The amount of energy consumed worldwide has increased significantly. Global social advancement and economic expansion depend on energy, and nonrenewable energy sources such as fossil fuels now provide around 65% of the world's energy demands.⁴ The potential production of hazardous greenhouse gases, including CO₂, CO, SO_x, and NO_x from nonrenewable energy sources, has a detrimental impact on society and industry. Additionally, these gases contribute to environmental contamination and global warming. By the year 2050, there will be a 10 TW demand to produce renewable energy as a result of the dwindling supply of fossil fuels and the rise in CO₂ emissions.^{5–7}

As a carbon-free alternative energy source, hydrogen might be used in future energy systems. It has the benefits of being environmentally friendly and having high energy density,^{8,9} as

presented in Table 1. The possibility of reducing dependence on fossil fuels generated considerable interest in the potential for a clean and renewable energy source.^{10–13} The energy output of hydrogen is about 2.75 times greater compared to the output of hydrocarbon fuels.¹⁴ The demand for hydrogen is expected to increase almost eight times by 2050.¹⁵ However, certain challenges may hinder the effective use of hydrogen technology in the energy industry.^{14,16,17} One well-established and extremely promising technique to produce hydrogen is alkaline water electrolysis (AWE).^{18,19} Using an alkaline electrolyte as a conducting medium, this electrochemical process splits water molecules (H₂O) into hydrogen (H₂) and oxygen (O₂) gases.²⁰ Hydrogen generated by water electrolysis

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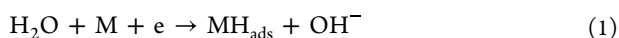
Table 1. Properties and Application of Common Fuels

fuel	LHV (MJ/kg)	HHV (MJ/kg)	energy density (MJ/kg)	applications
methanol	18.1	20	19.66	fuel cells, solvent, transportation fuel
diesel	42.5	44.8	42.5	heavy-duty vehicles, generators, marine engines
gasoline	44.5	47.5	44.5	automobiles, small engines, aerospace
ethane	47.8	51.9	53.2	feedstock for ethylene, fuel gas, chemical production
methane	50	55.5	55.6	natural gas, biogas, hydrogen production
hydrogen	119.9	141.9	120.1	fuel cells, energy storage, ammonia production

is considered truly green energy source, if the electricity driving the process is obtained from renewable sources.^{10,17,21} Hydrogen generation by electrolysis accounts for just 4% of total hydrogen production, indicating that water electrolysis is still too expensive due to low-energy efficiency and high expenditures.^{15,22–24} AWE is often preferred over proton exchange membrane (PEM) and solid oxide electrolysis (SOE) for hydrogen production due to its mature technology, lower cost, and operational stability under moderate conditions.²⁵ Unlike PEM, which requires expensive noble metal catalysts and highly acidic membranes, AWE uses cheaper and more durable electrodes and alkaline electrolytes, making it economically more feasible for large-scale applications. Compared to SOE, which operates at elevated temperatures requiring complex materials and intricate system management, AWE operates efficiently at lower temperatures, thereby reducing energy consumption and system complexity.^{26,27}

The water-splitting process usually occurs in multiple steps. The first step, also known as the Volmer step, is a primary dissociation that happens when adsorbed protons cover the metal surface, as explained by eq 1. The second step involves the catalytic recombination of the adsorbed intermediates (MH_{ads}), following the Tafel mechanism. Subsequently, the adsorbed species undergo electrodesorption through the Heyrovsky step, as described in eq 3.^{28–31}

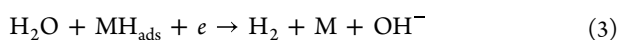
Volmer step (adsorption)



Tafel step (catalytic recombination)



Heyrovsky step (electrodesorption)



The performance of AWE, which uses KOH as an electrolyte, faces major technical problems, including lower electrolyte conductivity, lower energy efficiency, slow hydrogen evolution kinetics, undesirable side reactions, and less electrode stability.³² The use of potassium hydroxide (KOH) can lead to electrode degradation and decreased efficiency over extended operational periods.³³ The need for frequent maintenance and electrolyte replacement in KOH-based systems raises operational costs and reduces the overall sustainability of hydrogen production.³⁴

ILs have gained attention as beneficial additives in various electrochemical applications due to their unique properties, including high ionic conductivity, thermal stability, low vapor

pressure, a wide electrochemical window, and tunable properties.^{35–37} The addition of ILs to the electrolyte can enhance the efficiency of the hydrogen evolution reaction (HER) and improve the overall effectiveness of hydrogen production.³⁸ Commonly used ILs as electrolyte additives, based on imidazolium cations, possess environmental issues and toxicity, alongside their high costs.^{39–41} However, there is a lot of unexplored potential for amino-based ILs under these circumstances.

Choline-based amino acid ILs have emerged as viable alternatives to imidazole-based ILs due to their nontoxic, biocompatible, and cost-effective properties.^{42–48} Amino acid ILs (AAILs), such as [Cho][Pro], are characterized by strong ionic interactions and the capacity to form extensive hydrogen-bonding networks. These ILs consist of discrete ions, which enhance the ionic mobility and electrical conductivity within the electrolyte. This enhancement arises from functional groups present on both the choline cation (e.g., hydroxyl group) and the proline anion (e.g., carboxylate and amine groups). Recent research by Dean et al. demonstrates that the electrochemical properties and interfacial stability of choline-based ILs are significantly influenced by the nature of the anion. In electrolyte systems where the anion forms strong hydrogen bonds with choline, the resulting IL exhibits markedly improved thermodynamic stability and a more stable interfacial structure.⁴⁹ Choline-based ILs also display considerable stability and enhanced electrocatalytic activity in alkaline environments, particularly for the HER. Protchenko et al. reported that anodic treatment of nickel electrodes in these ILs promotes electropolishing, which in turn improves HER performance.⁵⁰ Furthermore, Gomes et al. provided additional evidence supporting the stability of choline-based ILs in aqueous electrolytes, confirming their suitability for electrochemical applications without significant side-product formation.⁵¹ Moreover, studies have demonstrated that choline-based ILs paired with amino acid anions, such as L-histidine and L-cysteine, maintain high stability and electrochemical efficiency. Aslam et al. observed that these ILs retain their stability and functionality for up to 72 h under dynamic conditions.⁵² Additionally, Ott et al. highlighted their excellent thermal stability and ionic conductivity.⁵³

This research investigated advanced electrolyte compositions to enhance the hydrogen production rate and examined the effect of [Cho][Pro] as an electrolyte additive in a 1 M KOH solution for AWE. Based on previous studies, a quantum chemical approach (COSMO-RS) was employed to evaluate prospective AAILs as electrolyte additives.^{54–56} According to Wlazlo et al., selecting potential ILs through experimental methods presents considerable challenges, including high cost and time consumption.⁵⁷ To overcome these challenges and minimize the costs associated with extensive experimental trials, the COSMO-RS method was employed. This computational technique provides critical insights into the physicochemical properties of ILs, facilitating effective prescreening before experimental validation.

2. MATERIALS AND METHODS

2.1. Chemicals. All of the chemicals, including L-proline, choline hydroxide solution, acetonitrile, graphite powder, and paraffin oil, were procured from Sigma-Aldrich, USA. [Cho]-[Pro] was synthesized by combining L-proline [(C₅H₈NO₂)[−]], acting as the anion, with choline [(C₅H₁₄NO)⁺] obtained from choline hydroxide solution (C₅H₁₅NO₂), which acted as the

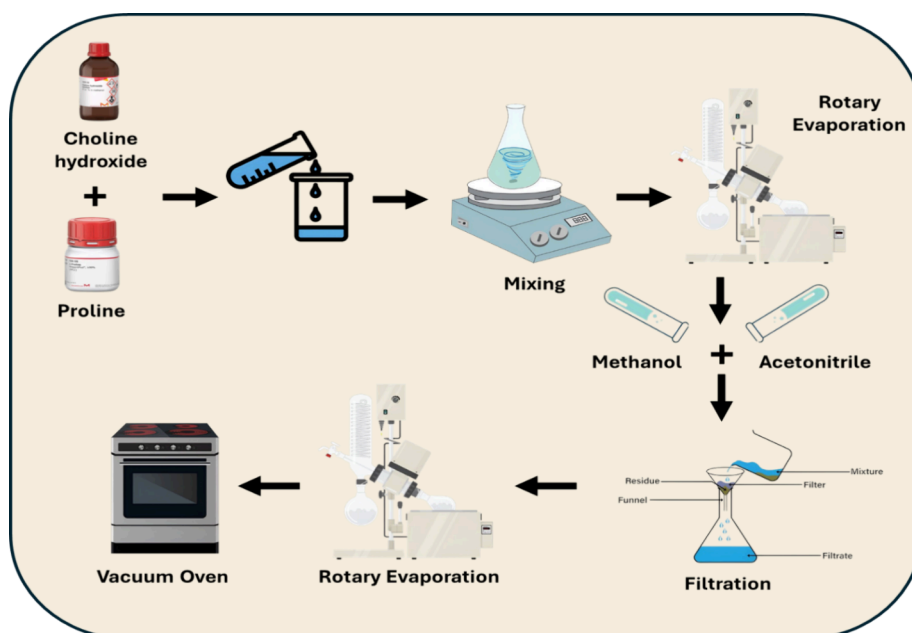


Figure 1. Synthesis process of choline proline IL.

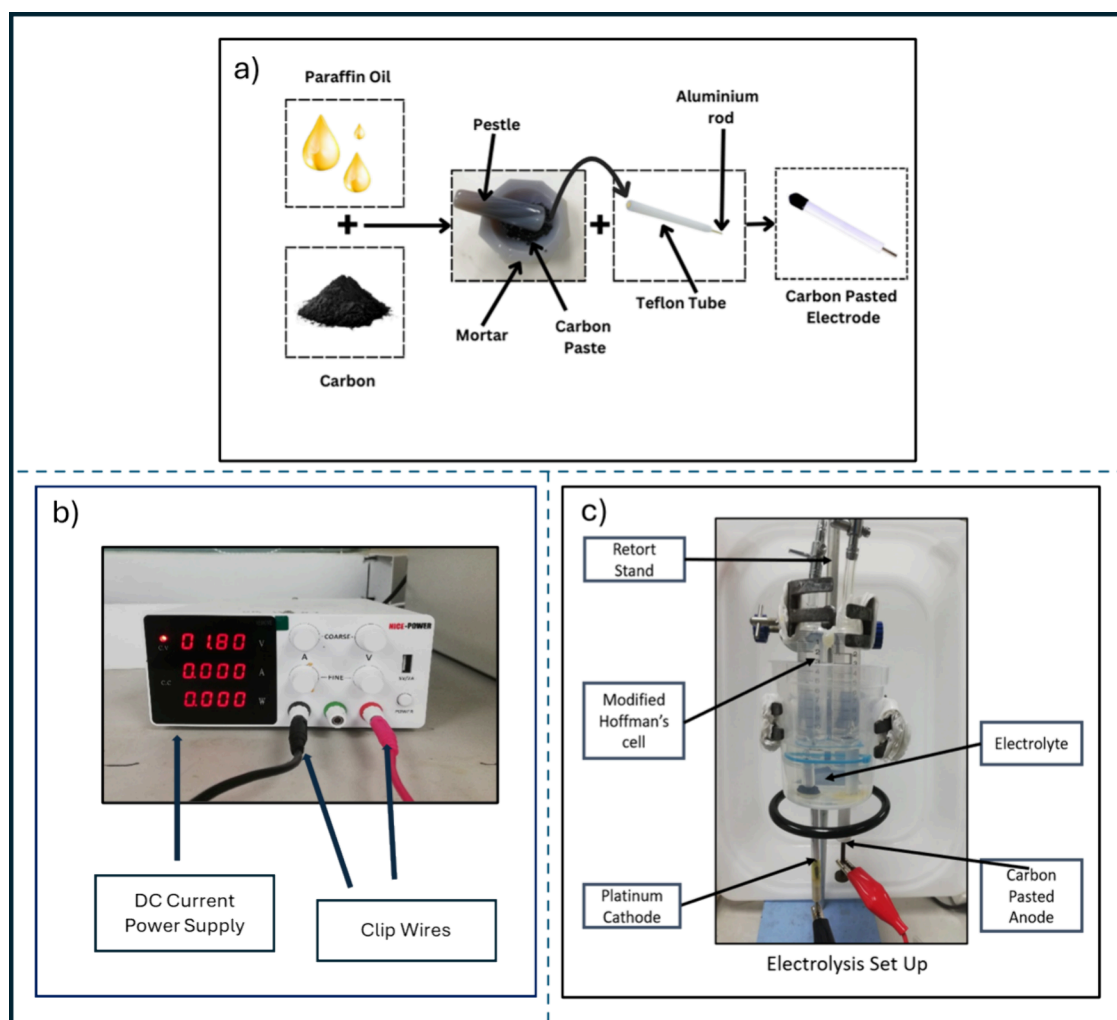


Figure 2. (a) Schematic illustration of the preparation process for the carbon paste electrode. (b) DC power supply used for electrochemical experiments. (c) Modified Hofman electrolysis setup employed for hydrogen production experiments

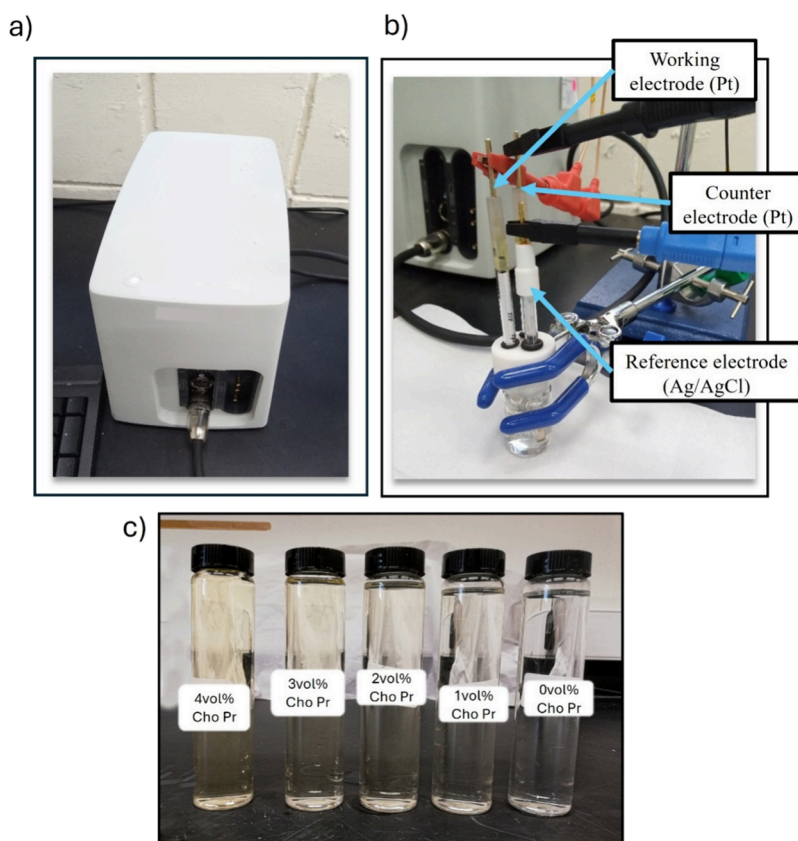


Figure 3. (a) Autolab potentiostat. (b) Three-electrode system. (c) 1–4 vol % samples of [Cho][Pro] in 1 M KOH.

cation. Methanol (Millipore, USA) and acetonitrile were used in the synthesis to precipitate excess amino acids. A carbon-paste electrode was prepared by using a paste of graphite powder and paraffin oil as a binder. The water-splitting experiments utilized a modified Hofman cell, with 0 to 4 vol % of [Cho][Pro] as an electrolyte additive in 1.0 M potassium hydroxide (MERCK, Germany). All reagents were of analytical grade and used without further purification. The materials were selected based on purity, availability, and suitability for experimental objectives, ensuring reliability and reproducibility in investigating the effect of AAILs as electrolyte additives for hydrogen production.

2.2. IL Screening. A quantum chemical technique was employed in this research to screen out the potential AAILs as an electrolyte additive.^{54–56} The COSMO-RS software was used to estimate the thermodynamic characteristics of AAILs, as it is not practically feasible to choose the possible ILs by experimental methods because of the time-consuming and costly nature of the process.^{58–61} The anions, cations, and water structures were created using TURBOMOLE version 21.0.0 (TmoleX) and the triple-valence polarized basis set (TZVP) program package. By measurement of the properties such as capacity, reliability, activity coefficient, and σ -profiles obtained, the AAIL with the highest suitability in water was chosen as an electrolyte additive.

2.3. IL Synthesis. The synthesis of [Cho][Pro] was carried out following the procedure described in previous studies.⁶² An equimolar ratio of choline hydroxide (26.34 g), $[(C_5H_{14}NO)^+]$, and L-proline $[(C_5H_8NO_2)^-]$ (11.51 g) was taken to start the neutralization reaction. This neutralization process was carried out by stirring the mixture at a constant room temperature for a time duration of roughly 48 h. A rotary

evaporator was used to evaporate the water once the stirring operation was finished, with low pressure and an evaporation process temperature of 80 °C. After that, methanol and acetonitrile were added in a 1:9 ratio, which allowed the excess amino acid to precipitate before finally filtering the liquid. Following the filtration, the [Cho][Pro] filtrate was dried using a vacuum oven for about 24 h and a rotary evaporator for 1 h, both of which were run at a temperature of 70 °C. The whole synthesis process of [Cho][Pro] is displayed in Figure 1.

2.4. Material Characterizations. The characterization of [Cho][Pro] was conducted using Fourier transform infrared spectroscopy (FTIR, Model: PerkinElmer FTIR Frontier) to assess the presence of functional groups. Proton Nuclear Magnetic Resonance Spectroscopy (1H NMR) was employed to further characterize the structure of [Cho][Pro]. A Bruker Advance DRX-400 spectrometer was used to record H NMR spectra using deuterium oxide (D_2O) as the solvent and at a proton frequency of 400 MHz. Furthermore, thermogravimetric analysis (TGA) was conducted to evaluate the thermal stability of synthesized [Cho][Pro]. The analysis utilized TGA (PerkinElmer, Model STA6000), with data processed through Pyris software. Approximately 1 mg of the IL sample was precisely placed into a crucible pan. The specimen was subsequently raised from ambient temperature to 500 °C at a uniform heating rate while subjected to a continuous flow of nitrogen gas at a rate of 19.8 mL/min. This measure was implemented to prevent oxidation and to preserve an inert environment.

2.5. Electrode Preparation. The carbon-pasted electrode was fabricated by mixing 0.4 g of graphite powder with an appropriate quantity of paraffin oil. Next, a small amount of the resultant paste was collected and placed at the other end of a 3

mm internal radius Teflon tube. This process was repeated until the paste was completely compacted within the Teflon tube to eliminate the possibility of a short circuit. An electrical connection was established using a brass rod that was connected directly to the paste, as shown in Figure 2a. To achieve this, a brass rod was inserted into the Teflon tube to an appropriate depth.

2.6. Electrolysis Setup. The electrolysis experiment was performed using a modified Hofman cell reaction setup, as shown in Figure 3c, where a carbon-paste electrode (CPE) was used as the anode and a platinum (Pt) electrode was used as the cathode. The production of hydrogen gas was recorded every 10 min alongside the current density J . For every run of the experiment, new CPE was prepared. The distance between the two electrodes and other parameters remained constant throughout the experimental series.

The power consumption in kWh/kg H_2 was measured by using experimental data, which included the volume of hydrogen produced, the observed current reading, and the voltage during the experiment. The formula used to calculate the power consumption per unit mass of hydrogen generated is provided in eq 4:

$$P = \frac{(I \times V) \times \left(\frac{1 \text{ kW}}{1000 \text{ W}}\right)}{\left(Q \times \left(\frac{1 \text{ m}^3}{1 \times 10^{-6}}\right)\right) \times \rho_{H_2}} \quad (4)$$

where P is power consumption per mass of hydrogen produced (kWh/kg of H_2), I is current reading (A), V is supplied voltage (V), Q is hydrogen production rate (mL/h), and ρ_{H_2} is density of hydrogen gas at STP (0.08375 kg/m³).

2.7. Electrochemical Analysis. Electrochemical analysis of synthesized [Cho][Pro] was performed using the linear sweep voltammetry technique to assess the current response of the system with an Autolab PGSTATION128N Potentiostat (Metrohm, Norway). A three-electrode system was used, where platinum electrodes were used as working electrode (WE) and counter electrode (CE), while Ag/AgCl was used as reference electrode (RE), as presented in Figure 3b. The voltage range was set to be from 0 to -1 V with a scan rate of 0.1 V/s.

Electrochemical impedance spectroscopy (EIS) was used with a frequency response analyzer (FRA) to assess electrolyte resistance using a three-electrode system. To examine the effect of the IL concentration on conductivity, electrolyte solutions were formulated with different concentrations of ILs. Impedance tests were performed in a frequency spectrum from 100 kHz to 0.1 Hz. To achieve a linear electrochemical response, the amplitude of the alternating current (AC) signal was meticulously calibrated to 10 mV, with 10 frequency points recorded for each decade. This method allowed an extensive examination of the system's behavior across a broad spectrum of frequencies. The acquired impedance measurements were then fitted to an analogous circuit model. The solution resistance (R_s) was determined using the optimal circuit model, which demonstrated minimal inaccuracy. The real component of the impedance (Z') at the high-frequency intercept, directly reflecting the electrolyte resistance, was derived from the raw impedance data. This approach allowed a comparative examination of electrolyte resistance relative to IL concentration

3. RESULTS AND DISCUSSIONS

COSMO-RS was employed to conduct advanced screening of AAILs, focusing on essential physicochemical properties, including σ -profiles and capacity reliability. To enhance computational efficiency, the AAILs were represented as discrete molecules with equimolar fractions in the COSMO-RS calculations.

The σ -profiles of water with various AAILs such as choline proline [Cho][Pro], choline glycine [Cho][Gly], choline serine [Cho][Ser], choline alanine [Cho][Ala], choline lysinate [Cho][Ly], choline leucinate [Cho][Leu], and choline asparagine [Cho][Asp] were examined. The integration of σ -profile probability distributions offers essential insights into the compatibility of cations and anions with water. The σ -profile graph is categorized into three distinct regions: H-bond donor ($\sigma < -1 \text{ e}/\text{\AA}^2$), nonpolar ($-1 \text{ e}/\text{\AA}^2 < \sigma < 1 \text{ e}/\text{\AA}^2$), and H-bond acceptor ($\sigma > 1 \text{ e}/\text{\AA}^2$). Figure 4 illustrates that the choline

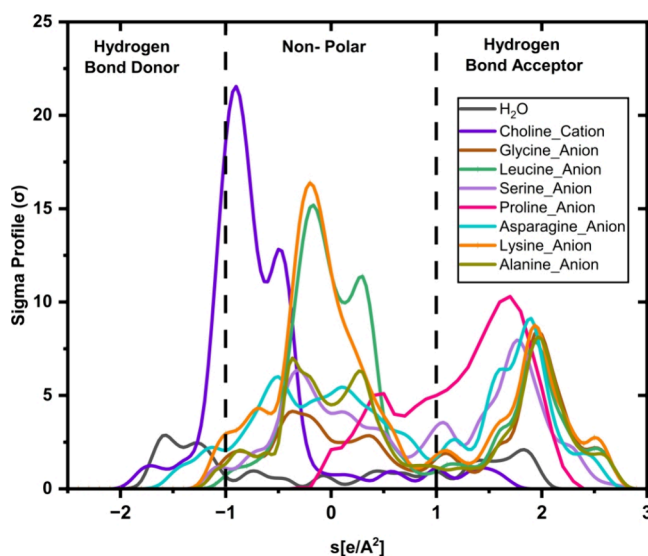


Figure 4. Sigma profiles of selected cations and anions.

cation displays a notable peak in the H-bond donor region, suggesting its capacity to engage with water molecules at their H-bond acceptor sites. In contrast, the anions originating from glycine, proline, serine, and alanine exhibit significant peaks in both the nonpolar and H-bond acceptor regions. This distribution suggests that these anions tend to interact with hydrogen-bond donor molecules. The observed peak for water molecules in the H-bond donor region supports the likelihood of strong interactions between these ions and water. This interaction pattern highlights the favorable water-soluble properties of these AAILs.

To predict the compatibility, solubility, and stability of ILs in water systems, we measured their capacity reliability. A higher value of capacity reliability indicates that the IL is suitable for addition to water.^{63,64} The capacity reliability of these AAILs was assessed using the "IL Screening" feature in the properties panel of COSMO-RS. In the screening process, L-proline, glycine, serine, lysine, leucine, asparagine, and L-alanine were employed as different amino acid anions, while choline hydroxide acted as the cation. Figure 5 illustrates the capacity reliability values of the choline cation in combination with amino acids as anions, which affect the water solubility. The order of AAILs according to their capacity reliability was as

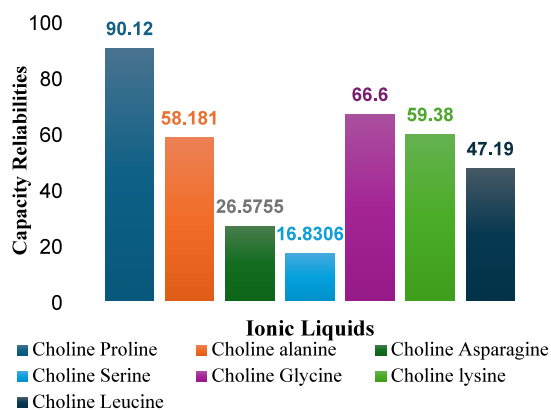


Figure 5. Predicted capacity reliabilities of the studied ILs using COSMO-RS.

follows: [Cho][Pro] > [Cho][Gly] > [Cho][Ly] > [Cho]-[Ala] > [Cho][Leu] > [Cho][Asp] > [Cho][Sr]. Since the cation was fixed during this screening procedure, the only factor affecting AAILs solubility in water was the amino acid anions. These results suggest that [Cho][Pro] is the most effective, whereas [Cho][Sr] and [Cho][Asp] exhibit lower effectiveness compared to the other ILs in water-based electrolyte systems.

FTIR (PerkinElmer FTIR Frontier) analysis of synthesized [Cho][Pro] was performed to confirm the structure and identify the functional groups. The peaks seen at 3340 and 3225 cm^{-1} correspond to the existence of $-\text{NH}_2$ stretching and $-\text{OH}$ stretching, respectively. Furthermore, the FTIR spectra clearly exhibit both $-\text{COO}^-$ -stretching and $-\text{COO}^-$ -twisting. The band associated with $-\text{COO}^-$ stretching is clearly visible at a peak at 1574 cm^{-1} , while the band associated with $-\text{COO}^-$ twisting is seen at a peak at 1478 cm^{-1} . Thus, the peaks corresponding to the synthesized [Cho][Pro] are observed when comparing the FTIR spectra of pure [Cho]-[Pro] with those shown in Figure 6b, as referenced in the paper by Zhang et al., which illustrates the FTIR spectra of pure [Cho][Pro] and confirms its structure in accordance with previous studies.^{43,65}

To further characterize the structure of the synthesized [Cho][Pro], ^1H NMR was performed. The analysis of the ^1H NMR spectrum of synthesized [Cho][Pro] indicates significant chemical shifts associated with different proton environments in the molecule. The spectrum displays distinct peaks attributable to the pyrrolidine ring of proline, the trimethylammonium group ($\text{N}-(\text{CH}_3)_3$), the $\text{N}-\text{CH}_2-$ group, and additional methylene ($-\text{CH}_2-$) groups. The purity and characterization of the synthesized [Cho][Pro] were confirmed by comparing its spectrum with that of pure [Cho][Pro] reported in reference Figure 7.⁶⁵

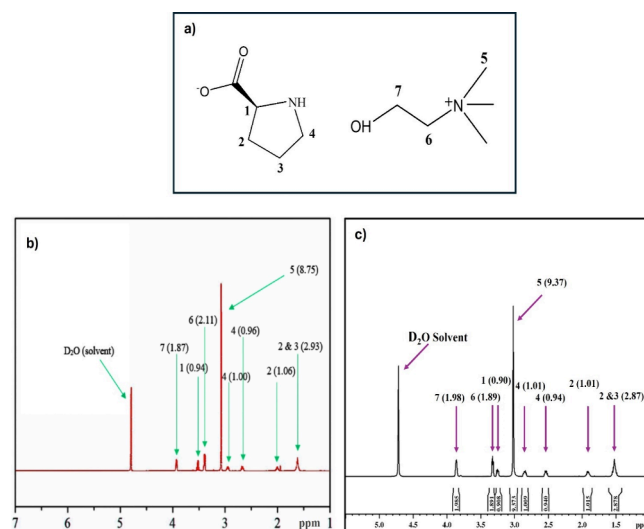


Figure 7. (a) Chemical structure of [Cho][Pro]. (b) ^1H NMR spectrum of pure [Cho][Pro]. Figure adapted with permission from ref 65 Licensed under CC BY 4.0. Copyright 2019 MDPI. (c) ^1H NMR spectrum of synthesized [Cho][Pro].

The peak at 3.0–3.1 ppm (Peak 5, integration 9.37) in our spectrum corresponds closely with the strong signal observed in the pure sample (integration 8.75), which is attributed to the nine protons of the $\text{N}-(\text{CH}_3)_3$ group in choline. Additional significant signals, including those at 3.5–3.6 ppm

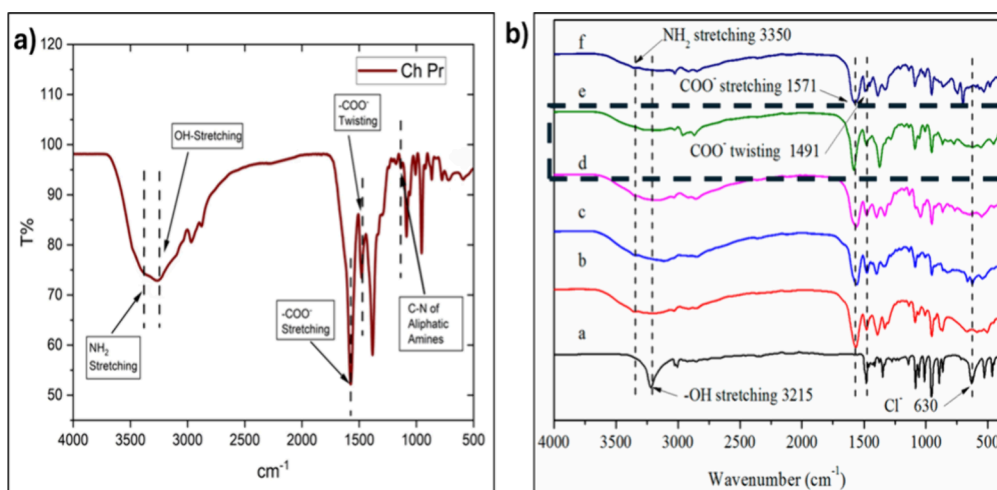


Figure 6. (a) FTIR spectrum of synthesized choline proline [Cho][Pro]. (b) FTIR spectra of choline-based ILs reported in the literature [Cho][Cl], [Cho][Gly], [Cho][His], [Cho][Ser], [Cho][Pro], and [Cho][Phe]. This figure is was adapted with permission from ref 65 Licensed under CC BY 4.0. Copyright 2019 MDPI.

peak 7, show the CH_2 group, while peak 6 at 3.35 ppm was assigned to the $\text{N}-\text{CH}_2$ group of choline, and 1.01 ppm (peak 2) and 2.87 ppm (peaks 2 and 3 combined) align closely with the peaks identified in the pure $[\text{Cho}][\text{Pro}]$ spectrum. The spectrum demonstrates reasonable agreement with the pure sample; however, little variation in chemical shifts and integrations may arise from variations in the concentration, pH, or instrument calibration. The D_2O peak is reliably detected at approximately 4.7–4.8 ppm in both spectra, although there are very small variations in peaks, which could suggest the presence of trace impurities from synthesis solvents such as methanol or acetone. However, the overall spectral pattern and peak distribution provide strong evidence for the successful synthesis and high purity of our $[\text{Cho}][\text{Pro}]$ sample.

The TGA of $[\text{Cho}][\text{Pro}]$ provided essential information regarding the thermal properties of $[\text{Cho}][\text{Pro}]$. The compound demonstrates significant stability at temperatures approaching 100 °C, retaining nearly 100% of its initial weight. A notable onset of decomposition occurs at approximately 150 °C, indicated by a dotted vertical line, succeeded by a rapid weight loss from 150 to 250 °C. At 300 °C, the weight percentage nears zero, indicating total decomposition with negligible residual mass as presented in Figure 8. The TGA profile is essential for analyzing the thermal stability of $[\text{Cho}][\text{Pro}]$, particularly in electrochemical applications such as water electrolysis systems.

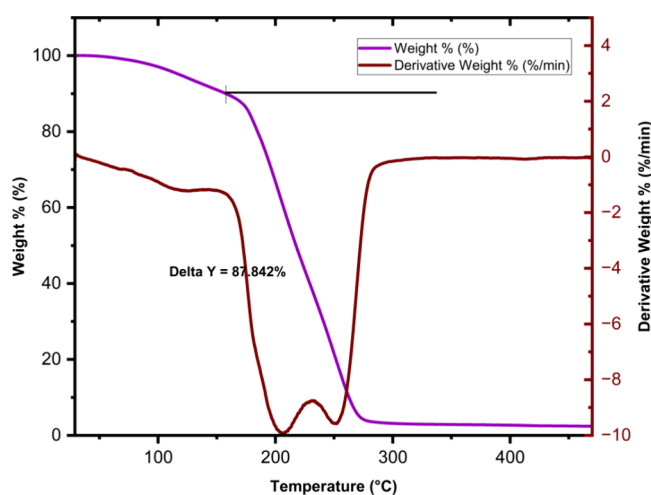


Figure 8. TGA curve for $[\text{Cho}][\text{Pro}]$, showing mass loss as a function of temperature.

The electrocatalytic response of the HER was investigated by using linear sweep voltammetry (LSV). Figure 10b shows the current response at the applied potential for different concentrations of $[\text{Cho}][\text{Pro}]$ in a 1 M KOH solution, measured at 25 °C with a scan rate of 0.1 V/s. Measurements were performed over a potential range of -1 to 0 V in 1 M KOH, both in the absence and presence of varying volume percentages of $[\text{Cho}][\text{Pro}]$. LSV measurements were conducted using the parameters summarized in Table 2. It was observed that the addition of 1 vol % $[\text{Cho}][\text{Pro}]$ IL to the 1 M KOH solution significantly increases the current density to approximately $-1.4 \text{ mA}/\text{cm}^2$. However, 4 vol % $[\text{Cho}][\text{Pro}]$ yields a lower current density of $0.75 \text{ mA}/\text{cm}^2$, while 2 vol % gives $0.72 \text{ mA}/\text{cm}^2$. In contrast, both the pure 1 M KOH solution and the addition of 3 vol % $[\text{Cho}][\text{Pro}]$ result in a similar current density of around $0.65 \text{ mA}/\text{cm}^2$. The 1 vol %

Table 2. Experimental Parameters Used for LSV Measurements

parameters	value	units
start potential	0	V
stop potential	-1	V
scan rate	0.1	V s^{-1}
final potential	$+1.0$	V
step potential	0.00244	V

curve shows the highest performance among all concentrations, indicating a reduction in overpotential for HER. At 0.5 V vs RHE, the current density increased to $-0.4 \text{ mA}/\text{cm}^2$, compared to just $-0.2 \text{ mA}/\text{cm}^2$ for pure KOH at the same potential. The observed shift indicates a reduction in the activation energy barrier for HER, most likely caused by the combined influence of choline and proline ions altering the interface between the electrode and electrolyte.

The shape of the LSV curves, particularly the steepness of the current rise, provides information about the reaction mechanism.^{66,67} The steeper slope observed for the 1 vol % $[\text{Cho}][\text{Pro}]$ indicates a more favorable reaction pathway, possibly due to enhanced proton transfer or altered electrode surface properties that facilitate the rate-determining step of HER.^{68,69} These findings suggest that the $[\text{Cho}][\text{Pro}]$ additive likely impacts both the Volmer step (initial proton adsorption) and the subsequent Heyrovsky or Tafel steps (hydrogen desorption) of the HER mechanism. The enhanced performance may be due to the choline element modifying the electric double-layer structure, while zwitterionic proline could increase local proton availability at the electrode surface, as mentioned in prior studies.^{70,71} The observed bending and fluctuations in the LSV curves after the initial rise in current density are primarily attributed to hydrogen gas bubble accumulation on the electrode surface during HER.⁷² These bubbles temporarily block active catalytic sites, causing a dip or plateau in current, which increases after bubble detachment.⁷³

Furthermore, Tafel analysis was performed to determine the kinetics and reaction rate of HER. Figure 10c shows that the addition of $[\text{Cho}][\text{Pro}]$ facilitates HER. The value of Tafel slope reduced from 188 to 139 as expected, indicating that adding 1% $[\text{Cho}][\text{Pro}]$ enhances catalytic activity toward HER. This enhancement may be due to the synergetic effect of the $[\text{Cho}][\text{Pro}]$ molecule. The zwitterionic character of proline may help to increase ionic conductivity and proton availability, whereas the quaternary ammonium group of choline probably changes the electric double-layer structure at the electrode–electrolyte interface, enabling proton transfer.^{74,75} A schematic representation of the proposed interfacial enhancement mechanism is provided in Figure 9. Additionally, the observed reduction in Tafel slope suggests a potential shift in the rate-determining step of the HER mechanism, possibly from the Volmer to the Heyrovsky step.⁷⁶ It was noted that while increasing $[\text{Cho}][\text{Pro}]$ concentration from 2 to 4 vol %, the Tafel slope starts increasing to 199 and 222, respectively, indicating mass transfer limitations at high concentrations.

The charge transfer and electrolyte resistance of the electrolyte were analyzed using EIS at varying electrolyte concentrations. In the Nyquist plot, the Y-axis component ($-Z''$) represents the imaginary part of the impedance, while the X-axis component (Z') corresponds to the real part of the solution resistance. The presence of semicircular arcs in the plot suggests the occurrence of charge transfer events at the

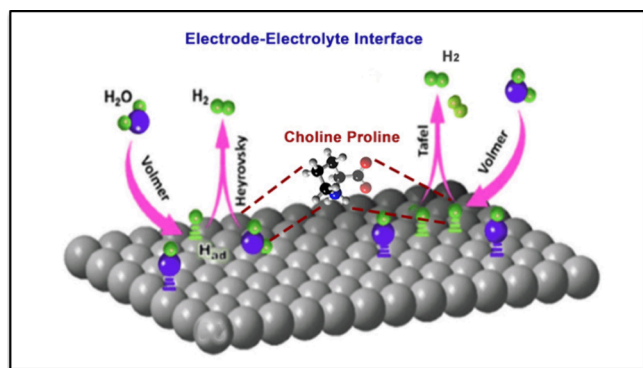


Figure 9. Illustration of the role of choline proline in HER at the electrode–electrolyte interface.

interface between the electrode and the electrolyte. As the diameter of semicircles represents the R_{ct} , the smaller diameter of the semicircle can be seen after the addition of [Cho][Pro] as compared to the 1 M KOH solution, indicating the ability of [Cho][Pro] to reduce R_{ct} .

Tafel plots were constructed from the polarization curve data, as shown in Figure 10d, and analyzed by using the Tafel equation (eq 5):

$$\eta = a + b \log j = \frac{2.3RT}{\alpha F} \log j_0 + \frac{2.3RT}{\alpha F} \log j \quad (5)$$

Here, the overpotential is represented by η , and the intrinsic rate of electron transfer is represented by the intercept, which is connected to the exchange current density (j_0). The charge transfer coefficient is denoted by α , and the Tafel slope, b , shows how the current density (j) varies with overpotential (η). F is Faraday's constant (96485 C mol^{-1}), T is the

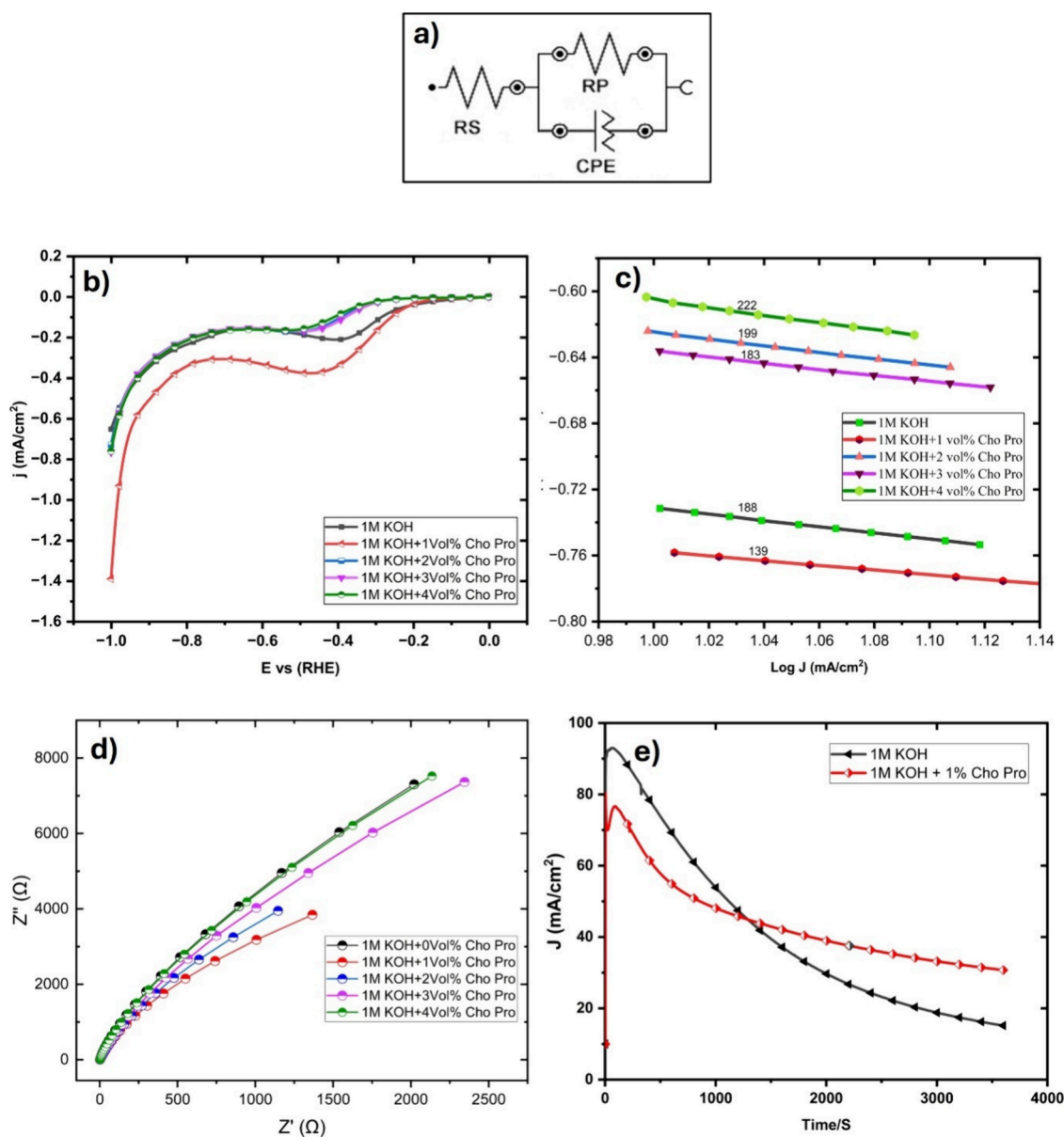


Figure 10. (a) Equivalent circuit used to fit EIS data. (b) LSV curves obtained at 25 °C. (c) Tafel slopes showing the effect of different [Cho][Pro] concentrations on HER kinetics in 1 M KOH. (d) Nyquist plots of 1 M KOH with different [Cho][Pro] concentrations as electrolyte additives. (e) Chronoamperometry results obtained at 25 °C for 1 h.

temperature in Kelvin, and R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$).

The EIS study demonstrates significant changes in the properties of the electrode–electrolyte interface with the incorporation of a minimal quantity of [Cho][Pro] into 1 M KOH. Results obtained after EIS measurements are indicated in Table 3. The solution resistance (R_s) significantly decreased

Table 3. Results Obtained from EIS after the Addition of 0–4 vol % of [Cho][Pro]

element	CPE ($\mu \text{ Mho} \cdot \text{s}^{\wedge} \text{N}$)	R_s ($\Omega \text{ cm}^2$)	R_{ct} ($\text{k}\Omega$)
1 M KOH	186	1.86	36.1
1 M KOH + 1% Cho Pro	283	1.06	20.5
1 M KOH + 2% Cho Pro	163	1.36	28.18
1 M KOH + 3% Cho Pro	164	1.93	32.4
1 M KOH + 4% Cho Pro	168	2.11	41.4

from $1.86 \Omega \text{ cm}^2$ in 1 M KOH to 1.06 and $1.36 \Omega \text{ cm}^2$ with the addition of 1 and 2 vol % [Cho][Pro], respectively, as shown in Figure 10d. This reduction indicates enhanced ionic conductivity at these concentrations, particularly at 1 vol %, which appears to be optimal. However, additional increments in [Cho][Pro] concentration result in a gradual rise in R_s values to 1.93 and $2.11 \Omega \text{ cm}^2$ at 3 and 4 vol % of [Cho][Pro], respectively. This trend indicates that moderate additions of [Cho][Pro] enhance ion transport, whereas higher concentrations could lead to increased electrolyte viscosity.⁷⁷ The values of the constant-phase element, which indicate nonideal capacitive behavior, demonstrate a notable increase from 186 to $283 \mu \text{ Mho} \cdot \text{s}^{\wedge} \text{N}$ with the addition of 1 vol % [Cho][Pro], suggesting an enhanced ability for charge accumulation at the interface and more effective charge distribution.^{78,79} The R_{ct} shows a comparable trend, declining from 36.1 to 20.5 $\text{k}\Omega$ with 1 vol % [Cho][Pro], then gradually rising to 28, 32.4, and 41.4 $\text{k}\Omega$ for 2, 3, and 4 vol % [Cho][Pro], respectively. The analysis of these parameters suggests that a concentration of 1 vol % [Cho][Pro] yields the best interfacial properties, promoting better charge transfer kinetics and superior electrochemical performance.

Stability analysis was carried out using chronoamperometric measurements at 25°C and -1.4 V using 1 vol % [Cho][Pro] IL in 1 M KOH and IL-free electrolyte. The stability and current response of the system were assessed for a 1 h duration. The first current density in a pure 1 M KOH electrolyte showed a sudden peak, reaching approximately 90 mA, followed by a rapid drop during the first 500 s, suggesting the formation of an electrochemical double layer and initial charge redistribution. After 3500 s, the current density showed a constant declining trend that finally stabilized at around 20 mA as shown in Figure 10e. This large current drop ($\Delta I = 70 \text{ mA}$) points to possible mass transfer constraints in the pure KOH solution and considerable electrode polarization. However, the electrochemical stability showed a significant increase when 1% IL was added to the KOH electrolyte. The first current spike was controlled to approximately 75 mA, suggesting that the IL modifies the dynamics of the electrode–electrolyte interface. More importantly, the following current decline curve showed a slower slope than pure KOH, stabilizing at around 32 mA after 3500 s ($\Delta I = 43 \text{ mA}$).

To investigate the increase in the amount of hydrogen production at different applied voltages (2, 4, 6, 8, and 10 V) during 1 h of experiment, a graph between hydrogen

production rate (mL/h) and applied voltage has been plotted. Experimental findings indicate an ongoing advancement in hydrogen production rates as the applied voltages increased from 2 to 10 V in the water electrolysis system. Figure 11

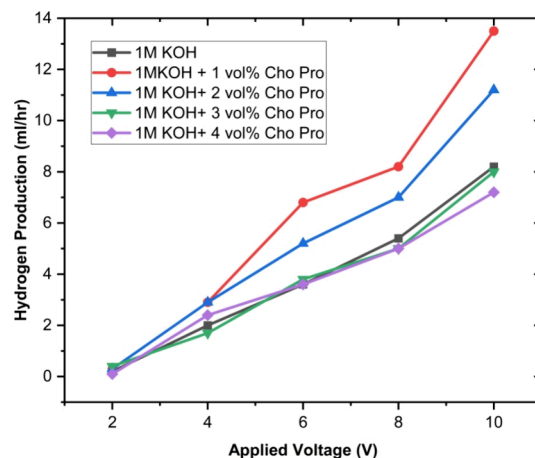


Figure 11. Hydrogen production rate measured at applied voltages ranging from 2 to 10 V during water electrolysis experiments

highlights the clear correlation between higher voltages and increased hydrogen production, mostly attributable to an increasing current density at the electrode surface. As the current density increases, it promotes an enhanced flow of electrons to the cathode, where they engage with the hydrogen (H^+) ions in the electrolyte. The increased electron flow at higher voltages results in more frequent and extensive electron transfers to H^+ ions, leading to enhanced hydrogen gas generation at the cathode surface.⁸⁰ ion of [Cho][Pro], which was 13.5, 11.2, and 8.2 mL/h, respectively. By comparing the hydrogen production rate, the maximum hydrogen produced at 1% [Cho][Pro] at the supplied voltage of 10 V was 13.5 mL/h. The overall trend indicates that increasing the concentration of [Cho][Pro] to 3 and 4 vol % does not enhance hydrogen production. Instead, higher concentrations of hydrogen appear to inhibit the hydrogen production rate. This observation can be attributed to the relatively high viscosity of choline proline, whereby increasing its volume percentage may hinder ion mobility within the electrolyte.⁷⁷ The expected increase in hydrogen production rates is supported by prior research indicating that IL cations may donate protons, thereby improving local proton availability at the catalyst surface.^{81,82} The formation of a H-bond network at the catalyst/IL interface promotes proton donation, thus improving the kinetics of the HER.⁸³

To investigate the relationship between hydrogen production rate and power consumption over a voltage range of 2–10 V, separate graphs were plotted for each concentration of [Cho][Pro] in KOH. Power consumption, expressed in kWh/kg H_2 , was calculated using experimental data, particularly the hydrogen production rate and the measured current during the experiment by applying eq 4. The optimum parameters in terms of maximum hydrogen production at the lowest power consumption were also calculated by comparing the results at each concentration of [Cho][Pro] in 1 M KOH solution. The hydrogen production rate (mL/h) is represented on the left y-axis, while power consumption is displayed on the right y-axis of the plot. Figure 12a–e presents the results of hydrogen production and power consumption at applied voltages of 2, 4,

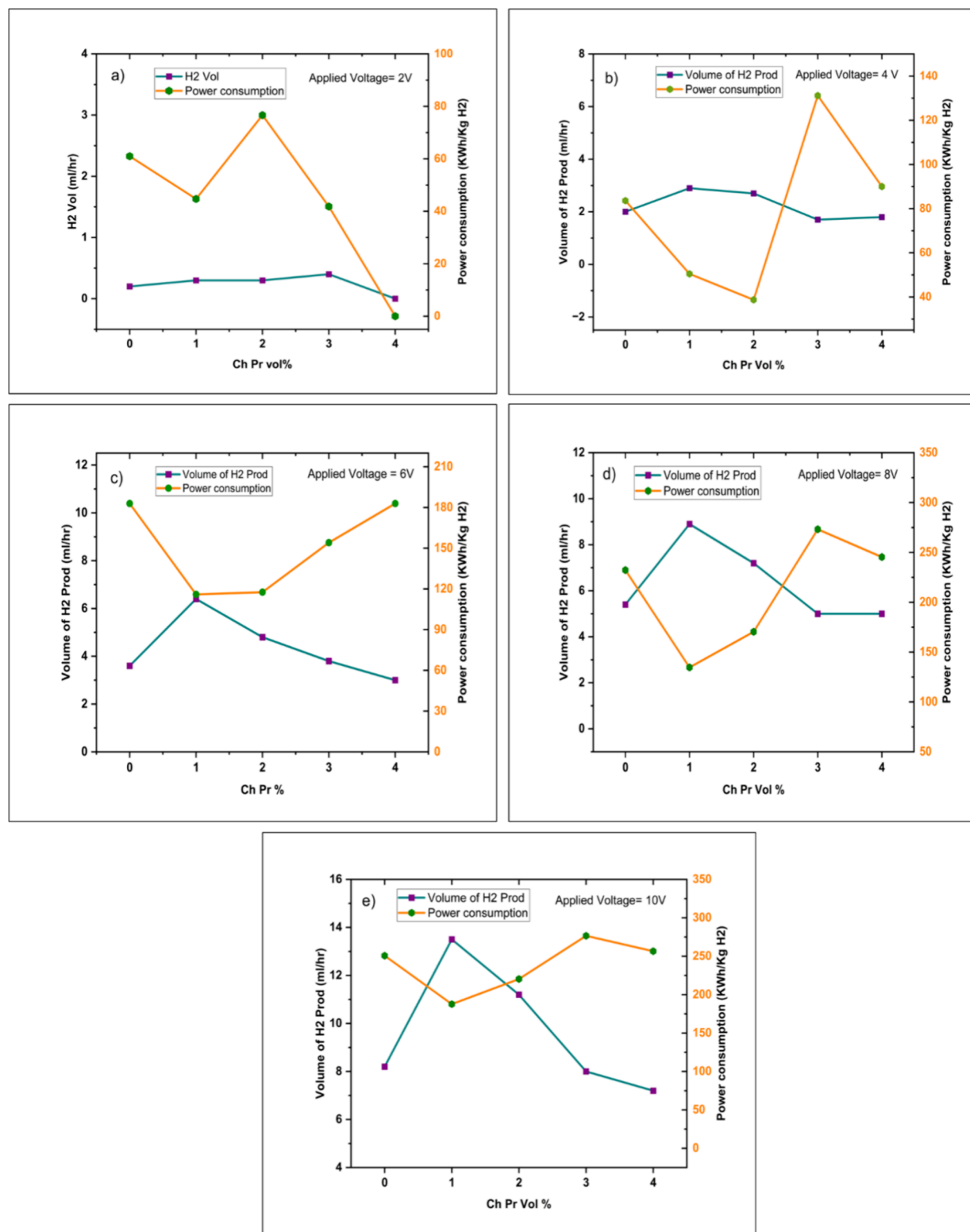


Figure 12. Correlation between hydrogen production rate and power consumption at applied voltages of (a) 2, (b) 4, (c) 6, (d) 8, and (e) 10 V.

6, 8, and 10 V, respectively. As shown in the graphs, the maximum hydrogen production at 10 V was achieved with a power consumption of 250.70 kWh/kg H₂. After the addition of 1 vol % [Cho][Pro], the maximum hydrogen production increased to 13.5 mL/h, with a reduced power consumption of 187.61 kWh/kg H₂. The observed correlation between H₂ production rates and power consumption trends indicates that

[Cho][Pro] influences both the kinetics of the HER and the overall cell impedance, as discussed above in electrochemical characterizations.

3.1. Gas Chromatography Analysis. The composition of the gas sample collected from the cathode during water electrolysis was analyzed by using a Clarus 580 gas chromatograph. A sample volume of 1.000 μ L was injected into the

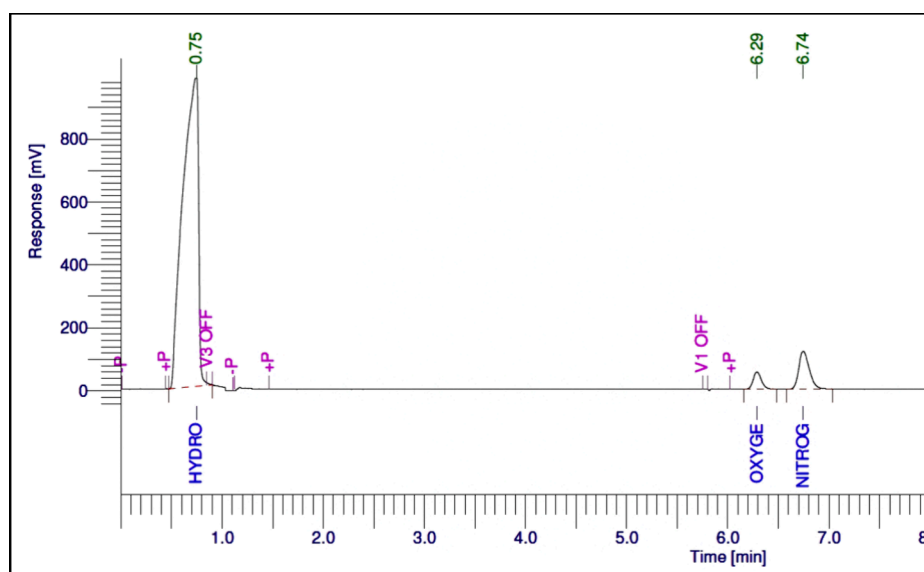


Figure 13. Gas chromatographic analysis of hydrogen gas evolved from 1 M KOH + [Cho][Pro] electrolyte at 25 °C.

system, and the analysis was performed with a sampling rate of 3.125 points/s over a total acquisition time of 12 min. The GC analysis of the cathodic gas sample yielded a chromatogram (Figure 13) showing distinct peaks for hydrogen, oxygen/argon, and nitrogen, with retention times of 0.75, 6.28, and 6.74 min, respectively. Hydrogen, the targeted gas of electrolysis, showed the highest peak area ($1.05 \times 10^6 \mu\text{V s}$), accounting for 89.92% of the normalized volume percentage (vol% Norm), confirming the efficient generation of hydrogen. The oxygen/argon peak was less prominent, with an area of $3.09 \times 10^5 \mu\text{V s}$ (2.64 vol % Norm), while the nitrogen peak, representing 7.44 vol % Norm, had an area of $8.72 \times 10^5 \mu\text{V s}$. The relatively low concentrations of oxygen and nitrogen suggest minor contamination of the air in the gas collection bag.

The sharp and well-separated hydrogen peak at 0.75 min indicates a high signal-to-noise (S/N) ratio, reflecting the efficiency of the chromatographic conditions for hydrogen detection. The GC-MS data of the gas sample collected during electrolysis, consisting of KOH + IL [Cho][Pro] electrolyte solution, indicate the hydrogen gas production at the cathode, with no detectable amount of volatile organic impurities. According to the findings, no peaks of volatile organic solvents were observed in the retention time window characteristic of the range 1.5–5.5 min. This confirms the absence of organic impurities, such as trimethylamine, methanol, or ethanol.

4. CONCLUSIONS

In this study, we use [Cho][Pro] as an electrolyte additive in KOH to improve the hydrogen production rate in AWE. To identify the most suitable IL, the COSMO-RS technique was employed as a screening tool to evaluate the various properties of seven AAILs. The σ -profile analysis revealed that the choline peak in the hydrogen-bond donor region facilitates interactions with water molecules at its acceptor sites. In contrast, the proline peak appears in both the nonpolar and hydrogen-bond acceptor regions, enabling contact with water molecules at the hydrogen-bond donor sites. Furthermore, capacity reliability results show that [Cho][Pro] is a more suitable IL in a water system.

Based on these computational studies, experimental research was conducted to validate the practical implications of our findings. The experimental study revealed a strong correlation between the applied voltage and hydrogen production in our electrolysis system. A rise in hydrogen production rate was observed as the voltage increased from 2 to 10 V. The addition of [Cho][Pro] as an electrolyte additive demonstrated beneficial, but its effectiveness was concentration dependent. The optimal performance was obtained with the addition of 1 vol % [Cho][Pro] in 1 M KOH at an applied voltage of 10 V, yielding a hydrogen production rate of 13.5 mL/h. This represents a significant improvement compared to 8.2 mL/h observed in the absence of the additive. However, higher concentrations of [Cho][Pro] (3 and 4 vol %) were less effective, hindering hydrogen production due to higher electrolytic viscosity. Electrochemical characterizations, including LSV and EIS, demonstrated that the addition of [Cho][Pro] reduces charge transfer and electrolyte resistances. This reduction leads to an increase in current density, and therefore, the hydrogen production rate is increased. This work highlights that the addition of a small amount of biodegradable ILs can be significantly beneficial for HER and potentially increases hydrogen production efficiency in industrial electrolyzers. The long-term stability and electrochemical performance of these biodegradable ILs require comprehensive research to assess their performance and scalability in continuous industrial operations. Future studies should explore a wider variety of AAILs with different combinations of cations and anions to uncover better options for hydrogen generation.

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Notes

The authors declare no competing financial interest.

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NOMENCLATURE

HER, Hydrogen evaluation reaction; ILs, Ionic liquids; Cho Pro, Choline proline; Cho Leu, Choline leucine; Cho Asp, Choline asparagine; Cho Gly, Choline glycine; Cho Sr, Choline serine; Cho Ala, Choline alanine; Cho Ly, Choline lysine; EIS, Electrochemical impedance spectroscopy; LSV, Linear sweep voltammetry; KOH, Potassium hydroxide; AAILs, Amino acid ionic liquids; CPE, Carbon-pasted electrode; CO₂, Carbon dioxide; CO, Carbon monoxide; SO_x, Sulfur oxides; NO_x, Nitrogen oxides; MH, Metal hydroxide; WE, Working electrode; CE, Counter electrode; RE, Reference electrode; Pt, Platinum; COSMO-RS, Conductor-like screening model for real solvents; H NMR, Nuclear magnetic resonance spectroscopy; FTIR, Fourier transform infrared spectroscopy; TGA, Thermogravimetric analysis; D₂O, Deuterium oxide; EIS, Electrochemical impedance spectroscopy; FRA, Frequency response analyzer; RHE, Reversible hydrogen electrode; Vol.%, Volume percent; R_{ct}, Charge transfer resistance; TW, Terawatts

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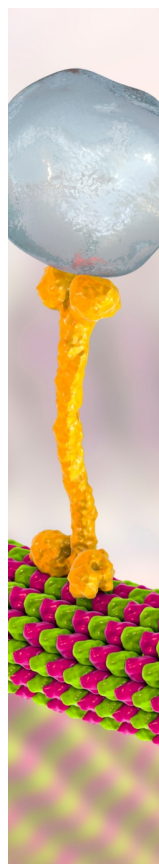
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