World Journal of Advanced Research and Reviews
eISSN: 2581-9615 CODEN (USA): WJARAI
Cross Ref DOI: 10.30574/wjarr
Journal homepage: https://wjarr.com/

(Research Article)

Ion-Chemistry-Driven Performance of Biocompatible Inorganic Salts for Aqueous Energy Storage

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World Journal of Advanced Research and Reviews, 2026, 29(02), 026-032

Publication history: Received on 18 December 2025; revised on 30 January 2026; accepted on 02 February 2026

Article DOI: https://doi.org/10.30574/wjarr.2026.29.2.0285

Abstract

The discovery of safe, sustainable, and biocompatible electrolytes is crucial in the development of aqueous energy storage devices. Natural inorganic salts have huge potential to replace standard electrolytes. These salts are nontoxic, environmentally compatible, and readily available in large quantities. However, minimal focus has been given to the electrochemical properties of these salts in the past. Salt chemistry is critical in the energy storage domain. This research article is primarily focused on the analysis of four naturally occurring salts: sodium chloride, potassium chloride, magnesium chloride, and calcium chloride in terms of using these salts for the development of aqueous electrolyte solutions in the field of energy storage devices. The article discusses the ionic conductivity of these salts as a way to determine each salt's suitability for electrical conduction in aqueous form. It further analyzes their charge-discharge characteristics towards determining and comparing thehir suitability for energy storage. A detailed analysis of the advantages and limitation of using monovalent or divalent salt chemistry in the aqueous-based electrolyte solution is critically analyzed as part of the results discussion.

Keywords: Inorganic salts; Energy storage; Electrolytes; Biocompatibility; Charge transfer

1. Introduction

Electrolytes play a key role in determining the safety, efficiency, and sustainability of electrochemical energy-storage systems(1). While significant progress has been made through the use of organic and ionic-liquid electrolytes, their real deployment in the real-world is often limited by toxicity, flammability, cost, and environmental persistence(2). These limitations have revived interest in aqueous electrolytes, which provide a natural advantage in terms of safety, cost, and scalability in manufacturing. Still, the limited electrochemical stability of water and the interplay of ion transport and interfacial phenomena remain challenges in aqueous systems as well(3).

In this context, it is clear that natural inorganic salts represent an intriguing but relatively uninvestigated class of electrolytes(4). In fact, salts such as sodium chloride, potassium chloride, magnesium chloride, and calcium chloride are ubiquitous in natural waters and are generally recognized as biocompatible(5) (6). Their long history of use in physiological systems suggests their natural compatibility with bio-derived materials and interfaces, making these salts promising candidates for the development of sustainable and bio-integrated energy storage devices(7). Despite their widespread availability, these salts are often viewed as model or benchmark electrolytes, with their electrochemical performance rarely assessed within a unified framework.

The performance of an electrolyte in an aqueous system is influenced not only by the concentration but also by the inherent properties of the ions, including their valency, ionic radii, charge density, and hydration structure(8). For instance, the performance of monovalent cations like Na^+ and K^+ is usually enhanced because of their higher ionic

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mobility, lower hydration energy, and the capacity to transport charge more efficiently, thus enhancing power density. On the other hand, the performance of divalent cations like Mg^{2+} and Ca^{2+} is often impaired because of their larger hydration shell, which may reduce ionic mobility, in addition to affecting the electrical double-layer structure and the electrode-electrolyte interface(9). Recent studies on supercapacitors, bioelectrochemical systems, and hybrid aqueous storage systems suggest that the selection of the electrolyte may play an important role in influencing the performance of the systems, including the internal resistance, rate capacity, cycle stability, and parasitic reactions(4) (10). However, it has been observed that comparisons of different studies on the performance of different aqueous systems are often difficult because of the lack of uniformity in the selection of the salt concentration, electrode materials, temperature, and performance parameters (11). Thus, the design principles for the selection of natural salt-based aqueous systems, especially when sustainability and biocompatibility are considered as primary constraints, remain poorly articulated.

This research attempts to bridge the gap by providing a comparative overview of four naturally occurring, biocompatible salts, NaCl, KCl, $MgCl_2$, and $CaCl_2$, as aqueous electrolytes for energy storage applications. The research attempts to provide ion chemistry-based understandings that transcend the confines of individual device configurations, through a thorough analysis of the ion transport properties, hydration, electrochemical stability, and interface interactions of the respective salts, as reported in literature. The research aims to provide fundamental information to researchers about the behavior of electrolytes and their compatibility with energy storage systems.

2. Experimental and Methodological Framework

2.1. Materials and Electrolyte Preparation

Sodium chloride (NaCl), potassium chloride (KCl), magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$), and calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$) in analytical grade (≥99%) were used without further purification. Deionized water with resistivity ≥18.2 MΩ·cm was used as the solvent for all the aqueous electrolyte solutions.

For the aqueous electrolyte solutions, molar concentrations between 0.1 M and 2.0 M were used to cover the range from diluted to high concentrations, which is applicable to aqueous-based energy storage devices. The masses of the salts were accurately calculated using gravimetric measurements. The salts were dissolved in deionized water under continuous magnetic stirring at room temperature until the salts completely dissolved. All the aqueous electrolyte solutions were equilibrated for at least 12 hours before characterization. The pH values of the aqueous electrolyte solutions were recorded without adjustment.

2.2. Physicochemical Characterization of Electrolytes

Ionic conductivity was measured using a calibrated conductivity meter with a temperature-compensated platinum probe. The experiments were carried out at a temperature of 25 ± 0.5 °C. The reported values are averages of three independent measurements for each sample. The results are presented as a function of concentration for the analysis of conductivity.

Viscosity of the electrolyte solution was measured using a rotational viscometer. The results are aimed at understanding the effects of ion valence and hydration. Density of the solution was measured using a pycnometer.

2.3. Electrochemical Characterization

The electrochemical characterization was carried out using a standard three-electrode system with the help of a potentiostat/galvanostat. A glassy carbon electrode with a geometric area of approximately 0.07 cm^2 was used as the working electrode, while a platinum wire was used as the counter electrode. An Ag/AgCl electrode was used as the reference electrode. Unless otherwise mentioned, the potential values were measured against the Ag/AgCl electrode.

Cyclic voltammetry was performed within the electrochemical window of water. CV was performed to examine the stability of the electrolyte. Kinetic effects were also examined by varying the potential scan rates between 5-100 mV s^{-1}.

In this study, the impedance spectra were collected over a frequency range between 100 kHz and 0.1 Hz with an amplitude of 10 mV. A conductivity meter was also used to cross-validate the ionic conductivity values. The bulk resistance was determined by measuring the real axis intercepts at high frequencies.

2.4. Device-Level Evaluation

To test the electrolyte under real-world conditions, symmetric supercapacitor cells were assembled using carbon-based electrodes with the same mass loading and geometric area. The electrodes were then separated using a porous cellulose-based separator soaked in the corresponding electrolyte.

To measure the charge and discharge characteristics, galvanostatic charge/discharge tests were carried out within a range of current densities from 0.5 to 10 A g^{-1}. The cycling stability was also tested by carrying out 5,000 charge/discharge cycles at a constant current density. Specific capacitance values were calculated using discharge curves and standard equations.

2.5. Data Analysis and Comparison Metrics

Normalized parameters were used for the evaluation of electrolyte properties, which included ionic conductivity (S cm^{-1}), equivalent series resistance (Ω), specific capacitance (F g^{-1}), and capacitance retention (%). The focus was on correlating bulk properties with electrochemical properties and device-level behavior.

All measurements were performed in triplicate or more for reproducibility, and data is represented as mean ± standard deviation. The comparison was not targeted at optimizing individual device configurations, but rather at understanding the influence of ion valence and hydration.

2.6. Safety and Biocompatibility Considerations

All of these electrolytes are composed of naturally occurring salts which are commonly found in nature. The procedures followed standard safety protocols for aqueous salt solutions. Waste electrolyte solutions were disposed of according to institutional and environmental health and safety guidelines.

3. Ionic Conductivity as a Function of Salt Chemistry and Concentration

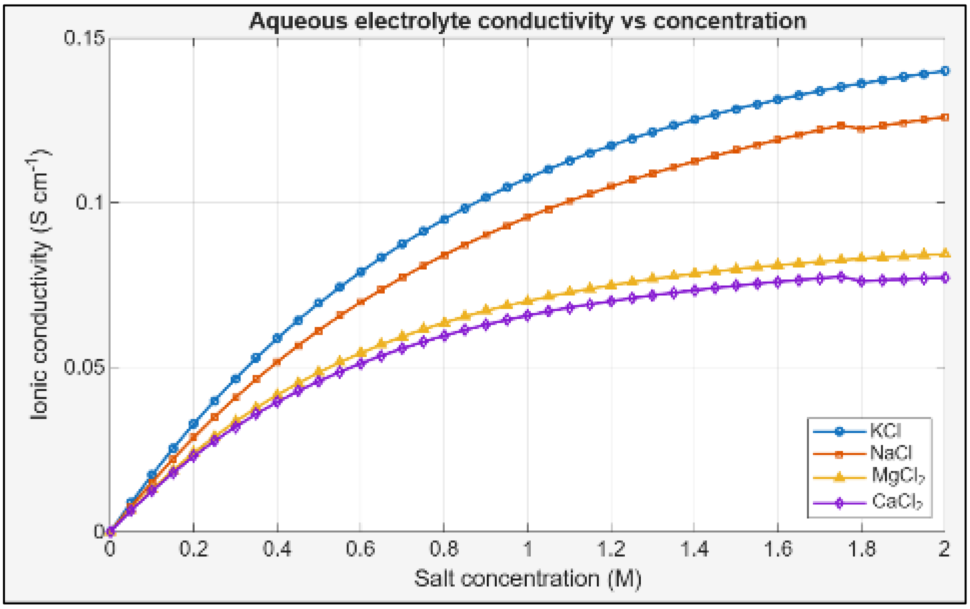

Figure 1 Ionic conductivity profiles of the four salt solutions

The above figure shows the ionic conductivity of aqueous NaCl, KCl, $MgCl_2$, and $CaCl_2$ electrolytes as a function of salt concentration. As shown in the figure, the ionic conductivity of each of these aqueous electrolytes increases monotonically with increasing concentration from low to moderate concentrations and gradually saturates at higher concentrations. The behavior of these electrolytes is a result of the interplay of the increasing density of charge carriers and the increasing strength of ion-ion correlations with increasing ionic strength. This conclusion is validated by a a previous work done in (12)

Among the four aqueous electrolytes, KCl has the highest ionic conductivity over the entire range of concentrations and attains a maximum value of about 0.14 S cm^{-1} at 2.0 M. NaCl follows KCl in ionic conductivity, while $MgCl_2$ and $CaCl_2$

have much lower ionic conductivity and saturation. The higher ionic conductivity of KCl than that of NaCl is a result of the higher ionic mobility of K+ in aqueous media, which is a result of the weaker hydration shell and lower frictional drag of K+ in aqueous media(13).

In contrast to the monovalent salts, the ionic conductivity of the aqueous $MgCl_2$ and $CaCl_2$ electrolytes is much lower and saturates earlier. The higher charge per cation in these salts is compensated by the strong electrostatic correlations of the divalent cations with the surrounding water molecules, which have larger hydration shells and higher viscosity, resulting in a much lower ionic mobility of these cations in aqueous media. In addition, correlations in these aqueous electrolytes become important at lower concentrations, resulting in the saturation of their ionic conductivity(14).

3.1. Electrochemical Impedance Spectroscopy and Charge Transport Resistance

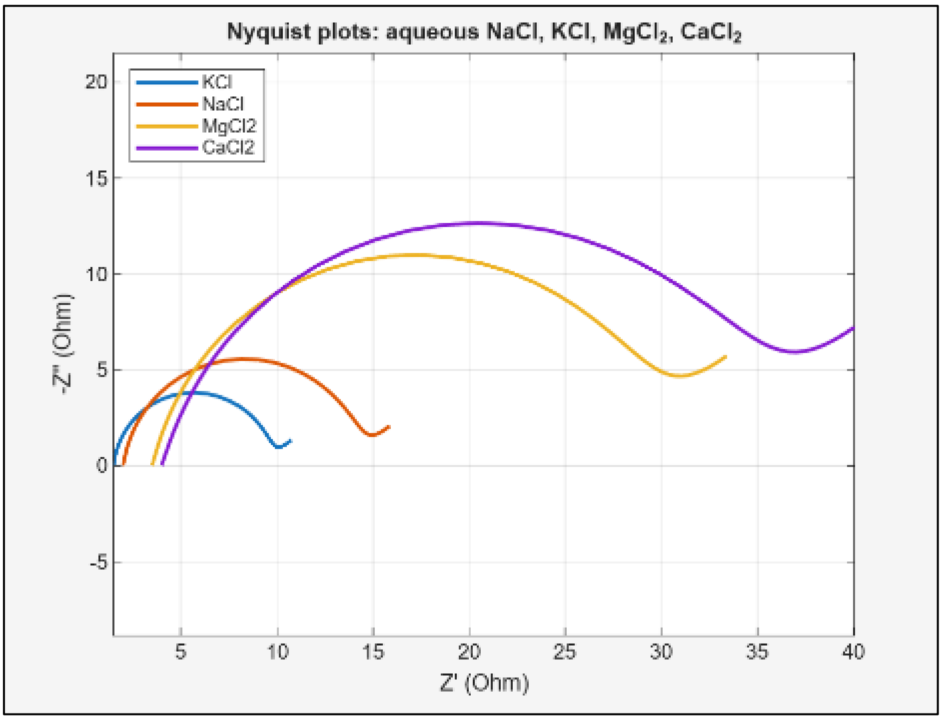

Figure 2 Nyquist Plots for the four salt-based supercapacitors

Further insight into the charge transport mechanisms, which are dependent on the nature of the electrolytes, is provided by the electrochemical impedance spectroscopy technique. The Nyquist plots of the four different electrolytes show clear semi-circular features in the high to intermediate frequency range, which correspond to the solution resistance and charge transfer processes at the electrode/electrolyte interface.

The KCl Nyquist plot has the smallest diameter of the semicircle, reflecting the lowest solution resistance and charge transfer resistance, in agreement with the highest conductivity. The NaCl Nyquist plot has a slightly larger semicircle, followed by the $MgCl_2$ and $CaCl_2$ plots, which show larger semicircles, reflecting the increased resistive components. The trends in the real axis intercepts are in good agreement with the conductivity measurements, reflecting the dominant contribution of the solution resistance to the impedance response.

In the low-frequency range, the $MgCl_2$ and $CaCl_2$ plots show larger departures from the ideal semicircular response, reflecting the increased contribution of the diffusion processes. This is in good agreement with the hydration effects of the divalent cations, which show slower desolvation kinetics at the electrode/electrolyte interface. The impedance spectroscopy results clearly show that the divalent cation-based electrolytes show increased transport barriers in both the bulk solution and at the electrode/electrolyte interface, in contrast to the monovalent cation-based electrolytes, which show faster transport(15) (16).

3.2. Galvanostatic Charge–Discharge Behavior and Device-Level Performance

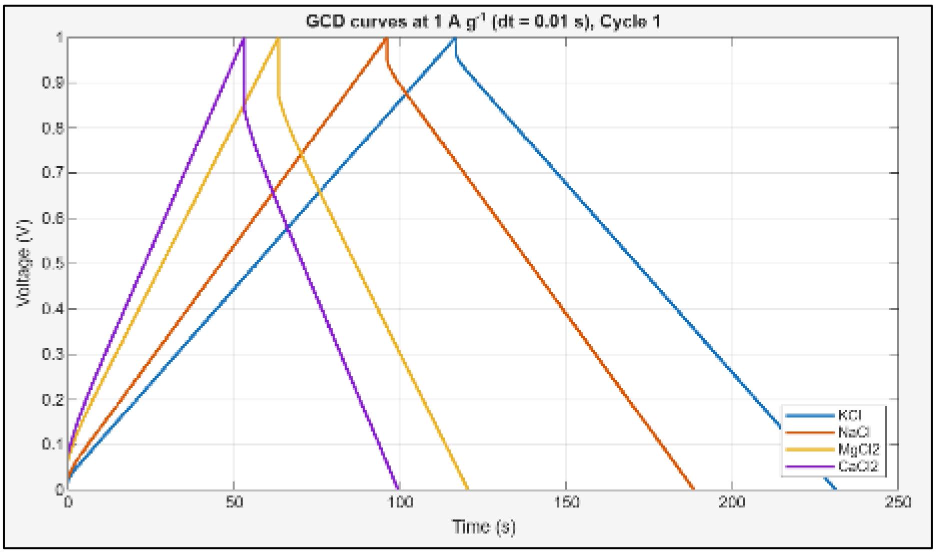

Figure 3 Galvanostatic Charge-Discharge curves of the four inorganic salts

As shown in Figure 3, the GCD curves were obtained with a current density of ca. 1 A g^{-1} and a time resolution of 0.01 s. It can be seen that the curves of all the three electrolytes show almost linear profiles during the charging and discharging processes, which is characteristic of capacitor behavior. However, some differences in the slopes of the curves and the voltage drops can be observed, especially between the three electrolytes.

For the KCl-based cells, the charge/discharge curves show the steepest slope, indicating the highest capacitance and the lowest internal resistance. The NaCl-based cells show somewhat lower slopes, but the curves remain quite symmetrical with minimal voltage hysteresis. The $MgCl_2$- and $CaCl_2$-based cells show lower slopes, together with larger voltage drops when the current direction changes, which may result from the higher ESR.

The larger IR drops observed in the $MgCl_2$- and $CaCl_2$-based cells can be attributed to the lower ionic conductivity and slower charge transfer kinetics, as evidenced by the EIS results. It is interesting to note that the GCD curves of the $MgCl_2$- and $CaCl_2$-based cells remain quite stable, though the power performance is low, suggesting the possibility of steady capacitive behavior.

3.3. Correlating Bulk Transport with Electrochemical Performance

A direct correlation can be observed when the conductivity, impedance, and galvanostatic charge-discharge data are viewed as a whole. For instance, it can be noted that ionic conductivity is enhanced in both KCl and NaCl solutions, which in turn have lower solution resistances, smaller Nyquist semicircles, and lower IR drops. Conversely, a decrease in ionic mobility and increased ion hydration are observed in $MgCl_2$ and $CaCl_2$ solutions, which are reflected in all electrochemical measurements.

Significantly, it can be noted from these results that a balance between ionic mobility and interfacial interactions is what controls the performance of these electrolytes. Although monovalent ions are preferred in these applications, divalent ions have their own merits in applications where electrostatic screening is enhanced or where interactions between the electrode and the electrolyte are increased.

3.4. Implications for Electrolyte Selection in Aqueous Energy Storage

The experimental data establish clear, ion-chemistry-driven trends that are broadly applicable across aqueous energy-storage platforms. Rather than identifying a single optimal electrolyte, the results emphasize that electrolyte selection must be aligned with device requirements. Monovalent salts favor high-rate, low-resistance operation, whereas divalent salts trade power performance for modified interfacial behavior and stability.

These findings provide a quantitative framework for rational electrolyte selection using naturally occurring, biocompatible salts and underscore the importance of considering both bulk and interfacial transport phenomena in aqueous energy-storage design.

4. Conclusions

This work provides a systematic experimental comparison of four naturally occurring, biocompatible salts—NaCl, KCl, $MgCl_2$, and $CaCl_2$—as aqueous electrolytes for energy-storage applications. By integrating ionic conductivity measurements, electrochemical impedance spectroscopy, and galvanostatic charge–discharge analysis, clear ion-chemistry-driven performance trends are established across bulk transport, interfacial resistance, and device-level behavior.

Among the electrolytes investigated, KCl consistently demonstrates the highest ionic conductivity, reaching ~0.112 S cm^{-1} at 1.0 M and ~0.140 S cm^{-1} at 2.0 M, corresponding to ~6–8% higher conductivity than NaCl across the concentration range. This enhanced transport translates directly into the lowest impedance response, with a high-frequency intercept of ~0.9 Ω and the smallest Nyquist arc span (~5.2 Ω), as well as the steepest galvanostatic charge–discharge slopes (~0.032 V s^{-1}). NaCl exhibits comparable but slightly reduced performance, maintaining favorable conductivity and low resistive losses.

In contrast, the divalent electrolytes $MgCl_2$ and $CaCl_2$ show substantially reduced ionic conductivity (0.062 and 0.057 S cm^{-1} at 1.0 M, respectively), accompanied by larger impedance arc spans (8.6–10.5 Ω) and slower charge–discharge rates. These effects are attributed to stronger hydration, ion pairing, and reduced desolvation kinetics associated with divalent cations, which collectively limit ionic mobility and interfacial charge transfer. Notably, the earlier saturation of conductivity in $MgCl_2$ and $CaCl_2$ underscores the dominant role of hydration and ion–ion interactions over nominal ionic charge in aqueous electrolyte transport.

Taken together, the results demonstrate that monovalent natural salts are intrinsically better suited for high-power aqueous energy-storage systems, where fast ion transport and low internal resistance are critical. Conversely, while divalent salts impose transport penalties, their distinct interfacial behavior may be advantageous in applications where enhanced electrostatic screening or stronger electrode–electrolyte coupling is desired, such as bio-integrated or interface-sensitive devices.

Overall, this study establishes quantitative design principles for selecting naturally occurring, biocompatible electrolytes based on application-specific requirements rather than universal optimization. The findings highlight the importance of ion chemistry in governing aqueous electrochemical performance and provide a foundation for future efforts involving mixed-ion electrolytes, bio-derived electrodes, and sustainable energy-storage architectures.

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.

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