Proceeding of International
Conference on Science and Technology
Lembaga Penelitian Pengabdian kepada Masyarakat dan Dakwah Islamiyah,
Universitas Islam Kuantan Singingi, Indonesia, August 5th 2026
DOI : https://doi.org/10.36378/internationalconferenceuniks.v3i1

ISSN 2985-8739
Page: 60-69

Designing Next-Generation PVDF-HFP Polymer Electrolytes: Insights from Ion Transport, Dielectric Studies, and Ex-Situ Filler Engineering

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Abstract

The development of safe, flexible, and high-performance solid polymer electrolytes is essential for next-generation lithium-based energy storage. PVDF-HFP remains a leading polymer system owing to its high dielectric constant, mechanical strength, and compatibility with lithium salts. However, its limited ion mobility and low room-temperature conductivity require targeted material enhancements. This review highlights recent progress in improving PVDF-HFP polymer electrolytes through ex-situ ceramic filler engineering, optimized plasticizer incorporation, and detailed dielectric–impedance analysis. Ex-situ synthesized fillers such as SiO_2 and TiO_2 have been shown to enhance segmental mobility, promote lithium-salt dissociation, and create continuous ion-conduction pathways within the semi-crystalline matrix. Reported dielectric and impedance studies reveal strong relationships between permittivity, relaxation behaviour, charge-carrier density, and ionic conductivity, with optimized systems achieving 10^{-4}–10^{-5} S cm^{-1}. This review consolidates key structure–property correlations and identifies the primary drivers of mobility enhancement, offering valuable guidance for designing next-generation PVDF-HFP-based solid polymer electrolytes for safe and efficient lithium-energy storage applications.

Keywords: *PVDF-HFP Polymer Electrolytes, Ion Transport Mechanisms, Dielectric Analysis, Ex-Situ Filler Engineering, Lithium-Ion Conductivity*

1.0 Introduction

The worldwide search for safer, high-efficiency, and more sustainable energy-storage systems has intensified interest in solid polymer electrolytes (SPEs), particularly for next-generation lithium-based batteries [1–3]. Among the various polymer hosts investigated, poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) has emerged as a promising candidate because of its relatively high dielectric constant, broad electrochemical stability, chemical resistance, and favourable mechanical properties [4–6]. The incorporation of hexafluoropropylene units disrupts the regular packing of PVDF chains, reducing crystallinity and increasing the amorphous fraction available for ionic transport [4,6]. Nevertheless, pristine PVDF-HFP remains semi-crystalline and generally exhibits insufficient room-temperature ionic conductivity, making further structural and interfacial engineering necessary for high-performance electrochemical applications [1,2,7].

Recent studies have demonstrated that the strategic incorporation of ex-situ ceramic fillers and plasticizers can substantially modify Li^+ transport within PVDF-HFP matrices [1–3,8]. Ex-situ synthesized fillers such as SiO_2, TiO_2, and Al_2O_3 can disrupt ordered polymer-chain packing, suppress crystalline domains, and generate polymer–filler interfacial regions favourable for ionic migration [8–10]. Surface-active sites on these ceramic particles can additionally participate in Lewis acid–base interactions with the polymer and ionic species, weakening cation–anion association and promoting lithium-salt dissociation [9,10]. Plasticizers provide a complementary function by softening the polymer environment, increasing free volume and segmental mobility, and lowering the energetic constraints associated with ion hopping [3,11]. The resulting conductivity enhancement therefore reflects more than an increase in charge-carrier concentration; it arises from the coupled effects of salt dissociation, polymer dynamics, structural disorder, and interfacial transport [2,3,12].

Understanding these coupled processes requires characterization approaches capable of connecting molecular-scale dynamics with macroscopic electrochemical behaviour. Dielectric analysis provides valuable information on permittivity, polarization, relaxation behaviour, and the response of mobile charge carriers, whereas electrochemical impedance spectroscopy enables bulk resistance and ionic conductivity to be evaluated across different frequencies and temperatures [3,12–14]. When these measurements are interpreted alongside structural and morphological analyses, they provide a more complete picture of how polymer modification, filler interfaces, and molecular relaxation collectively regulate Li^+ migration [1,2,14,15]. Such structure–dynamics–transport correlations are increasingly important for moving beyond empirical conductivity optimization toward the rational design of polymer electrolytes. Accordingly, this review critically examines recent advances in filler engineering, polymer modification, dielectric behaviour, and ion-transport characterization to establish an integrated framework for designing next-generation PVDF-HFP polymer electrolytes for safer, efficient, and adaptable lithium-energy-storage systems.

1.1 Polymer Electrolytes for Lithium-Based Energy Systems

Solid polymer electrolytes (SPEs) are increasingly being explored as safer alternatives to conventional flammable liquid electrolytes in lithium-based batteries, offering reduced leakage risk, improved mechanical flexibility, and compatibility with thin-film energy-storage configurations [15–17]. Despite these advantages, achieving sufficiently high ionic conductivity at room temperature remains a major challenge because ion migration within a solid polymer matrix is strongly influenced by polymer-chain mobility and the availability of favourable coordination environments [16–19]. Effective Li^+ conduction therefore requires a polymer host capable of supporting lithium-salt dissociation while providing sufficient segmental motion for ions to migrate between transient coordination sites [16–19]. The extent of amorphous character, polymer–ion interactions, free volume, and segmental dynamics collectively determines the concentration and mobility of available charge carriers and, consequently, the macroscopic ionic conductivity [17–20]. Understanding these fundamental structure–transport relationships is therefore essential before introducing plasticizers or inorganic fillers to enhance electrolyte performance, particularly when considering the properties and limitations of PVDF-HFP as a host polymer [19,20].

1.2 Properties and Limitations of PVDF-HFP as a Host Polymer

PVDF-HFP has become one of the most extensively investigated host polymers for lithium-based polymer electrolytes because of its favourable combination of dielectric, chemical, electrochemical, and mechanical properties [19,20]. Its relatively high dielectric constant ($\varepsilon \approx 8–12$) can support ionic dissociation, while its chemical resistance, mechanical integrity, and broad electrochemical stability make it attractive for solid and composite electrolyte configurations [19,20]. The incorporation of hexafluoropropylene units disrupts the regular packing of PVDF chains, reducing crystalline ordering and increasing the amorphous fraction available for ionic migration [19,20]. This structural modification provides greater local chain flexibility, creating a more favourable environment for segmental-assisted Li^+ transport [16–19]. Nevertheless, PVDF-HFP remains intrinsically semi-crystalline, and residual ordered domains can restrict segmental motion and interrupt continuous long-range ion-transport pathways [19,20]. Moreover, unlike oxygen-rich polymer hosts such as PEO, PVDF-HFP lacks strongly coordinating carbonyl functionalities, limiting direct coordination between the polymer backbone and Li^+ and increasing the importance of the surrounding electrolyte environment [16–19]. Consequently, unmodified PVDF-HFP systems generally exhibit relatively poor room-temperature ionic transport, motivating strategies that increase charge-carrier concentration while simultaneously improving polymer dynamics and ion-conduction pathways [19,20]. These limitations make electrolyte-salt selection, salt dissociation, and polymer–ion interactions particularly important in defining the Role of Lithium Salts in Enhancing Ion Transport [17–20].

1.3 Role of Lithium Salts in Enhancing Ion Transport

Lithium salts such as $LiClO_4$, LiTFSI, and $LiPF_6$ are central to the ionic transport process because their dissociation characteristics, anion size, charge delocalization, and interactions with the polymer environment determine the availability of mobile charge carriers. Effective salt dissociation increases the population of free Li^+ ions that can participate in conduction, while bulky, charge-delocalized anions can weaken cation–anion association and favour greater ionic mobility. LiTFSI, for example, contains the large $TFSI^-$ anion with highly delocalized charge, which generally promotes salt dissociation and increases the concentration of mobile Li^+ species. Nevertheless, generating more free ions does not necessarily guarantee efficient long-range transport; within a relatively rigid or semi-crystalline polymer matrix, Li^+ migration can remain constrained by insufficient chain motion and limited free volume. Overcoming this dynamic limitation therefore requires modification of the polymer environment, particularly through plasticizer inclusion and segmental relaxation.

1.4 Plasticizer Inclusion and Segmental Relaxation

Plasticizers such as ethylene carbonate (EC), propylene carbonate (PC), and polyethylene glycol (PEG)-based additives are widely employed to improve ion transport by creating a more dynamically responsive polymer environment [20,21]. Once incorporated into the electrolyte, these additives can disrupt regular polymer-chain packing, weaken intermolecular interactions, and suppress crystalline ordering, thereby increasing the proportion of ionically favourable amorphous domains [20–22]. The resulting structural rearrangement can increase free volume and chain flexibility while lowering the glass-transition temperature (T_g), allowing polymer segments to reorganize more readily around migrating ionic species [22,23]. Enhanced segmental relaxation consequently

facilitates the continuous formation of transient coordination environments through which Li^+ can migrate, strengthening the coupling between polymer dynamics and ionic transport [22–25]. In suitably optimized polymer electrolyte systems, these combined effects can substantially increase room-temperature ionic conductivity, with values approaching the $\sim 10^{-4}$–10^{-5} S cm^{-1} range depending on polymer composition, salt concentration, plasticizer content, and electrolyte architecture [20,21,23–26]. Nevertheless, plasticization involves an inherent conductivity–mechanical stability trade-off; excessive plasticizer loading may soften the polymer network, compromise dimensional stability, and adversely affect long-term electrochemical performance [20,22,25–28]. Achieving enhanced Li^+ mobility while preserving the structural and interfacial integrity required for practical solid-state batteries therefore motivates complementary reinforcement strategies, particularly Ex-Situ Filler Engineering to Improve PVDF-HFP Performance [20–22,25,26,29,30].

1.5 Ex-Situ Filler Engineering to Improve PVDF-HFP Performance

Ex-situ fillers are prepared independently before their incorporation into the polymer matrix, allowing greater control over particle size, morphology, surface chemistry, and interfacial characteristics [20–22]. Ceramic materials such as SiO_2, TiO_2, Al_2O_3, ZnO, and lithium lanthanum zirconium oxide (LLZO) have been extensively investigated as functional components of composite polymer electrolytes because they can simultaneously influence structural, interfacial, mechanical, and electrochemical properties [20–25]. Their incorporation can disturb regular polymer-chain packing, suppress crystalline ordering, and promote amorphous domains that provide a more favourable environment for ionic migration [20–22]. At polymer–filler interfaces, Lewis acid–base interactions may weaken cation–anion association, facilitate lithium-salt dissociation, and consequently increase the availability of mobile Li^+ species [20–22]. When uniformly dispersed, nanoscale fillers can additionally generate extended interfacial regions that facilitate ion migration while reinforcing the mechanical and thermal integrity required for solid-state electrolyte operation [20–25]. The ex-situ strategy further offers the advantage of independently tailoring nanoparticle characteristics before electrolyte fabrication, providing greater control over filler-dependent structure–property relationships [20–22]. Establishing how these structural and interfacial modifications ultimately influence polarization, molecular relaxation, and charge-carrier mobility requires Dielectric Studies: Linking Permittivity and Ion Dynamics [20–22].

1.6 Dielectric Studies: Linking Permittivity and Ion Dynamics

Dielectric spectroscopy provides a sensitive window into the molecular and ionic dynamics governing charge transport in polymer electrolytes, complementing conventional conductivity measurements by revealing the frequency-dependent response of the electrolyte system [20–22,25]. Rather than describing ionic conduction through a single macroscopic parameter, dielectric analysis examines how dipoles, mobile ions, and interfacial charges respond to an applied alternating electric field through dielectric permittivity, dielectric loss, polarization behaviour, and characteristic relaxation processes [20,22,26]. In PVDF-HFP-based electrolytes, a favourable dielectric environment can promote lithium-salt dissociation by screening the electrostatic attraction between Li^+ and its counter-anion, thereby increasing the population of mobile charge carriers available for conduction [20–22,27,28]. Frequency-dependent dielectric loss and relaxation behaviour further provide insight into the ability of polymer segments and ionic species to reorganize under the applied field, helping to elucidate ion hopping,

electrode/interfacial polarization, and the dynamic processes associated with ionic migration [20,22,25–28]. Correlating these dielectric characteristics with structural and electrochemical properties therefore provides a more complete understanding of the relationship between molecular relaxation, charge-carrier availability, and macroscopic ionic transport [20–22,26,28]. Establishing how these dynamic dielectric processes ultimately translate into measurable bulk resistance and ionic conductivity naturally leads to Impedance Analysis for Ion Transport Behaviour [20–22,25,28].

1.7 Impedance Analysis for Ion Transport Behaviour

Electrochemical impedance spectroscopy (EIS) is a well-established method for analysing the ionic transport in polymer electrolytes and identifying the resistive processes that control charge migration [19-22]. The frequency-dependent impedance response allows for the estimation of bulk resistance (Rb), which is then used to compute ionic conductivity using the formula, where is the electrolyte thickness and represents the effective electrode-electrolyte contact area [19,20,22]. Impedance spectra, in addition to determining conductivity, provide essential information on bulk ion transport, electrode polarisation, and processes that occur at the electrode-electrolyte interface [21, 22, 25–26]. Variations in composite polymer electrolytes can be attributed to differences in polymer-chain mobility, amorphous-phase development, charge-carrier availability, and polymer-filler interfacial interactions, all of which influence Li^+ migration (19-22). A decrease in, when supported by complementary structural and dielectric evidence, can imply the formation of a more conducive environment for long-range ionic conduction; nevertheless, such alterations should not be assigned to a single mechanism without further characterisation [20-22]. Integrating EIS with structural, morphological, thermal, and dielectric analyses provides a more physically meaningful interpretation of how material engineering influences macroscopic ionic transport, laying the groundwork for understanding recent advances in PVDF-HFP composite electrolytes [19-22,25].

1.8 Recent Progress in PVDF-HFP Composite Electrolytes

Recent studies have demonstrated substantial improvements in polymer-electrolyte performance through careful control of composition, microstructure, and interfacial chemistry [20–22]. Plasticization with carbonate-based solvents such as propylene carbonate (PC) and ethylene carbonate (EC) can enhance polymer-chain flexibility, increase the amorphous fraction, and facilitate lithium-salt dissociation, collectively promoting Li^+ mobility and improving room-temperature ionic conductivity [20–22,27,28,30]. In optimized polymer electrolyte formulations, conductivity can approach the order of $\sim 10^{-4}$ S cm^{-1}, although the achievable value strongly depends on polymer composition, salt concentration, plasticizer loading, temperature, and electrolyte architecture [20–22]. The incorporation of nanoscale ceramic fillers provides an additional route for transport enhancement by disturbing crystalline packing and generating polymer–filler interfacial regions that can favour lithium-ion migration [20–22,25,26]. More recently, hybrid and multifunctional filler strategies have been explored to balance ionic conductivity with mechanical reinforcement and interfacial stability, addressing the inherent conductivity–mechanical strength trade-off encountered in polymer electrolytes [20–22,25,26]. Despite this progress, important challenges remain in translating material-level improvements into practical cells, particularly in achieving stable electrode–electrolyte interfaces, sustained electrochemical and thermal stability, reproducible processing, and scalable manufacturing for commercial solid-state

battery applications [21–26].

2. METHODOLOGY SECTION

2.1 Materials Selection

The materials selected for this study comprise a polymer host, lithium salt, plasticizer, and ex-situ inorganic filler. Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) was employed as the host polymer because of its favourable electrochemical stability, relatively high dielectric constant, chemical resistance, and mechanical integrity, which make it an attractive matrix for lithium-based polymer electrolytes [1–4,31,32]. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) or lithium perchlorate ($LiClO_4$) was incorporated as the lithium-salt source to provide mobile Li^+ charge carriers, with salt dissociation and polymer–ion interactions playing central roles in determining ionic transport [16–19,33,34]. Propylene carbonate (PC) was employed as a plasticizer to increase polymer-chain flexibility, promote a more dynamically favourable amorphous environment, and facilitate Li^+ migration through the polymer matrix [19,27,28,30,33]. In addition, synthesized silicon dioxide (SiO_2) or titanium dioxide (TiO_2) nanoparticles were introduced as ex-situ fillers to modify polymer packing and polymer–filler interfacial interactions, with the aim of improving ionic transport while supporting the thermal and mechanical properties of the composite electrolyte [1,5,11–14,20]. Collectively, these components were selected to establish a polymer–salt–plasticizer–filler system in which molecular mobility, salt dissociation, and interfacial effects can be systematically correlated with electrolyte performance [1–4,20].

2.2 Ex-Situ Filler Synthesis

The ex-situ inorganic fillers were synthesized using a sol–gel route to obtain nanoscale SiO_2 or TiO_2 particles for subsequent incorporation into the polymer electrolyte matrix [11–13,20]. For SiO_2 synthesis, tetraethyl orthosilicate (TEOS) was employed as the precursor and subjected to controlled hydrolysis and condensation reactions, with solution pH regulating the kinetics of sol formation and network development [11,12]. The resulting sol was subsequently aged to promote further condensation and development of the inorganic network, followed by drying to remove residual solvent and volatile species. The dried gel was then calcined under controlled thermal conditions to remove residual organic components and stabilize the resulting oxide structure before further processing. The morphology, surface characteristics, degree of agglomeration, and particle-size distribution of the synthesized fillers were subsequently examined using scanning electron microscopy (SEM) or field-emission scanning electron microscopy (FESEM), providing information relevant to their subsequent dispersion and interfacial behaviour within the polymer electrolyte [11–14,20].

2.3 Electrolyte Film Preparation

Polymer electrolyte films were prepared using the solution-casting technique, a widely employed approach for producing homogeneous and flexible PVDF-HFP-based electrolyte membranes [1–4,14]. PVDF-HFP was initially dissolved in a mixed acetone/DMF solvent system under continuous stirring until a homogeneous polymer solution was obtained. A predetermined amount of lithium salt, either LiTFSI or $LiClO_4$, was subsequently introduced to provide mobile Li^+ species and establish favourable polymer–salt interactions within the electrolyte matrix [17,19,33]. Propylene carbonate (PC) was then incorporated as a plasticizer to increase chain flexibility, promote segmental mobility, and create a more favourable environment for ionic migration [19,27,28,30,33]. The independently synthesized ex-situ filler was subsequently dispersed into the polymer–salt–plasticizer solution, with ultrasonication employed to

minimize particle agglomeration and promote more uniform filler distribution throughout the matrix [1,11–14,20]. The resulting homogeneous dispersion was cast onto a Petri dish and subjected to controlled solvent evaporation at room temperature, allowing gradual formation of the polymer electrolyte membrane [1,14,20]. Finally, the resulting films were vacuum-dried to minimize residual solvent before subsequent structural, thermal, dielectric, and electrochemical characterization [1–4,14,20].

2.4 Characterization and Physicochemical-Electrochemical Analysis

The prepared polymer electrolyte films were comprehensively characterized to establish the interrelationship between their structural organization, morphology, thermal response, dielectric behaviour, and electrochemical transport properties [1–4,19,20]. X-ray diffraction (XRD) was employed to assess crystalline ordering and amorphous-phase development, particularly the structural changes induced by lithium salt, plasticizer, and filler incorporation [1,4,14,19]. Fourier-transform infrared spectroscopy (FTIR) was used to probe changes in characteristic vibrational bands and elucidate molecular interactions among the polymer, salt, and inorganic filler, including coordination and intermolecular interactions within the electrolyte matrix [1,3,14,19]. Surface morphology, filler dispersion, and possible nanoparticle agglomeration were examined using scanning electron microscopy (SEM), providing complementary evidence of microstructural evolution and polymer–filler interfacial characteristics [1,11,12,14,20]. Thermal behaviour was investigated using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) to evaluate thermal transitions, polymer-chain organization, and the thermal stability of the resulting electrolyte films [1,19,20]. Dielectric measurements were performed over the selected frequency range to determine dielectric permittivity, dielectric loss, polarization behaviour, and relaxation dynamics, thereby providing insight into the molecular and ionic responses governing charge-carrier mobility [3,19,32,34]. Electrochemical impedance spectroscopy (EIS) was subsequently employed to determine bulk resistance and ionic conductivity, while the complex impedance response was interpreted using physically representative equivalent-circuit modelling to resolve the dominant resistive, capacitive, and interfacial contributions to ion transport [1–3,19,20]. Collectively, these complementary analyses establish an integrated structure–interaction–morphology–thermal–relaxation–ion transport relationship, which forms the scientific basis of the proposed Conceptual Framework Diagram.

3. Conceptual Framework Diagram

Incorporation of ex-situ fillers can progressively modify the local environment governing ion transport within a polymer electrolyte, as illustrated in Figure 1. Well-dispersed SiO_2 nanoparticles interfere with regular polymer-chain packing, suppressing crystalline ordering and promoting the formation of more dynamically active amorphous domains. This structural reorganization enhances segmental mobility and generates transient free volume that can facilitate Li^+ migration. At the same time, surface functionalities on SiO_2 may interact with the polymer and ionic species through Lewis acid–base interactions, weakening ion association and promoting lithium-salt dissociation. The combined effects of enhanced chain dynamics, increased charge-carrier availability, and polymer–filler interfacial interactions can therefore establish more favourable pathways for long-range ionic conduction and improve overall electrolyte performance. Nevertheless, these benefits are strongly dependent on filler concentration and dispersion, as excessive loading or nanoparticle agglomeration may restrict

polymer mobility, interrupt conductive pathways, and ultimately reduce ionic conductivity—a critical consideration addressed in the conclusion.

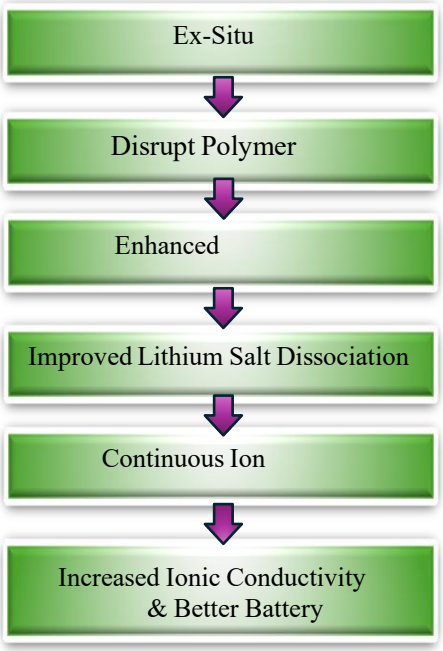

Figure 1: Flow Conceptual Framework Diagram

Conclusion

The development of next-generation PVDF-HFP polymer electrolytes represents a promising strategy for achieving safer, high-performance solid-state lithium-ion batteries. This study highlights the importance of understanding ion transport mechanisms, dielectric properties, and ex-situ filler engineering in enhancing the electrochemical performance of PVDF-HFP-based composite polymer electrolytes. Appropriate incorporation of inorganic fillers can reduce polymer crystallinity, improve dielectric permittivity, promote salt dissociation, and create continuous pathways for lithium-ion migration, resulting in higher ionic conductivity and improved electrochemical stability. Dielectric analysis provides valuable insights into polarization behaviour, charge carrier dynamics, and relaxation processes, offering a deeper understanding of the factors governing ion mobility within the polymer matrix. Furthermore, ex-situ engineered fillers with tailored morphology, particle size, and surface functionality strengthen polymer–filler interactions, contributing to enhanced mechanical integrity, thermal stability, and interfacial compatibility with lithium electrodes. The synergistic relationship between polymer structure, dielectric response, and filler characteristics provides an effective framework for designing advanced composite polymer electrolytes. Future research should focus on multifunctional nanofillers, interface engineering, scalable fabrication techniques, and advanced characterization methods to further optimize electrolyte performance. Integrating experimental investigations with computational modeling and machine learning approaches may also accelerate material discovery and electrolyte design. Overall, these strategies offer significant potential for advancing reliable, durable, and high-energy-density solid-state lithium battery technologies for next-generation energy storage applications.

Acknowledgement

The authors would like to express their sincere appreciation to the entire research team from Universiti Teknologi MARA (UiTM) Cawangan Perak, Kampus Tapah, Universiti Teknologi MARA (UiTM) Shah Alam, and Universiti Kebangsaan Malaysia (UKM), Bangi, for their invaluable collaboration, technical expertise, and continuous support throughout this research. The authors also gratefully acknowledge the financial support provided by the Ministry of Higher Education (MOHE/KPT), Malaysia, through its research grant(s), which made this study possible. The authors further appreciate the laboratory facilities, research infrastructure, and administrative assistance provided by the participating institutions, as well as the constructive discussions and contributions from all collaborators that significantly enhanced the quality of this work. The wording of the funding acknowledgement should be updated to

include your specific grant scheme and grant number (e.g., FRGS, PRGS, TRGS, or LRGS), in line with MOHE publication acknowledgement guidelines.

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