UNIVERSITI TEKNOLOGI MARA

ELECTRICAL CONDUCTIVITY IN SALT – POLYMER SOLUTIONS

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ABSTRACT

ELECTRICAL CONDUCTIVITY IN SALT-POLYMER SOLUTIONS

Electrolytic conductivity (κ) at 25.0 °C was measured in liquid electrolyte and liquid polymer electrolyte as a function of salt concentration (C_{salt}) by AC conductivity meter. The effect of adding polymer into liquid electrolyte was discussed. Molar conductivity at infinite dilution (Λ_0) of weak electrolyte lithium perchlorate (LiClO₄) in tetrahydrofuran (THF) and acetronitrile (ACN), respectively was estimated from Ostwald's dilution law. The estimated Λ_0 values for both LiClO₄ in THF and LiClO₄ in ACN are 76 and 24200 S cm² mol⁻¹. The expected values for both systems are 155.3 ± 2.0 and 173.0 ± 2.0 S cm² mol⁻¹. The limitation of Oswald's dilution law in estimation of Λ_0 values for weak electrolytes is demonstrated in this study. We propose, a double-logarithmic plot of κ versus C_{salt} (power law) was introduced to determine the Λ_0 for weak electrolytes. The power law proposed is linear for certain (finite) range of C_{salt} . The reference salt concentration (C_{ref}) of the systems has to be estimated carefully. It is noted that, C_{ref} for each system that corresponding to the Λ_0 is approximately half of the lowest C_{salt} concentration that still obeys the power law before the data starts to divert from the linearity of the power law. In order to estimate Λ_0 value at 25.0 °C for LiClO₄ in poly(ethylene oxide) (PEO) solution (PEO + ACN), $C_{ref} = 3.0 \cdot 10^{-9}$ mol cm⁻³ is adopted. PEO with different molecular weights, $M_{\rm n}s = 3 \cdot 10^5$, $6 \cdot 10^5$, $1 \cdot 10^6$ and $4 \cdot 10^6$ g mol⁻¹ were studied and are denoted as PEO₁, PEO₂, PEO₃ and PEO₄ respectively. The κ of the LiClO₄ in PEO solutions was measured as a function of C_{salt} . The PEO solutions comprise of fixed PEO concentrations (C_{PEO}) of PEO₁, PEO₂, PEO₃ and PEO₄ from 0.0005 to 0.010 g cm⁻ ³. In general, as C_{PEOS} increase for LiClO₄ in PEO solutions, Λ_0 values of the systems tend to show a descending trend. It is also noted, higher M_{η} of PEOs at C_{PEO} = constant demonstrate a descending tendency in Λ_0 . This indicates lower ion mobility (K') in the electrolyte as calculated in this study. Finally, the degree of dissociation (α) for LiClO₄ in PEO solution was calculated as a function of C_{salt} for different PEOs at different C_{PEOS} . Higher M_n PEOs result in the improvement of dissociation of LiClO₄ in PEO solutions as compared to LiClO₄ in ACN. At C_{PEO} = constant, α values are insignificantly different at higher C_{PEO} .

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CHAPTER 1

INTRODUCTION

1.0 Introduction

Power sources for electric vehicles and portable electronic equipment have attained attention upon the discovery of electrochemical systems that store a large amount of energy, deliver high power output and utilize lightweight materials. Depending on the application, ideally they can be reversibly recharged. Most importantly, they should be mechanically and chemically stable in all environments for realistic commercial application [1]. Most of the commercially known electrolytes contribute to one or two of the above-described attributes, but the ideal electrolyte that fulfils all the mentioned requirements has remained very elusive to those involved in electrochemistry research. The discussion in the following section will start with electrolyte and afterwards will be extended to polymer electrolyte.

1.1 Electrolytes

In chemistry, an electrolyte is any substance containing free ions that make the substance electrically conductive. Electrolyte solution is normally formed when salt is placed into solvent such as water and the individual components dissociate due to the thermodynamic interactions between solvent and solute molecules, in a process called salvation [2-4]. For example, when table salt, NaCl, is placed in water, the salt (solid) dissolves into its component elements [c.f. Eq. (1)], according to the dissociation reaction.