An application of bio-degradable polymers for electrolyte inside Lithium ion batteries including (m, m) SWCNTs as anodic material

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ABSTRACT
We report the stability and electronic structures of bio-degradable polymers as electrolyte inside Lithium ion batteries including various nanotubes carbon (SWCNTs) to interact with anodic materials. Lithium ion conducting polymer blend electrolyte films based on polyvinyl alcohol (PVA) and polyvinyl pyro lidone (PVP) within SWCNT has produced a large potential as anodic-electrolyte material for lithium ions batteries due to their unique structural geometry, mechanical construction, and electrical properties. The measured reversible lithium ion of (m, m) SWBNTs// (Li+)//PVA and (m, m)SWBNTs// (Li+)//PVP are improved compared to the conventional graphite’s-based/(Li+)//LiClO4. In this work (5, 5), (7,7) and (10,10) SWCNTs as anode material to interact with bio-degradable polymers (PVA and PVP) have been investigated. Additionally, we have found the structure of (7, 7) SWCNTs can be to improve the capacity and electrical transport in anode-based LIBs with this kind of electrolytes.

Keywords: lithium ion battery; SECNTs; PVA; PVP; bio-degradable polymers.

1. INTRODUCTION
LiBs generally consist of a (+) electrode, a (-) electrode and conducting electrolytes where store electrical energies in the two electrodes in the form of Li-intercalation compounds. Electrolytes, two electrodes, and separators are the main component of the lithium ion batteries where the two electrodes within interaction to electrolytes play an essential role in the efficiency of these kind batteries.

In the structure PVA and PVP electrolytes, the hydroxyl and carbonyl structures act as the pair electrons donor which enable complexion with lithium ion. Moreover, PVP and PVA both are important electrolytes because of filming properties, without toxic, cheap price, and other important items which are biodegradable. PVA is semi-crystalline macromolecules and its crystalline natures are reduced via an extra concentration from amorphous natures (PVP). Both of them are soluble in polar solvent such as DMSO with a high-degree complexion within the large variety of dopants.

During the discovery of reversible, Li-intercalation carbonaceous compounds and low-voltage battery, Sony’s company discover the commercialization of xC6/Li 1-x CoO2 cells in 1991 [1]. Lithium ion batteries (LiBs) are amazing energy storage devices for electrochemical energies, generally used in the small storage systems. The favorable electrochemical efficiency of LiBs regarding energies and power density, as well as in manufacturing of a cell designing, has made LiBs greatly successful for electronics instruments.

During LiBs charging, lithium ions released from the cathode through the electrolytes (PVP and PVA) which is a bio-degradable polymer and is important for interacting with the anodic (SWCNTs) compounds. Although those electrolytes establish a large ionic conductivity between SWCNTs electrodes, the PVP and PVA are not related to the conduction of free electrons and so the electrons complete the half reactions via an extra moving in external wire. In discharging, the lithium ions are extracted from the SWCNTs and move back to the cathode. SWCNTs presently are the most important molecules used for the anodic materials of batteries because of its capability for reversible lithium intercalation in the layered crystals [2].

There are no works for experimenting with the cylindrical nanotube to increase lithium storage capacity or improving recharging cycle efficiency. There are many reviews on the anode carbon sheet [1-11] which most of them have focused on inorganic electrolyte compounds. By this work, a semi-empirical study and also first-principal investigation have been used for calculating the amount of lithium ion storages between SWCNTs and these kinds of electrolytes, as well as some heteroatom-substituted carbon materials [12-17].

Although a lot works have been made for finding the suitable replacement, currently only LiClO4 and LiPF6 are important and used for a commercial electrolyte which are much more dangerous for the environment and also are bio-degradable polymers in contrast of PVP and PVA. For those degradable polymers, there are no theoretical or experimental reports for these kind electrolytes in LiBs.

This work has investigated to find the suitable replacement for carbonaceous materials with interacting to PVP and PVA Fig.1. The efficiencies of LiB including cycle lives, power densities and energies densities are extremely influenced by electrolyte-anodic compounds. The items are including fast diffusivities of lithium ion into the PVP and PVA, critical changes in crystal structures of anodic material, required low potential of anode materials for supplying the high cell voltages with the
cathodes and capabilities of storing significant amounts of charges per unit mass.

Conduction in anode’s material is complex due to continuous phase transformations and the formation of the PVP and PVA–electrolytes interphase (SEI) layer [18, 19]. In other words, conduction is strongly dependent upon the degree of bio-degradable polymers.

![Fig. 1: Li⁺ intercalate with (7,7)SWCNTs.](Image)

The SWCNTs layer display much lower electronic and ionic conductivity compared to the bulk electrodes. The diffusion process can vary widely from graphene sheet to SWCNTs materials [20-22]. SWCNTs have also been researched as an option to enhance electrochemical efficiency [21]. Although the nano-size diameter dimension and other superior material properties of carbon nanotubes (CNTs) is suitable for anode materials, CNTs are not successful as anode materials [21, 22], due to the commercial electrolytes such as LiPF6 (in contrast PVP or PVA). So, instead of graphene the bio-degradable polymers as electrolyte inside Lithium ion batteries applied for electrolyte materials in LIBs.

Most, reports on Li-ion diffusivities adders improving measurement technique and not the diffusion mechanisms by themselves. This may derive from the various phase mixtures, the staging phenomenon of PVP and PVA, and the complexity caused by the solvents [20-23].

Using the cylindrical carbon materials as two electrodes including vacuum dielectric in anode and PVP electrolytes has been shown to increase cell performance by this work (Figs.2&3).

![Fig. 2: Operating Li-ion battery including (7, 7) SWCNTs for diffusion Li⁺ into PVP electrolyte.](Image)

2. EXPERIMENTAL SECTION

2.1. Li⁺ diffusivity in PVP and PVA electrolytes.

In contrast to graphite, CNTs are transparent and is an insulator. Electronic properties of CNTs and CNTs are radically different from each other and can be shown by theoretical calculations [28] for band structures of a single layer of CNT. For a single layer of graphite, a Graphene, two bands cross each other at fermi energy. In this study, charging and discharging of Li-ions has investigated in (m, m)SWCNTs with the positive electrode reaction as: \( \text{LiCoO}_2 \rightarrow \text{Li}_{1-x} \text{CoO}_2 + x \text{Li}^+ + xe^- \) and the negative electrode reaction as: \( x(7,7)\text{SWCNTs} + x \text{Li}^- + xe^- \rightarrow x \text{Li} (7,7)\text{SWCNTs} \), where the whole reaction is: \( \text{LiCOO}_2 + x \text{(7,7)SWCNTs} \rightarrow \text{Li}_{1-x} \text{CoO}_2 + x \text{Li} (7,7)\text{SWCNTs} \). Recently many works have been investigated to describe the intercalation and diffusion of Li at different sites on CNTs and many studies have been performed in order to explain the mechanism by which lithium ions are stored in CNTs, including theoretical works (Fig.1). Yang et al. [24] imaged the surfaces mechanisms by which the naked surfaces of CNTs and are able for storing lithium species, via investigation of the electrochemical intercalation of lithium into PVA and PVP electrolytes. Both side (outside and inside) of the nanotubes are susceptible to lithium intercalations and achieved a high Li density.

2.1.1. Diffusion’s mechanism in matrix.

Li⁺ diffusion determines some of the important keys performance metrics of Li-ion batteries cells (Fig.3), including the charge and discharge rates, practical capacities and cycling stabilities. The equations describing the diffusion process are known as Fick’s law:

\[ j_i = -D_i \nabla C_i \] (1)

And \( \frac{\partial C_i}{\partial t} = \nabla (D_i \nabla C_i) \) (2) which “\( j_i \)” is an ionic flux, \( \text{mol cm}^{-2} \text{s}^{-1} \), \( D_i \) are diffusivities of solutes (PVP and PVA), \( \text{cm}^2 \text{s}^{-1} \) [25]. Factors D are the diffusivities coefficient \( D_i = \frac{K_i T}{6 \pi \eta R_0} \) (3) [26, 27].

In PVP or PVA electrolytes, diffusions are governed through a random jump of Li⁺, leading to position exchange with their neighbors.

The kinetics of these mechanisms is temperature dependence rate = \( \exp \left( \frac{-\Delta G}{K T} \right) \) (4) [25-27].

In PVP and PVA electrolytes, the temperature dependence of the diffusions is much less than in solids. (Eq. 2) [24-27].

Although the Li-ions are one of the smallest ions, they are still quite bigger when compared to an electron, the radius of a Li-ions are ten times larger than that of the electrons [25-27]. Also, the motion of a Li-ion is strongly barricaded via the potential created through the presence of adjacent ions. The van der Waals non-bonded forces, illustrated as the Lenard–Jones interaction, are strongly weak despite exhibiting a longer interaction range. In the case of the SWCNTs, the Li-ions can easily diffuse parallel rather than the graphite layer during intercalation. Thus in order to
understand the diffusion of the Li-ion, it is important to consider SWCNTs structures as well as the surrounding potentials.

**2.2. Density energies of lithium in diffusion into PVP and PVA**

The electron densities have been defined as \( \rho(r) = \sum_i \eta_i \varphi_i(r)^2 = \sum_i \eta_i \left( \sum_j C_{i,j} \chi_j(r) \right)^2 \). [28] Where \( \eta_i \) is orbital (i), \( \varphi \) are orbital wave functions, \( \chi \) are basis functions. Atomic unit for electron density can be explicitly written as e/Bohr^3. \( \nabla \rho(r) = \left[ \frac{\partial \varphi(r)}{\partial x} \right]^2 + \left[ \frac{\partial \varphi(r)}{\partial y} \right]^2 + \left[ \frac{\partial \varphi(r)}{\partial z} \right]^2 \).

The positive and negative values of these functions correspond to electron densities are locally depleted and locally concentrated respectively. The relationships between \( \nabla^2 \rho \) and valence shells electron pair repulsions, chemical bond type, electron localization and chemical reactivity have been exhibited by Bader [29].

The kinetic energy densities are uniquely defined as:

\[ < \varphi | \left( \frac{1}{2} \nabla^2 \right) \varphi > \quad (8) \]

The general definitions are: \( k(r) = -\frac{1}{2} \sum_i \eta_i \varphi_i(r)^2 \nabla^2 \varphi_i(r) \) Relative to \( K(r) \). The Lagrangian kinetic energy densities, \( "G(r)" \) is also known as: \( G(r) = \frac{1}{2} \sum_i \eta_i \nabla \varphi_i(r)^2 = \frac{1}{2} \sum_i \eta_i \left( \frac{\partial \varphi(r)}{\partial x} \right)^2 + \left( \frac{\partial \varphi(r)}{\partial y} \right)^2 + \left( \frac{\partial \varphi(r)}{\partial z} \right)^2 \) \quad (10).

\( K(r) \) and \( G(r) \) are directly related by Laplacian of electron density \( \frac{1}{4} \nabla^2 \rho(r) = G(r) - K(r) \) \quad (11).

Becke [30] noted that spherically averaged conditional pair probabilities with the Fermi hole and then exhibited electron localization function (ELF) \[ \text{ELF}(r) = \frac{1}{1+ |D(r)/D_0(r)|^2} \] \quad (12).

where \( D(r) = \frac{1}{2} \sum_i \eta_i \nabla \varphi_i^2 - \frac{1}{4} \sum_i \left[ \frac{\varphi_i}{\rho_a(r)} + \left( \frac{\varphi_i}{\rho_b(r)} \right)^2 \right] \) \quad (13) and

\( D_0(r) = \frac{3}{10} (6\pi^2)^2 (\rho_a(r)^2 + \rho_b(r)^2) \) \quad (14) for close-shell system, since \( \rho_a(r) = \rho_b(r) = \frac{1}{4} \rho \). \( D \) and \( D0 \) terms can be simplified as

\( D(r) = \frac{1}{2} \sum_i \eta_i \nabla \varphi_i^2 - \frac{1}{4} \sum_i \left[ \frac{\varphi_i^2}{\rho(r)} \right] \) \quad (15), \( D_0(r) = \frac{3}{10} (3\pi^2)^2 \rho(r)^2 ) \quad (16).

Savin has reinterpreted the ELF [31], which makes a meaningful for Kohn-Sham DFT equations. They \( D(r) \) reveals the excess kinetic energy densities caused by Pauli repulsions [32]. Localized orbital locators (LOL) are important function for locating high localization regions as the same ELF, defined by Schmidt [33].

\( LOL(r) = \frac{\sum_i \eta_i \nabla \varphi_i(r)^2}{\sum_i \eta_i \varphi_i(r)^2} \) \quad (18).

**3. RESULT AND DISCUSSION**

A listed data of density energies, electron localization functions (ELF), localized orbital locators (LOL) and local entropies including gap energies, charges from ESP, electrostatic potentials, ionization energies, the charges of (m, m)SWCNTs and the stability energies are shown in tables 1,2 and these data have been plotted in the figures (Figs.1-10). We have calculated the gradient norm and the Laplacian of electron densities via Eqs \((5-7)\) for the lithium diffused in the PVP and PVA electrolytes respectively.

![Fig. 3: Possible interaction between polymer PVP and Li^+](image)

**Table 1:** Density, energy, Electron localization function (ELF), The localized orbital locator (LOL) and Local Entropy for each Li of 5 lithium ion diffused on PVP & PVA.

<table>
<thead>
<tr>
<th>Lithium</th>
<th>Density</th>
<th>Energy</th>
<th>ELF</th>
<th>LOL</th>
<th>Entropy</th>
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<td>Li1</td>
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<td>Li3</td>
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<td>Li4</td>
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<td>Li5</td>
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In this work, we have mainly focused on getting the optimized results for each tube of SWCNTs from DFT methods including the m06 and m06-L. The m062x, m06-L, and m06-HF are strong Meta hybrid DFT functional in non-bonded calculations and are suitable for calculating the energies of the distance between tubes and electrolytes (PVA and PVP). Pm6, Extended-Huckel, and Pm3MM including pseudo-lanl2z calculations using abintio program have done for the non-bonded interaction between tubes and electrolytes.

M06 and m06-L (DFT) functionalism are based on an iterative solution of the Kohn-Sham equations [49] of those density functional theories in the plane-wave sets with the projector-augmented wave pseudo-potential. The Perdew-Burke-Ernzerhof (PBE) [50] exchange-correlation of the generalized gradient approximations (GGA) is adopted.

A fixed SWCNTs geometry with electrolytes of PVP and PVA and Li_x for various tubes is chosen with no further geometry optimization.

We further calculated the interaction energies between x lithium of the SWCNTs with electrolytes. The interaction energies were calculated via Mp6 methods in all items according to eq.19: \( \Delta E_S(eV) = (E_{\text{total}} - (E_{Li} + E_{SWCNTs} + E_{PVP})) + E_{\text{BSE}} \) \quad (19).

Where the \( \Delta E_S \) is the stability energy of system.
For calculation the electron spin densities from the difference between alpha and beta densities, we have used the spin polarization parameter functions will be returned instead of spin densities $\xi(r) = \rho^\alpha(r) - \rho^\beta(r)$. The kinetic energy densities, Lagrangian kinetic energy densities, and the electrostatic potential from nuclear / atomic charges can be calculated as eqs. (9), (10) and $V_{nuc}(r) = \sum_A \frac{Z_A}{|r - R_A|}$ where RA and ZA denote position vector and nuclear charge of atom A, respectively and are listed in tables 1, 2.

Bader found that the regions which have large electron localization must have large magnitudes of Fermi hole integrations. However, the Fermi holes are a six-dimension function and thus difficult to be studied visually.

Since $D_0(r)$ from eqs 11-16 is introduced into ELF as references, what the ELF reveals is exactly a relative localization {ELF is within the range of [0, 1]}. A large ELF value indicates that electrons are greatly localized, indicating that the PVP and PVA are suitable interface electrolyte for Li+ diffusion. ELFs have been widely used for the wide varieties of systems, such as organic and inorganic small molecules, atomic crystals, coordination compounds, clusters, and for different problems, such as the revealing atomic shell structure, classification of chemical bonding, verification of charge-shift bond, studying aromaticities.
LOLs have similar definition compared to ELFs. Actually, the chemical regions that highlighted by the LOLs and ELFs are basically qualitative comparable, while Jacobsen pointed out which LOLs conveys more deceives and clearer the pictures than ELFs, Obviously LOLs can be interpreted in kinetic energies way as for ELFs; however LOLs can also be interpreted in view of localized orbitals.

As lithium has a single electron in the last orbital, leading to a difference in spin-up and spin-down, when two lithium atoms are adsorbed simultaneously electrons get paired and magnet moment disappears. So, spin polarized clusters have some gaps which size depends on adsorbed electron spin polarization.

In this work, we have shown SWCNTs does demonstrate high performance with PVP and PVA electrolytes, good mechanical strengths, excellent flexibilities, great chemical stabilities and high surfaces. This is especially noticeable when SWCNTs are converted with PVP and PVA electrolytes, proving that it is suited for use as a base composite electrode material.

4. CONCLUSION

Increasing oil difficulties estimates that by 2020, hybrid vehicles are to account for more than 10% of the global transportation markets. Growing of hybrid vehicles is driving the global demand for lithium ion batteries but what about when those vehicles reach the end of usage? Is it possible for Li-ion easily recycling of this instrument? The rechargeable batteries recycling is the most challenges for new worlds especially the electrolyte of these batteries are dangerous for environments. Via this work, it has been exhibited that the PVA and PVP are suitable electrolytes for lithium ion batteries in view oint of 1-increasing the efficiency of the voltage and amperage and 2-They are bio-degradable polymers electrolyte which are suitable for ecology.

5. REFERENCES

6. ACKNOWLEDGEMENTS

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