

MECHANISM OF INTERCALATION OF POLY(ETHYLENE OXIDE) IN BENTONITE CLAY

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Innumerable, potential technological applications of solid polymer electrolytes have spurred attempts to understand ion-transport behavior of solid electrolyte systems, especially polymer solid electrolyte systems. These materials show ionic conductivity when ionic salts are dissolved in them. The mechanism of ionic mobility is still controversial. We have addressed these problems by choosing Bentonite/poly(ethylene oxide)(PEO)/cations as a model system and systematically investigating the bonding, intercalation and ionic conductivity by Fourier Transform Infrared spectroscopy (FTIR), X-ray diffraction spectroscopy (XRD) and AC-impedance spectroscopy respectively. The FTIR, XRD and AC-impedance characteristics were studied for Na⁺-Bentonite, Li⁺-Bentonite and Li⁺-Bentonite-PEO.

The XRD data reveal that the Na⁺-Bentonite has a d-spacing of 15.49 Å attributed to the presence of Na⁺ and two water layers within interlayers at room temperature. The removal of water brings the d-spacing to 9.97 Å. The Li⁺ exchange gives a d-spacing of 15.57 Å which on dehydration gives a d-spacing of 9.97 Å. Solution intercalation of PEO into Li⁺-Bentonite results in the enhancement of d-spacing up to 18.73 Å which readily takes up water, enhancing the d-spacing to 23.33 Å. These results show clearly that PEO is readily intercalated in Bentonite at a composition of 6% PEO. The enhancement of d-spacing at 6% PEO composition has not been observed previously.

FTIR is a powerful tool for investigating bonding, and ordinary Bentonite (Na⁺-Bentonite) shows typical vibrational modes at 916 cm⁻¹ $\bar{\nu}_{\text{Al-OH}}$, 1040 cm⁻¹ $\bar{\nu}_{\text{Si-O}}$ and a band in the region of 3300 cm⁻¹ - 3700 cm⁻¹ due to $\bar{\nu}_{\text{OH}}$ stretching. Clearly two types of $\bar{\nu}_{\text{O-H}}$ are seen: isolated OH groups and those involved in hydrogen bonding. The Li⁺ exchange decreases the extent of isolated hydroxyl groups, but the extent of H-bonding increases. This suggests that Li⁺ is coordinated by the octahedral unit of the clay, through the O atoms (ions) of free Al-O-H groups. The enhancement of ionic conductivity measured using AC impedance analyzer supports this arrangement.

The intercalation of PEO in Li⁺-Bentonite reverses the above process by forming H-bonds with Li⁺. The amount of free O-H then increases and the extent of hydrogen bonded O-H decreases.

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