

Water transport in non-aqueous electrolytes associated with ion transport and intercalation

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Non-aqueous electrolytes are very popular for many battery systems. For example, carbonate solvents are extensively used in Li-ion batteries. The performance and long term stability of batteries is determined by side reactions of impurities present in electrolytes, and water is one of the most critical impurities. Although water solubility in carbonates is very low, of ~0.1 wt%, its concentration at the electrodes can locally deviate from the average concentration. Transport of solvated water with ions supports water concentration gradients.

The solvation shell surrounding ions, in binary solvents, is determined by the size and polarity of the two types of solvent molecules. Small and polar water molecules have a tendency to replace bigger or less polar solvent molecules in the solvation shell. Thus, ion movement in the electrolyte may preferably drag water molecules. Intercalation of ions in electrode material should reduce the number of solvated molecules in the solvation shell. Depending on the material, intercalation of Li-ions into carbon or oxide electrodes could lead to almost naked Li-ions, but intercalation into conducting polymers may conserve a significant part of the solvation shell. A three step process of solvation, movement, and de-solvation, acts to concentrate water in non-aqueous electrolytes. Here we report on experimental studies of water transport in several carbonate electrolytes (PC, DMC, PC+DMC) associated with transport of Li-ions, as well as with ion intercalation into carbon, CoO_3 , and polypyrrole electrodes.

We simultaneously measured electrical current and humidity changes in an electrochemical cell. The cell was composed of a porous liquid membrane filled with electrolyte, sandwiched between two porous electrodes. Each electrode was adjacent to a gas compartment fitted with humidity meters. Water in the electrolyte equilibrated with the water vapor in the adjacent gas compartments through the electrode pores. Partial water vapor pressure changes in each compartment of a cell consisting of CoO_3 :Li anode and a high surface

carbon (PAC MM 203, $1200 \text{ m}^2/\text{g}$) cathode after a constant voltage of 3.0 V was applied across the cell are shown in Figure 1. Intercalation of Li-ions into carbon enhanced the water concentration near the cathode and de-intercalation of Li-ions from the oxide anode diminished the water concentration.

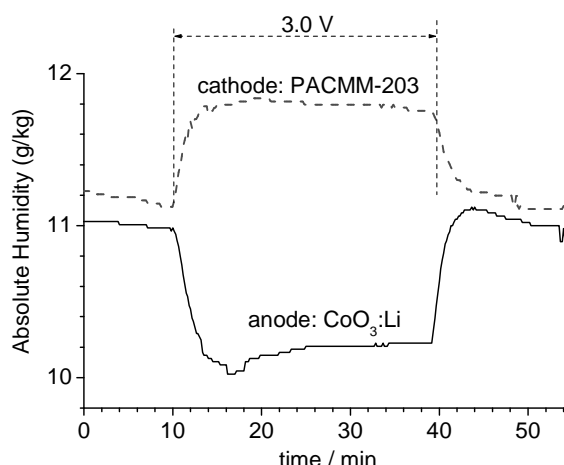


Figure 1. Absolute humidity changes in cathodic (dashed line) and anodic compartments (solid line) of a two-electrode cell consisting of a high surface porous carbon cathode, porous CoO_3 :Li anode, and a porous liquid membrane filled with LiBF_4 /PC electrolyte. A constant voltage of 3.0 V was applied for 30 min.

Water transport numbers α (water molecules per unit charge) were estimated from the experimental data. It was found that for carbonate electrolytes α is about 0.01-0.1, depending on the system. The influence of the solvent and the electrode material on α will be discussed. Water concentration enhancement of 25% above average values was estimated at the cathode.

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