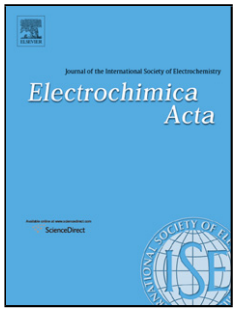

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PII: S0013-4686(17)30941-6
DOI: http://dx.doi.org/doi:10.1016/j.electacta.2017.04.158
Reference: EA 29416

To appear in: *Electrochimica Acta*

Received date: 31-12-2016
Revised date: 28-4-2017
Accepted date: 28-4-2017

Please cite this article as: Elshad Allahyarov, Hartmut L*ddoto*wen, Philip L. Taylor, Simulation Study of Ion Diffusion in Charged Nanopores with Anchored Terminal Groups, *<![CDATA[Electrochimica Acta]]>* (2017), http://dx.doi.org/10.1016/j.electacta.2017.04.158

Available online at www.sciencedirect.com

ScienceDirect

Electrochimica Acta 00 (2017) 000–000

Invited article for Electrochimica Acta, guest edited by Michael Eikerling

Simulation Study of Ion Diffusion in Charged Nanopores with Anchored Terminal Groups

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Abstract

We present coarse-grained simulation results for enhanced ion diffusion in a charged nanopore grafted with ionomer sidechains. The pore surface is hydrophobic and its diameter is varied from 2.0 nm to 3.7 nm. The sidechains have from 2 to 16 monomers (united atom units) and contain sulfonate terminal groups. Our simulation results indicate a strong dependence of the ion diffusion along the pore axis on the pore parameters. In the case of short sidechains and large pores the ions mostly occupy the pore wall area, where their distribution is strongly disturbed by their host sulfonates. In the case of short sidechains and narrow pores, the mobility of ions is strongly affected by the structuring and polarization effects of the water molecules. In the case of long sidechains, and when the sidechain sulfonates reach the pore center, a radial charge separation occurs in the pore. Such charge separation suppresses the ion diffusion along the pore axis. An enhanced ion diffusion was found in the pores grafted with medium-size sidechains provided that the ions do not enter the central pore area, and the water is less structured around the ions and sulfonates. In this case, the 3D density of the ions has a hollow-cylinder type shape with a smooth and uninterrupted surface. We found that the maximal ion diffusion has a linear dependence on the number of sidechain monomers. It is suggested that the maximal ion diffusion along the pore axis is attained if the effective length of the sidechain extension into the pore center (measured as twice the gyration radius of the sidechain with the Flory exponent 1/4) is about 1/3 of the pore radius.

Peer-review under responsibility of the scientific committee of the 19th CIRP Conference on Electro Physical and Chemical Machining.

Keywords: ionomer, ion transport, molecular dynamics, charged pores

1. Introduction

Over the past decade there has been a growing interest in ion transport phenomena in restricted geometries and porous networks. The development of many applications relies on a fundamental understanding of the diffusion properties of particles in cylindrical pores. For example, transport properties of the catalyst layer of polymer electrolyte fuel cells are largely regulated by the electrostatic interaction of the ion with the charges on the cylindrical pore in the Pt electrode [1,2,3]. The charge storage in conducting narrow nanopores relies

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Peer-review under responsibility of the scientific committee of the 19th CIRP Conference on Electro Physical and Chemical Machining.