The IMA Lighthill Lecture at BAMC

Shock Waves and Phase Transformations in Electrochemistry

Delivering the **2016 IMA Lighthill Lecture** was not only a great honour, but also an opportunity to reflect on the influence of Sir Michael James Lighthill (1924–1998). Of course, he is well known to this audience as the founder of the IMA and Lucasian professor at Cambridge. He is remembered worldwide as a pioneer in theoretical fluid mechanics, especially in aeroacoustics and swimming, which was also his passion in real life.[1]

Personally, I first came across the work of Lighthill, when I was trying to calculate the induced-charge electro-osmotic flow around a polarisable particle and its resulting electrophoretic motion.[2] Half a century later, his seminal paper on the 'squirming' motion of micro-organisms[3] provided a useful mathematical framework that could also be applied in this context. Lighthill's emphasis on broken symmetries in swimming also foreshadowed recent developments in induced-charge electrophoresis.[4]

Like many applied mathematicians, I also came to know the Lighthill-Whitham theory of kinematic waves, in traffic flow[5] (Figure 1) through my teaching. This turned out to be a fateful experience, since it prepared me to understand shock waves in other, unexpected areas of my research. This background helped me to develop (with A. Mani) a simple mathematical model of deionisation shocks in charged porous media[6] sustained by surface conduction and electro-osmotic flow[7] (Figure 2). Guided by the theory, I set out to develop the principles and applications of 'shock electrochemistry' in my new experimental laboratory, after I joined the Department of Chemical Engineering in 2008. Recent examples (Figure 3) include shock electrodialysis,[8] a method of water desalination and purification, and shock electrodeposition,[9, 10] a means of controlling metal growth for nanotechnology or batteries.

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In the lecture, my reflection on Lighthill thus naturally led to the main topic of *Nonequilibrium thermodynamics of Li-ion batteries*. For the mathematical details and a historical account of this work, let me refer to a recent review[11] and simply provide some highlights from the lecture. Traditional battery models describe ion transport by diffusion, in both the liquid electrolyte and the solid electrode, but this assumption breaks down for some of the most popular advanced electrode materials, such as iron phosphate and graphite, which separate into stable phases with different lithium concentrations. To address the problem, over the past ten years, I developed general modelling framework unifying non-equilibrium thermodynamics with electrochemistry. The theory is based on the Cahn-Hilliard equation,[12] extended for chemical kinetics and charge transfer,

$$\frac{\partial c_i}{\partial t} = \nabla \cdot M c_i \nabla \frac{\delta G}{\delta c_i} + R\left(\left\{\frac{\delta G}{\delta c_j}\right\}\right)$$

where the reaction rate R may be localised on a boundary for heterogeneous reactions (the 'Cahn-Hilliard reaction model') or distributed throughout a volume for homogeneous reactions (the 'Allen-Cahn reaction model').[11] In traditional battery modelling, the open circuit voltage versus state of charge is fitted to experimental data, which amounts to relating the lithium chemical potential in the solid to the (assumed) uniform concentration in equilibrium, when diffusion stops. In multiphase systems, however, equilibrium does not imply constant concentration, but instead constant (diffusional) chemical potential, defined as the variational derivative of the total Gibbs free energy functional. The new theory thus has a fundamentally different starting point, putting all the constitutive physics into the free energy functional, rather than the voltage profile. In this way, complicated effects of configurational entropy, elastic coherency strain and diffuse charge are consistently incorporated into the formulation of chemical reaction kinetics.

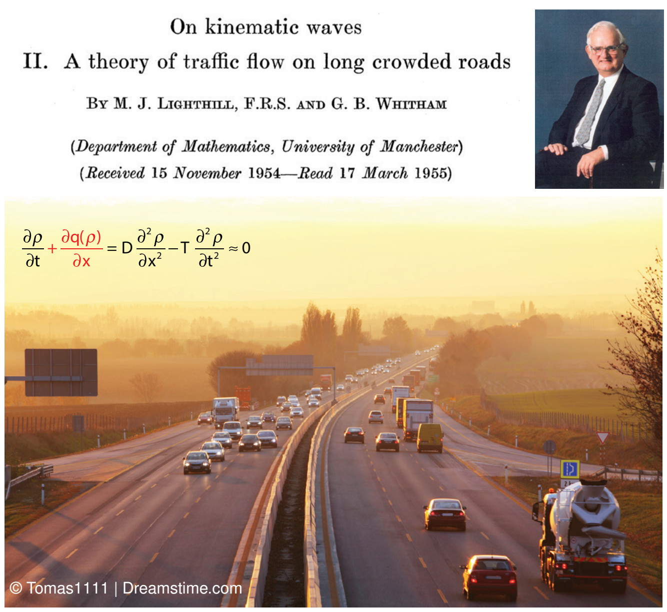

Figure 1: The Lighthill-Whitham theory of traffic flow.[5]

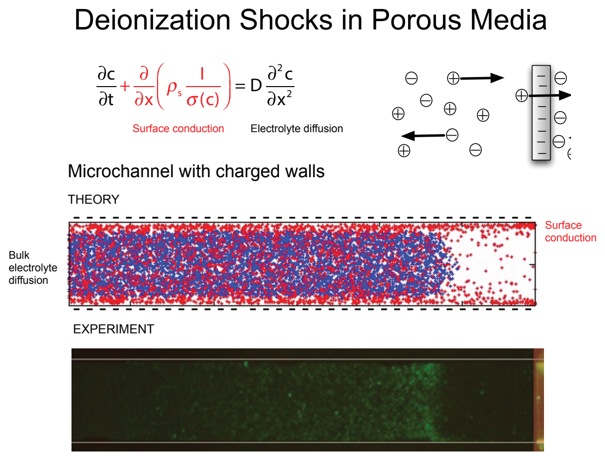

Figure 2: Theory[6] and experiments[7] on deionisation shocks.

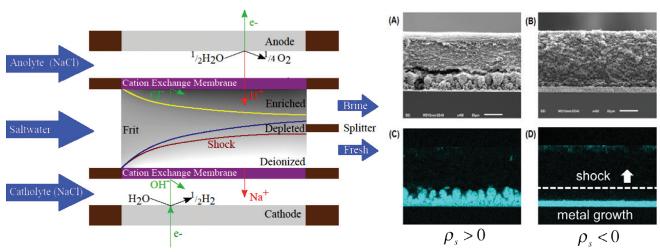

Figure 3: Left: shock electrodialysis.[8] Right: shock electrodeposition.[10]

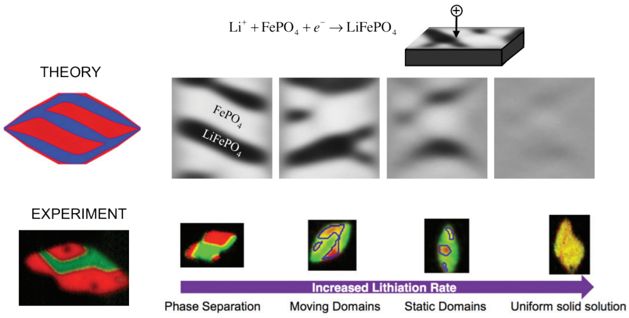

Figure 4: Phase separation patterns in lithium iron phosphate nanoparticles, which become suppressed with increasing discharge current. Top row: theoretical predictions.[11,14,15] *Bottom row: subsequent experimental observations by in operando x-ray imaging from the group of W.C. Chueh.*[18]

The mathematical theory has led to some surprising predictions about nanoscale kinetics in the prototypical two-phase battery material, lithium iron phosphate (LFP):

- Intercalation waves (moving phase boundaries) sweeping across the active crystal facet,[12] rather than penetrating the bulk like a shrinking core;
- Suppression of phase separation in nanoparticles during battery discharge;[13]
- Striped patterns of phase separation, resulting from coherency strain;[14]
- Nucleation by surface 'wetting' of solid phases in nanoparticles;[15]
- Mosaic instability (discrete particle transformations) in porous electrodes, depending on the applied current and particle size distribution.[16]

All of these predictions have since been visualised *in situ* during battery operation (Figure 4), a remarkable feat that will continue to shed light new phenomena, guided by mathematical modeling.[17,18] This connection between theory, experiments, and applications follows in the tradition of British applied mathematics, led by Lighthill.

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