

Capacitive De-ionisation: An Electrochemical Perspective

Robert A.W. Dryfe^{1,2*} and John M. Griffin^{3,4}

1 = Dept. of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL, UK

2 = Henry Royce Institute, University of Manchester, Oxford Road, Manchester M13 9PL,
UK

3 = Dept. of Chemistry, Lancaster University, Lancaster LA1 4YB, UK

4 = Materials Science Institute, Lancaster University, Lancaster LA1 4YB, UK

e-mail: robert.dryfe@manchester.ac.uk

Abstract: Capacitive de-ionisation is emerging as a viable technology for water desalination. The technique is based on electrochemical fundamentals: it rests on the potential-dependent adsorption of ions within the pores of high surface area electrode materials. The adsorption process is normally capacitive, although Faradaic approaches have been reported recently. Most of the rapidly expanding literature on this topic focusses on the material science aspects: namely the effect of electrode and membrane composition/structure on the performance metrics associated with this technique. In this short review, we focus on how electrochemical methods can be used to further understanding of this promising technology for water purification. We also highlight complementary analytical techniques which can be applied in tandem with the electrochemical signals.

Introduction: The literature on capacitive de-ionisation (CDI) can be traced back to the 1960s. The concept is simple: on application of a voltage between two high surface area electrodes, the resultant adsorption of ions can be used to purify water. Concerns about water resources and the energetic footprint of alternative water purification technologies have led to a dramatic upsurge in recent activity related to CDI. Most recent literature uses (at least) one membrane material in conjunction with the electrode materials, the rationale (discussed further below) being that ion-exchange membranes prevent the adsorption of co-ions and hence increase the Faradaic efficiency of CDI. Most of the recent literature discusses new electrode and/or membrane materials, thus focusing on the relation between the composition/micro-structure of these materials and the performance of the CDI system. Rather than the empirical, materials aspects which have been reviewed elsewhere [1,2], here we seek to survey the most recent (2018 onwards) literature concerning the electrochemical aspects of CDI, focussing on the general physico-chemical principles which underpin the technique. We discuss the interpretation of the electrochemical response itself and outline complementary spectroscopic, and other analytical, techniques that can be harnessed to increase mechanistic understanding of the CDI process.

The CDI experiment is critically dependent on transport over a variety of length scales. Transport and sorption of ions within micropores is the basis of the approach, however CDI is almost always performed under flowing conditions, hence the flow regime established, and coupling of the flow profile with the electric field established within the cell, means transport on a macroscopic level must also be considered. This hierarchy of length-scales makes accurate modelling of CDI particularly complex, although some notable works to address these multi-scale challenges have recently appeared [3]. Modelling of transport and sorption within CDI cells is an active area of research which has been reviewed recently [4].

From the experimental perspective, a range of metrics are used to describe CDI performance: new materials are often reported in terms of their salt adsorption capacity, charge efficiency, salt adsorption rate and energy normalised to salt adsorption [5]; standardisation of these metrics has been a recurring theme in the CDI literature [6,7]. Finally a weakness of most experimental studies of CDI is their reliance on a “remote” probe, normally the outlet conductivity. By definition, this approach can only sample an average ion concentration of the purified water and does not offer any specificity, which is of interest in multi-component (and hence “real-world” applications). A recent perspective article has highlighted that the gap between expected and observed CDI performance is largely due to our imperfect understanding of physico-chemical processes within the micropores inherent to electrode structure used in CDI [8]. We therefore highlight possible *in situ* structural studies, capable of giving local and ion-specific information on the mechanism of the CDI process.

The simplest CDI configuration: The simplest configuration for CDI involves flowing an electrolyte solution between - or through - two high surface area electrodes, normally formed from a nominally inert carbon material material (illustrated in Figure 1a). This type of configuration is, of course, unlikely to yield optimal device performance, but its simplicity does make it more tractable to modelling, either using numerical or analytical approaches. One intrinsic challenge in CDI cells is to understand which of the electrodes acts as the “process-limiting” one. Even for an electrolyte containing only Na^+ and Cl^- , the different interactions of

the ions with the (for example) carbonaceous electrode means that the sorption capacities on each electrode will not necessarily balance.

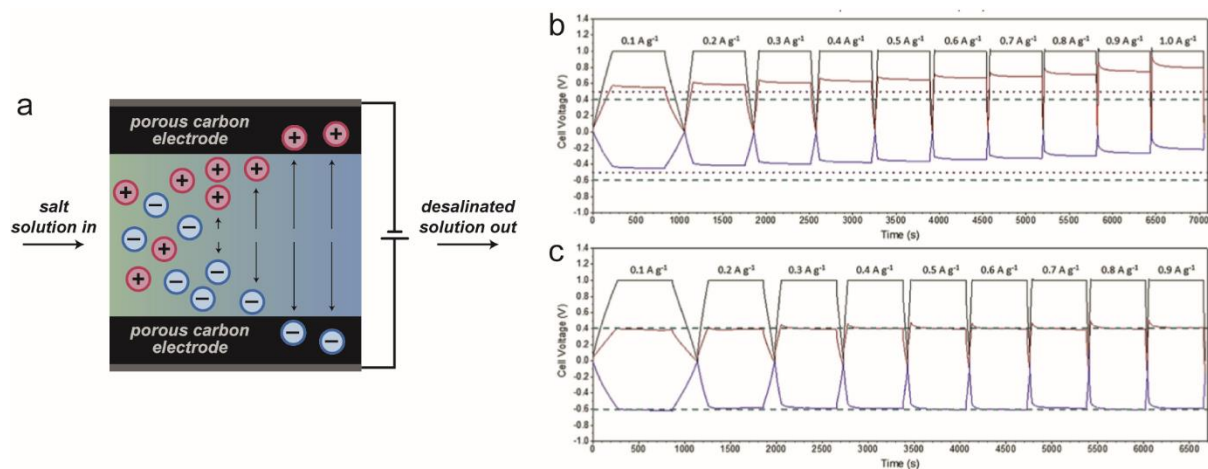


Figure 1. (a) Schematic representation of the simplest CDI cell configuration whereby a salt solution is desalinated as it flows between two high-surface area electrodes under a potential difference. Constant current charge-discharge data is shown for (b) electrode mass-symmetric and (c) mass-asymmetric CDI cells, illustrating how choice of an appropriate mass balance ratio based can keep the individual electrode potentials within the electrochemically stable potential window (green dashed line) [(b) and (c) Reprinted from *Electrochim. Acta*, 325, A. Carmona-Orbezo, L.W. Le Fevre and R.A.W. Dryfe, Performance optimization of carbon electrodes for capacitive deionization by potentiostatic analysis, 134898, Copyright (2019), with permission from Elsevier].

For this reason, it is useful to optimise the mass ratio of the electrodes, to ensure that both anode and cathode are fully utilised during the capacitive charging process, an approach familiar to those working in the battery and supercapacitor fields. One example of such an “asymmetric” CDI cell was reported by Presser and co-workers who showed that lignin-derived activated carbon was more susceptible to oxidative decomposition, thus the mass of the positive electrode should be increased to compensate for the lower stability of the electrode material. In the same study, carbon materials with different potentials of zero charge were also

used to create the symmetry required to overcome the asymmetric adsorption (and eventually) degradation processes [9]. The inclusion of a reference electrode into the CDI cell enables the ready determination of the optimal mass ratio [10], an approach we have adapted from previous work with coin cells in the supercapacitor context [11,12]. The work by Zornitta *et al* is also notable because the authors explore the stability window, with respect to cell voltage, of their system [9]. 1.2 V has become a default voltage, generally applied to CDI cells [13,14], apparently without much consideration of whether this voltage range is necessarily optimal for the electrode material/geometry/mass-transport/electrolyte combination employed. In terms of the CDI performance parameters outlined above, there will be a trade-off between salt adsorption capacity and rate (favoured by a higher cell voltage) vs. charge efficiency and energy normalised to salt adsorption (favoured by a lower cell voltage), although why 1.2 V is optimal is far from clear. The thermodynamic stability window of water is, of course, 1.23 V, although kinetic factors are likely to extend the achievable window, given that the kinetics of water decomposition on carbon are generally slow [15]. Set against this is the occurrence of competing processes, including chloride and carbon surface oxidation, however CDI studies rarely determine the optimal voltage for the system under study, which is an oversight, particularly when new materials are reported.

Electrochemical responses are sensitive to local mass-transport, as well as any inherent kinetic factors. So, in principle, a voltammetric signal could be used to report on local mass transport. An attempt to relate the electrochemical signal to mass-transport within the CDI cell has been reported by Simon and co-workers. They added a simple redox couple (the ferri/ferrocyanide couple) to the solution and used the Faradaic response of the couple as a proxy to understand mass-transport in the CDI case, comparing the simple case of a flat Pt foil, then extending the experiments to activated carbon films where the transport will become dominated by inter-pore transport [16]. Only empirical relations between the current and the flow regime are drawn, which is surprising because channel and tubular configurations exist which allow quantification of current in terms of flow rate, at least for the case of non-porous

electrodes [17]. Another complexity is that a much larger fraction of the transport of the redox-active probe will be due to diffusion, whereas migration of the salts will dictate transport in the regular CDI case. Even so, the approach is a promising preliminary one and suggests that insight can be obtained through the use of “voltammetric probes” of transport within CDI systems.

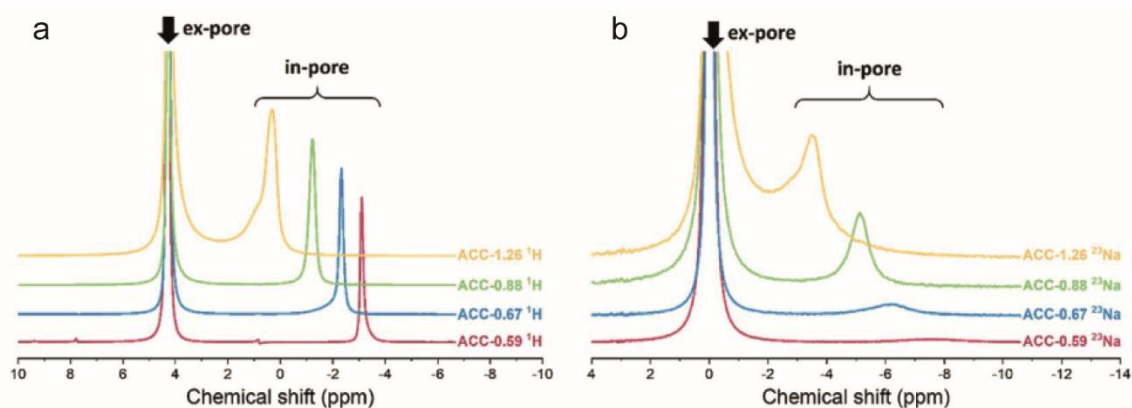


Figure 2. (a) ^1H and (b) ^{23}Na NMR spectra of activated carbons soaked in aqueous 0.80 M NaCl. In-pore (adsorbed) species can be readily distinguished from ex-pore species in the bulk electrolyte via a pronounced diamagnetic shift. Integration of the in-pore and ex-pore resonances enables the relative proportions of the two types of environment in the sample to be determined. [Reproduced from Ref. [18] with permission from the Royal Society of Chemistry].

Complexity 1, adding membranes: It has long been recognised that the addition of a membrane to one, or both, of the electrodes within the CDI cell improves the desalination performance [19]. The rationale for the greater charge efficiency seen in the “membrane-CDI” configuration is the repulsion of co-ions by the ion-exchange membranes, and the ability to provide some selectivity with respect to counter-ion transport in the case of multi-component systems. The addition of membranes, however, makes ion-transport and the potential distribution within the cell a less tractable problem, hence we consider the development of *in situ* probes of ion distribution to be desirable. Present-day work normally relies on *ex situ*

characterisation of such membranes (for example, their water uptake, ion-exchange capacity and microscopic morphology [20]) whereas the quantities of most interest are the relative distributions of the ions within the cell as a function of voltage, and the rate of change of these distributions as voltage (or flow rate, or salt concentrations) is altered. Particularly for cases where the selective uptake on a particular ion is intended, *in situ* spectroscopic methods will be key to quantifying selectivity. NMR spectroscopy shows considerable potential in this regard, owing to its ability to quantify in-pore (adsorbed) species within porous carbons, as illustrated in Figure 2 [21,22]. Recent *ex situ* NMR studies have already revealed differences in spontaneous uptake of salt solutions by microporous carbons, suggesting that salt concentration, pore size and ion-specific solvation properties may play an important role [18,23]. The implementation of *in situ* NMR approaches, similar to those already introduced for studying supercapacitors [24], will enable the influence of specific ion effects and membrane properties on the CDI mechanism to be characterised.

Complexity 2, Faradaic processes: A further important development in the CDI field has been the application of “battery” electrode materials. The concept is that the charge transfer reaction leads to the incorporation (e.g. by intercalation) of one of the electrolyte ions. In terms of charge stored per unit mass, or area, the capacity of Faradaic materials is normally in considerable excess over the capacitance of non-Faradaic materials, although there can be disadvantages in terms of conductivity, response time, and cycle life with Faradaic processes. A further advantage of the Faradaic approach, however, is that it may be more readily tuned to specific ions, taking the advantage of redox chemistry (and associated ion incorporation) over the less specific potential-dependent adsorption process. The complexity of these processes require the development of techniques capable of detecting them *in situ*. For example, Presser and co-workers have described a vanadyl phosphate material which is able to take up Na^+ , and although spectroscopic methods (specifically infra-red spectroscopy) were used to monitor the phase changes within the solid, these approaches were applied *ex situ* [25]. The same laboratory exploited the aforementioned potential dependence to tune the

extraction of divalent ions over monovalent ions, exemplifying their approach with Mg^{2+} (vs. Cs^+) uptake using a TiS_2 electrode [26]. *In situ* Raman spectroscopy has been combined with *in situ* X-ray diffraction as a route to determine fluoride sorption in a CDI cell [27]. Although the title of the work in question implies that the process is “capacitive”, the *in situ* analytical techniques demonstrate the reversible formation of fluoride phases of Al, through the presence of alumina particles decorating the electrode surfaces.

Complexity 3, “flow-able” electrodes: As indicated above, the flow regime established in CDI cells is a relatively complex one. The flow and voltage profile becomes further complicated when the “flow electrode” CDI configuration is considered: these systems consist of flowing suspensions of particles (typically carbon). The rationale behind their introduction is their ability to achieve significant de-ionisation, even at enhanced salt concentrations, i.e. those approaching sea-water, due to the high surface area of the suspensions [28]. One of us has recently described the application of channel flow cells to CDI [29], the rationale being that the well-defined mass-transport in the channel cell [17] simplifies the analysis of CDI response. The flow-able electrode configuration is particularly complex because of the interdependence of suspension loading (mass fraction), particle size (surface to volume ratio) and solution viscosity, all of which will affect cell conductivity and thus the resultant efficiency of the de-ionisation process. For most variables, an optimal value of these parameters was found. An attempt to present the data in terms of a single dimensionless number was made in this work, where the number depended on suspension viscosity, channel dimensions and suspension flow rate [29]. Rommerskirchen *et al* have proposed AC impedance methods as a diagnostic tool by which the electrical characteristics of different carbon suspensions, e.g. establishment of a percolation threshold, can be judged [30]. Finally, we note that another recent study with flow-able electrodes has systematically explored the voltage range and found an optimal voltage of 2.5 V (i.e. well above the “default” 1.2 V discussed above) for an activated carbon suspension [31].

Conclusion:

Most of the current work on CDI is largely empirical: the composition or micro-structure of one (or both) electrodes is changed and the resultant effect on performance is observed. Meaningful progress in our knowledge of CDI requires a mechanistic understanding of the physico-chemical processes occurring at/within the electrodes as a function of cell voltage. Bone *et al* have discussed the application of various X-ray and neutron based scattering techniques to achieve this goal, although it is not necessarily clear that some of these techniques can be readily applied to porous materials *in situ*, i.e. under potential control [*Bone again*]. We advocate the application of *in situ* spectroscopic methods coupled with careful electrochemical analysis, preferably in the three-electrode configuration, to build up a detailed picture of the CDI mechanism. Methods based on NMR spectroscopy show particular promise in this regard, as they have already proved to be very powerful probes of ion fluxes within porous materials in the supercapacitor context [21,32,33]. A longer-term challenge will be the integration of such microscopic structural studies with those of fluid flow and potential distribution on macroscopic scales.

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* * of outstanding interest

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This article highlights the power of *in situ* NMR methods as a probe of ion adsorption processes, under voltage control, in supercapacitors.

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