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Elektrolyytti käytettäväksi superkondensaattorissa ja suuritehoisessa akussa

Elektrolyt att användas för superkapacitor och högeffektsbatteri

ELECTROLYTE FOR SUPERCAPACITOR AND HIGH-POWER BATTERY USE

(57) Tiivistelmä - Sammandrag - Abstract

Esillä oleva hakemus koskee sähkökemiallista kennoa, joka käsittää nitriilipohjaiseen liuottimeen perustuvan elektrolyytin, jossa elektrolyyttisuola käsittää $NaClO_4$:n, ja sähkökemiallisen kennon varauksen missä tahansa vaiheessa elektrolyyttisuolalla on korkea molaarinen konsentraatio purkautuneessa tilassa.

The present application relates to an electrochemical cell comprising a nitrile-based solvent based electrolyte wherein, the electrolyte salt comprises $NaClO_4$ and, at any stage of charge of the electrochemical cell, the electrolyte salt has a high Molar concentration in the discharged state.

ELECTROLYTE FOR SUPERCAPACITOR AND HIGH-POWER BATTERY USE

FIELD OF THE INVENTION

The invention relates to rechargeable electrochemical cells such as batteries, for instance high-power batteries or fast-charging and supercapacitors. In particular, the present invention concerns the improvement of electrolytes for these electrochemical cells.

BACKGROUND OF THE INVENTION

High performance and low cost supercapacitors and fast batteries are advantageous for many applications in e.g., starter batteries or fast charging electric vehicles.

Electrolyte salts employed for supercapacitors or high-power or fast-charging batteries are generally in the 1 to 1.5 Molar concentration range, which corresponds to the ionic conductivity maxima of currently used salts. The use of $NaClO_4$ as a possible electrolyte salt with acetonitrile solvent has been previously known in the art. However, all related publications describe electrolyte formulations employing $NaClO_4$ salt concentration of 1 Molar or less in the acetonitrile solvent.

As the technology advances for making electric double-layer supercapacitor electrodes with ever higher volumetric capacitance, the use of highly concentrated supercapacitor electrolytes becomes essential. For instance, publication [2] describes porous carbon

based supercapacitor electrodes achieving 170 F/cm^3 volumetric capacitance with acetonitrile solvent based electrolytes. These electrodes have 70% space filling, i.e. is only 30% of the electrode volume is empty space for the electrolyte. Based on the data of publication [2], charging up such symmetric supercapacitor to 2.7 V voltage would require 4 Molar initial salt concentration, if all the electrolyte would be within the symmetric electrode volume. Under existing electrolyte formulations, significant excess electrolyte is required to use this capacity. Novel electrolyte formulations allowing increased volumetric capacity by minimizing the need of such excess electrolyte are a benefit to industry and commerce.

SUMMARY OF THE INVENTION

In the current invention, highly concentrated salts which have high ionic conductivity, are cost effective and support a wide voltage window are disclosed. Previously known highly concentrated electrolytes were poorly conductive and expensive.

Acetonitrile is frequently employed as an electrolyte solvent in supercapacitors. It can be also used as electrolyte solvent in certain high-power and/or fast-charging batteries, where the electrode cycling voltages are compatible with its voltage window. This invention discloses significant improvements in the acetonitrile solvent based electrolytes' conductivity, cost-efficiency, and compatibility with advanced electrode structures. These improvements are realized through the use of highly concentrated $NaClO_4$ containing electrolyte salt - either as a sole electrolyte salt or in combination with other salts

(co-salts) in combination with nitrile-based solvents. The current invention advances the state-of-the art in supercapacitors and high-power batteries for these and other applications. The improvements are realized in terms of the electrolyte's conductivity, cost-efficiency, and compatibility with advanced electrode structures. The described invention is, thus, beneficial to industry and commerce.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows the capacity evolution of a symmetric supercapacitor employing 3 Molar $NaClO_4$ salt concentration in acetonitrile solvent. Both electrodes are made from porous carbon on aluminum substrate. The supercapacitor has been charged up to 2.7 V during the cycling. The initial 30 cycles were performed at 0.5 mA/cm^2 current rate, and subsequent cycles were performed at 2 mA/cm^2 current rate.

DETAILED DESCRIPTION OF THE EMBODIMENTS

Detailed embodiments of the present invention are disclosed herein with the reference to accompanying drawings.

An electrochemical cell may comprises, at least, an anode, a cathode and an electrolyte at least partially between the anode and cathode. An electrochemical cell may further comprise a separator between the anode and cathode. An electrochemical cell may further comprise one or more charge carriers. An electrochemical cell may further comprise a housing. The electrolyte of an electrochemical cell may comprise a sodium-based salt. The electrolyte of an electrochemical cell may comprise a nitrile-based solvent. The sodium-based

salt of the electrolyte may be $NaClO_4$. The electrochemical cell may be symmetric in which case both the anode and cathode materials are essentially the same. The electrochemical cell may be asymmetric in which case the anode and cathode materials are essentially not the same. The electrochemical cell may be a supercapacitor or a battery. The battery may be a primary (single-use) or secondary (rechargable) battery.

The ionic conductivity maximum of $NaClO_4$ electrolyte salt with acetonitrile solvent has been previously stated to occur at 0.55 Molar concentration [1], however, we have surprisingly discovered that, contrary to other commonly used electrolyte salts, the ionic conductivity of the electrolyte comprising $NaClO_4$ salt in acetonitrile solvent increases with high molar concentration. After some point, the conductivity was found to decrease as the $NaClO_4$ concentration became over concentrated. Specifically, it was found that the ionic conductivity of the electrolyte increases with increasing $NaClO_4$ concentration, and reaches a conductivity maximum at approximately 3 Molar concentration.

At electrolyte salt Molar concentration above 1, the electrolyte salt may be considered to be highly concentrated. At Molar concentration at or above 1.25, the electrolyte salt may be considered to be highly concentrated. At Molar concentration above 1.5, the electrolyte salt may be considered to be highly concentrated. At Molar concentration at or above 1.75, the electrolyte salt may be considered to be highly concentrated. At Molar concentration at or above 2, the electrolyte salt may be considered to be highly concentrated. At Molar concentration at or above 2.25, the electrolyte salt may be considered to

be highly concentrated. At Molar concentration at or above 2.5, the electrolyte salt may be considered to be highly concentrated. At Molar concentration at or above 2.75, the electrolyte salt may be considered to be highly concentrated. At Molar concentration of at or above approximately 3, the electrolyte salt may be considered to be highly concentrated.

At electrolyte salt Molar concentration at or below 1, the electrolyte salt may be considered to be low concentration. At Molar concentration below 0.95, the electrolyte salt may be considered to be low concentration. At Molar concentration below 0.7, the electrolyte salt may be considered to be low concentration. At Molar concentration below 0.5, the electrolyte salt may be considered to be low concentration. At Molar concentration below 0.35, the electrolyte salt may be considered to be low concentration. At Molar concentration below 0.25, the electrolyte salt may be considered to be low concentration. At Molar concentration below 0.2, the electrolyte salt may be considered to be low concentration. At Molar concentration below 0.15, the electrolyte salt may be considered to be low concentration.

The lower bound of the electrolyte salt concentration between charge and discharge state of the electrochemical cell may be its highly concentrated value. The upper bound of the electrolyte molar concentration may be at or near its solubility limit in the electrolyte solvent. The Molar concentration of the electrolyte salt may be between any combination of lower (high concentration) and upper (solubility limit in the electrolyte solvent) bounds. Said solubility limit varies according to the solvents and salts present. Near, in terms of solubility limit, here may

mean an electrolyte Molar concentration above 70% of its solubility limit in the electrolyte solvent. Near, in terms of solubility limit, here may mean an electrolyte Molar concentration above 85% of its solubility limit in the electrolyte solvent. Near, in terms of solubility limit, here may mean an electrolyte Molar concentration above 90% of its solubility limit in the electrolyte solvent. Near, in terms of solubility limit, here may mean an electrolyte Molar concentration above 95% of its solubility limit in the electrolyte solvent. Near, in terms of solubility limit, here may mean an electrolyte Molar concentration above 98% of its solubility limit in the electrolyte solvent. Near, in terms of solubility limit, here may mean an electrolyte Molar concentration above 99% of its solubility limit in the electrolyte solvent.In the case when the electrochemical cell is a supercapacitor, the Molar concentration refers to the concentration in the fully discharged state or the assembled state and corresponds to the highest Molar concentration in the charge/discharge cycle. In the case of a supercapacitor, the Molar concentration may decrease during charging and may even drop to approximately zero in the fully charged state (the Molar concentration cannot drop to exactly zero or the electrolyte would no longer conduct ions). In the case when the electrolytic cell is a battery, the Molar concentration does not essentially change between charge and discharge states and the Molar concentration refers to the essentially constant Molar concentration.

Any combination of the described high concentration bound, solubility limit bound and/or ranges are possible. For the avoidance of doubt, when a co-salt is present in an electrolyte, as described below, the

electrolyte salt concentration (or salt concentration) refers to the combined $NaClO_4$: co-salt concentration.

Table 1 shows the dependence of the electrolyte conductivity on the $NaClO_4$ concentration in a system without co-salt. Other solvents are possible, most preferably nitrile-based solvents are possible.

$NaClO_4$ concentration	0.5 M	2 M	2.5 M	3 M	3.5 M
Electrolyte conductivity	31 mS/cm	35 mS/cm	36.5 mS/cm	38.5 mS/cm	35.5 mS/cm

Table 1: Ionic conductivity of the $NaClO_4$ salt in acetonitrile solvent, as a function of salt concentration

It has been furthermore discovered, that it is feasible to maintain the same 38.5 mS/cm conductivity maximum at an even higher electrolyte salt concentration by employing a mixture of electrolyte salts in the acetonitrile solvent, where $NaClO_4$ a salt component. As an example, Table 2 shows the electrolyte conductivity development obtained with a 4:1 ratio mixture of $NaClO_4$: $NaPF_6$ salts in acetonitrile solvent. The 38.5 mS/cm ionic conductivity maximum is reached at 3.5 Molar total electrolyte salt concentration. Other sodium containing co-salts besides $NaPF_6$ are possible; examples of suitable co-salts include but are not limited to Sodium-triflate (CF_3SO_3Na, denoted as NaTriflate) or Sodium-difluoro(oxalato)borate ($C_2O_4BF_2Na$, denoted as NaDFOB). Other ratios of $NaClO_4$: sodium containing co-salts are possible. The $NaClO_4$: sodium containing co-salt ratio may be between 0.5:1 and 32:1. The $NaClO_4$: sodium containing co-salt ratio may be between 1:1 and 16:1. The $NaClO_4$: sodium

containing co-salt ratio may be between 2:1 and 8:1, and more preferably between 3:1 and 6:1 and most preferably approximately 4:1. Any combination of the described upper and lower limits of the listed $NaClO_4$: sodium containing co-salt ratios are possible.

Total salt concentration	1 M	1.5 M	2 M	3 M	3.5 M
Electrolyte conductivity	31 mS/cm	34 mS/cm	34.5 mS/cm	37 mS/cm	38.5 mS/cm

Table 2: Ionic conductivity of the 4:1 ratio of $NaClO_4$: $NaPF_6$ salt mixture in acetonitrile solvent, as a function of total salt concentration

The abovesaid electrolyte formulations enable the cost-effective production of highly conductive supercapacitor and/or battery electrolytes, which are compatible with the full voltage window of the acetonitrile solvent. These electrolyte formulations are furthermore compatible with aluminum current collector substrates, as evidenced by the stable cycling capacity shown in Figure 1.

During cycling of an electric double-layer supercapacitor with a high volumetric capacitance, the ideal electrolyte salt concentration strongly can vary between high concentration (e.g. 3-3.5 Molar in the discharged state) and low concentration (e.g. 0.2-0.5 Molar in the charged state). The use of the highly concentrated electrolyte salt described here, therefore, becomes an important consideration for high volumetric capacity supercapacitors in order to minimize the needed excess electrolyte, and thus

maximize the device-level energy density. The use of the herein disclosed electrolyte formulations is therefore particularly advantageous, as such electrolytes are able to deliver >30 mS/cm ionic conductivity over a wide range of Molar salt concentrations as may exist between charge and discharge state (e.g. from below 0.5 Molar concentration to above 3.5 Molar concentration).

REFERENCES

[1] G. Herlem et al, Journal of Solution Chemistry, Vol. 28 (1999), No. 3, Pp. 223-235.

[2] Y. Tao at el, DOI: 10.1038/srep02975

CLAIMS

1. An electrochemical cell comprising a nitrile-based solvent based electrolyte wherein, the electrolyte salt comprises $NaClO_4$ and, at any stage of charge of the electrochemical cell, the electrolyte salt has a high Molar concentration in the discharged state.

2. The electrochemical cell of claim 1 wherein the nitrile-based solvent is acetonitrile.

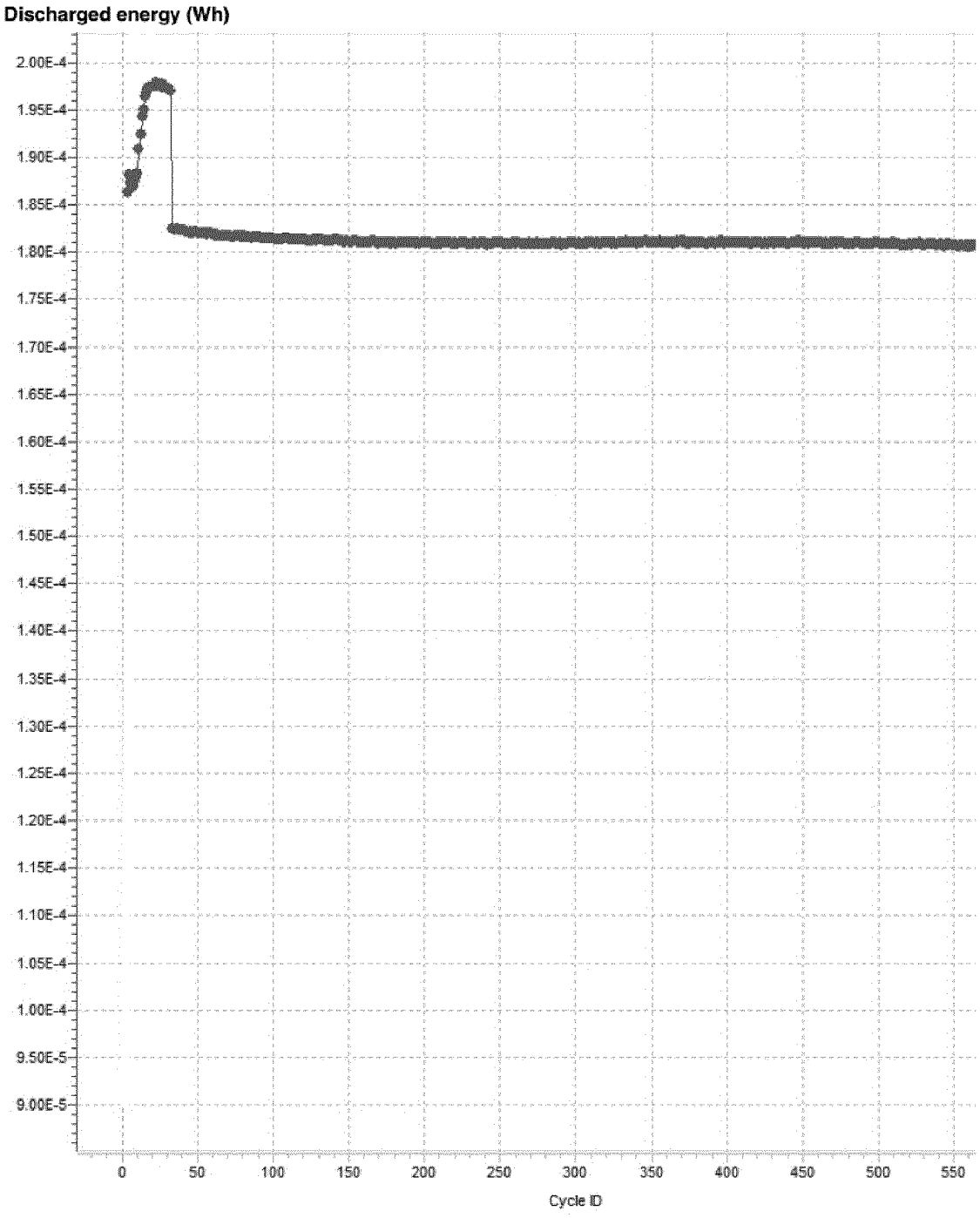
3. The electrochemical cell of any of claims 1 - 2 wherein the electrolyte salt further comprises a sodium containing co-salt.

4. The electrochemical cell of any of claims 1 - 3 wherein the co-salt is $NaPF_6$, NaTriflate, NaDFOB, or any combination thereof.

5. The electrochemical cell of any of claims 1 – 3 wherein, at any stage of charge of the electrochemical cell, the electrolyte salt is at or near its solubility limit in the electrolyte solvent.

FIGURES

Figure 1



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SEARCH REPORT

PATENT APPLICATION No.	**CLASSIFICATION**	
20175239	IPC ***H01G 11/62*** (2013.01) ***H01G 11/60*** (2013.01) ***H01G 11/58*** (2013.01) ***H01M 10/056*** (2010.01)	CPC **H01G 11/62** **H01G 11/60** **H01G 11/58** **H01M 10/056**

PATENT CLASSES SEARCHED (classification systems and classes)
IPC: H01G, H01M
DATABASES CONSULTED DURING THE SEARCH
EPODOC, EPO-Internal full-text databases, Full-text translation databases from Asian languages, WPIAP, CA, XPESP, COMPDX, PRH-Internal

DOCUMENTS CONSIDERED TO BE RELEVANT

Category*)	**Bibliographic data on the document and relevant passages**	**Relevant to claims**
X	US 2016071658 A1 (AZAIS PHILIPPE [FR] et al.) 10 March 2016 (10.03.2016) paragraphs [0074], [0091-0093], [0152], [0178]; claims 1, 2, 11, 14, 15, 16, 17 and 21	1-5
A	WO 2015072577 A1 (SUMITOMO CHEMICAL CO [JP]) 21 May 2015 (21.05.2015) & abstract [online] EPOQUENET & WPI & machine translation into English By Thomson Reuters [online] EPOQUENET TXPWOTEA claims 1-3	1-5
A	US 2016260551 A1 (NANDA JAGJIT [US] et al.) 08 September 2016 (08.09.2016) claims 1,3	1-5

Continued on the next sheet ☒

*) X Document indicating that the invention is not novel or does not involve an inventive step with respect to the state of the art.
Y Document indicating that the invention does not involve an inventive step with respect to the state of the art if combined with one or more other documents in the same category.
A Document representing the general state of the art.

O Document referring to disclosure through lecture, use or other non-written means.
P Document published prior to the filing date but not prior to the earliest priority date.
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D Document that is mentioned in the application.
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This document has been electronically signed. **Further information given in the annex** ☐

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SEARCH REPORT

PATENT APPLICATION No.
20175239

DOCUMENTS CONSIDERED TO BE RELEVANT, CONTINUED		
Category*)	**Bibliographic data on the document and relevant passages**	**Relevant to claims**
A	JP 2010165674 A (EQUOS RES CO LTD) 29 July 2010 (29.07.2010) & abstract [online] EPOQUENET & WPI & machine translation into English EPOQUENET TXPJPEA claims 1,4,5,6	1-5
A	FI 126390 B (BROADBIT BATTERIES OY [FI]) 15 November 2016 (15.11.2016) claim 1	1-5