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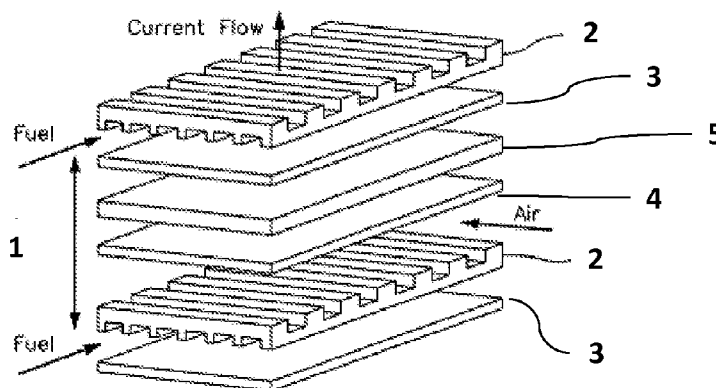
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Fig. 1



(57) Abstract: The present invention concerns a carbon-polymercomposite material containing at least one thermoplastic polymer, at least two carbon fillers, one beingselected fromgraphites, and at least one additive selected from flow modifiers.The invention also concerns a moulded composite structure, such as a plate,moulded from said composite material, a process for compounding and moulding said material into said structure, as well as the use of this composite in electrochemical applications.

# CARBON-CONTAINING COMPOSITES AND THEIR ELECTROCHEMICAL APPLICATIONS

## Background of the Invention

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### Field of the Invention

The present invention concerns carbon-polymer composite materials, as well as a process for compounding such a composite material and moulding it into the desired shape. This material can be used in various applications, but is particularly suitable for use in electrochemical applications, such as fuel cells.

10

### Description of Related Art

15

Graphite components are commonly used for electrochemical applications like stationary fuel cells and flow batteries, as well as heat exchangers. Due to its properties, graphite is highly suitable for use even in corrosive environments. Thus, graphite materials can be shaped into, e.g. bipolar plates for use in fuel cells, which plates are mainly responsible for distribution of reactants and other materials, as well as electron transport, but also provide mechanical support for membrane electrodes and separation of unit cells in stacks. The electrical conductivity of these plates and other similar components is essential, as well as the chemical resistance of the plate material.

20

Since pure graphite is brittle and expensive to machine (or shape), graphite components have lately been replaced in said electrochemical applications by graphite-polymer composites, which exhibit a higher strength than the corresponding pure graphite components, and at least a similar durability.

25

Common composites include graphite-thermoset composites, prepared for example using an epoxy or a vinyl ester polymer as the thermoset component. Such a composite has been described in, among others, US 6248467 B1 and WO1999019389A1. These materials, however, tend to exhibit poor dimensional tolerances, and they are more difficult to recycle and remould than thermoplastic materials.

30

Other common composites are graphite-thermoplastic composites, prepared for example using polypropylene as the plastic component. Mixtures of more than one thermoplastic have also been investigated, e.g. by Mighri F. et al. (Polym. Eng.Sci. 2004, 44:1755–  
5 1765). These simple thermoplastic-carbon composites, however, tend to exhibit poor strengths at high temperatures. For example, the mentioned polypropylene cannot withstand high temperatures (generally limited to 70–80°C), which limits the range of applications.

10 For the above described electrochemical applications, high thermal and chemical stability and good electric and thermal conductivity is, however, needed.

As described above, the stability of the mentioned composites can vary depending on the choice of materials. However, also the contents of the materials have an effect. Polyarylene  
15 sulphides have been found to provide the composites with relatively high stabilities, and these can endure high temperatures. For example, polyphenylene sulphide (PPS) is one of the most stable, chemically resistant, and temperature resistant engineering thermoplastics. High contents of carbon should be used to prepare electrically highly conductive materials from this polymer, but such high carbon contents generally give the resulting PPS  
20 compounds high melt viscosities, low strengths and low durabilities compared to the pure PPS materials.

The production and moulding of these graphite-polymer composites is cost-effective compared to the production of the conventional graphite components. Compression  
25 moulding is commonly used (see e.g. EP 1736295 A1, JP 2008078023 A and JP 2006019227 A), but this technology offers a poor precision due to variations in the stage of closing the mould.

Particularly for fuel cell applications, precision is, however, essential. These fuel cells  
30 generally include the above mentioned cell plates that in turn include a complex network of channels that guide liquid flow. Poor precision in forming these channels would result in poor function of the fuel cell.

Therefore, injection moulding would be a more advantageous alternative, due to its higher precision compared to compression moulding. Injection moulding, however, also has higher requirements regarding the melt flow characteristics, particularly melt viscosity, of the composite, and the temperature resistance, which the common graphite-polymer  
5 composites have not been able to fulfil. For example, graphite-polypropylene composites can be injection moulded but the operating temperature is limited to 90 °C.

Therefore, there exists a need for carbon composite materials that have high thermal and chemical stability, while maintaining the good electrical conductivity commonly provided  
10 by graphite. High thermal stability of these composites enables their use at higher application temperatures (e.g. at 100 °C to 200 °C). Thus, new applications can be found for electrically conductive thermoplastic composites.

### 15 **Summary of the Invention**

It is an object of the present invention to provide a carbon composite material, which exhibits high electrical conductivity, high stability and strength, even at high temperatures.

20 Particularly, it is an object of the present invention to provide such a carbon composite material in a cost-effective manner.

A further object of the invention is to provide a process for compressing such a material, and for moulding it with high precision.

25 These and other objects, together with the advantages thereof over known materials and processes, are achieved by the present invention, as hereinafter described and claimed.

The invention is based on improving the electric conductivity of conventional graphite-  
30 polymer composite materials. This improved conductivity is achieved by using a combination of at least two carbonaceous fillers, including graphite powder, and a polyarylene sulphide as the polymer.

Since the thermal and chemical stability of the polymer is critical for the feasibility of the composite materials, a polyarylene sulphide, such as polyphenylene sulphide (PPS), is used, preferably in powder form to enable homogeneous polymer-carbon premixing before compounding. To make the material more suitable for use with injection moulding, the melt viscosity of the composite is decreased, for example by using titanates as flow modifiers (or coupling agents).

More specifically, the composite material of the present invention is characterized by what is stated in the characterizing part of Claim 1, while the composite structure is characterized by what is stated in Claim 10.

Further, the process of the present invention is characterized by what is stated in Claim 13 and the use of the composite in electrochemical applications is characterized by what is stated in Claim 16.

Considerable advantages are obtained by means of the invention. Thus, the present invention provides a composite material with high stability and strength, even at high temperatures.

This material also has a sufficiently good electric conductivity to be used as a replacement of pure graphite in electrochemical applications. Further, the material has a sufficiently low melt viscosity to allow processing in high temperatures, such as by injection moulding.

Particularly, the present invention provides means for achieving both high strength and electrical conductivity, simultaneously, in the same material.

Next, the invention will be described more closely with reference to the attached drawings and a detailed description.

### Brief Description of the Drawings

Figure 1 is a schematic drawing of a preferred application for the present invention, i.e. of the unit of a fuel cell that includes a bipolar plate.

5

Figure 2 shows the measured resistivities of polyphenylene sulphide (PPS) composites with carbon nanotube filler (CNT), and with or without titanate additive.

Figure 3 shows the measured resistivities of polyphenylene sulphide (PPS) composites with different grades of graphite filler and with 0.75w-% or 3w-% titanate additive.

10

Figure 4 shows the measured resistivities of polyphenylene sulphide (PPS) composites with graphite filler, 3w-% titanate additive, and optional further carbon filler in the form of CNT in different contents.

15

Figure 5 shows the measured resistivities of polyphenylene sulphide (PPS) composites with graphite filler, 1.5w-% or 3w-% titanate additive, and optional further carbon filler in the form of CNT.

Figure 6 shows the required specific energy input and torque required when compounding by Berstorff ZE 25 x 48D twin screw extruder various PPS composites including varying contents of graphite, varying contents of CNT, and optionally 3w-% titanate.

20

Figure 7 shows the results of steady state testing of an in-house PPS composite, at a current density of 0.2 Acm<sup>-2</sup>, ambient pressure and 200 °C, with BASF standard flow field plates for reference.

25

### Detailed Description of Preferred Embodiments of the Invention

The present invention concerns a carbon-polymer composite material containing at least one thermoplastic polymer as well as at least two carbonaceous fillers.

5

Due to its advantageous properties, one of the carbonaceous fillers is graphite, preferably in the form of graphite powder (generally used in either spherical or flake form), most suitably spherical graphite powder. The average particle size (diameter) of this graphite is preferably  $<300\mu\text{m}$ , more preferably  $30\text{--}200\mu\text{m}$ , and most suitably  $50\text{--}150\mu\text{m}$ .

10

This graphite is typically the main filler, i.e. it typically forms at least 50 w-% of the total amount of carbonaceous fillers, preferably 60–95w-%.

The further carbonaceous filler(s) is/are selected from any carbonaceous materials that can be processed and which can promote the electrical conductivity (i.e. not diamond) of a composite, particularly from materials formed of pure or essentially pure carbon, such as carbon black, carbon fibres, carbon nanofibres, carbon nanotubes, graphene or a type of graphite that is different from the graphite used as the main carbonaceous filler.

For example, spherical graphite can be used as the main filler, whereby the further filler(s) can be selected from flaky graphite, carbon black, carbon fibres, carbon nanofibres, graphene and carbon nanotubes.

The optionally used carbon black is preferably selected from powders having an average diameter of primary particles of  $10\text{--}20\text{nm}$ . Similarly, the optionally used carbon fibres preferably have an average length of  $5\text{--}1000\mu\text{m}$  and an average diameter of  $5\text{--}15\mu\text{m}$ , while the optionally used carbon nanotubes preferably have an average length of  $1\text{--}50\mu\text{m}$  and an average diameter of  $8\text{--}100\text{nm}$ . The carbon nanofibres are naturally of nano-size.

Of these further fillers, carbon nanotubes (CNT) can be used in contents of up to 10w-% of the entire composite material, carbon black can be used in contents of up to 20w-% of the composite material, and carbon fibres can be used in contents of up to 10w-% of the composite material.

The total content of carbonaceous filler in the resulting composite is preferably >50w-%, more preferably 50 – 95w-%, and most suitably 60–80w-%. A high carbon filler content is needed to provide a sufficient electric conductivity (commonly of the level of 10 S/cm or higher).

5

According to a preferred embodiment of the invention, graphite (preferably as purely spherical graphite or a mixture of spherical and flaky graphite) is mixed with either carbon nanotubes or with both carbon black and carbon fibres, to form the filler mixture of the composite.

10

Thus, the composite material of the invention can contain, for example, 75w-% graphite powder, 2w-% carbon black and 0.5w-% carbon fibres, or 67w-% graphite powder and 2.5w-% carbon nanotubes, calculated based on the total weight of the composite material.

15 Combinations of two or more carbon materials in polymer composites have been found to provide synergistic effects (for example a lower resistivity). The further carbon filler(s) provides a lowered contact resistance between the graphite particles forming the main filler.

20 At least one thermoplastic polymer is used, as a binder, to facilitate plastic processing type of manufacturing of the composite article. This thermoplastic is preferably selected from polyarylene sulphides, more preferably being polyphenylene sulphide. Most suitably, this polyarylene sulphide is used as the only organic polymer.

25 The content of thermoplastic polymer in the composite material is preferably 10–45w-%, more preferably 10–35w-%, and most suitably 15–30w-%, although it is mainly guided by the required content of carbonaceous filler, since high carbon contents cause the desired increased electrical conductivities (or lower resistivities).

30 To provide a further possibility of using higher carbon contents in the composite material, and to provide a lower viscosity, flow modifier(s) (or coupling agents) can be added to said composite material.



The term “flow modifier” is intended to mean a group of additives that lower the melt viscosity of materials, such as composites. The same group of additives can be called “coupling agents” due to their further capability of influencing the interaction between particles and polymers, most likely by facilitating the breakdown of agglomerates. The  
5 breakdown of agglomerates also causes an increase in electrical conductivity.

Preferably at least one flow modifier is selected from the group of titanates. Titanate flow modifiers in the composition reduce the melt viscosity allowing high temperature processing and, thus, making the material more suitable for injection moulding. Examples  
10 of suitable titanates include organotitanates, preferably organotitanates based on the titanium(IV) atom, more preferably divalent or multivalent organotitanates, most suitably with one or more C<sub>1-18</sub> ligands attached to the titanium atom, particularly two or more C<sub>1-18</sub> ligands.

15 These C<sub>1-18</sub> ligands, as well as optional further ligands, commonly include also ether groups, hydroxyl groups, ester groups, halogens (-Cl, -Br or -I), amine groups or phosphate groups within the ligands, or more than one type of such functional groups.

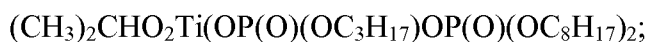
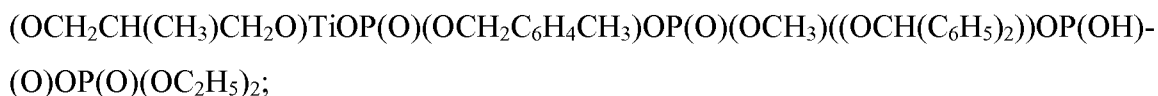
Examples of ligands that can be attached to the titanium atom include the following:

- 20        -alkoxy;  
          -aryloxy;  
          -alkylate;  
          -alkoxy-halogen;  
          -aryloxy-halogen;  
25        -alkoxy-amine;  
          -aryloxy-amine;  
          -PO<sub>2</sub>-alkoxy;  
          - PO<sub>2</sub>-alkoxy-halogen;  
          - PO<sub>2</sub>-OH;

30 wherein the alkoxy and the alkylate each independently can be linear or branched, can include 1–18 carbon atoms, and in case the alkoxy or alkylate contains 2–18 carbon atoms, the group can further contain one or more double or triple bonds.

Typical examples of titanates that have been found suitable for the present purpose (use as flow modifiers in materials intended for electrochemical applications) are the simple: hydroxy-acetate-titanate,

5 or the more complex alternatives:



10  $(\text{CH}_3)_2\text{CHOTi}(\text{OC}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NH}_2)_3;$



15 A particularly preferred example of the titanate suitable for use in the context of the present invention is the 2-propanolato-(tris-isooctadecanoato-O)-titanium(IV).

The titanate is preferably used in a content of 0.5–10w-%, more preferably 0.075–5w-%, of the entire composite material. If further additives are used, their content generally does  
20 not exceed 5w-%.

The present invention also concerns a structure made of the above described composite material. Examples of such structures are plates, which are commonly used in, among others, fuel cells (e.g. as bipolar plates), as well as in batteries (including liquid flow  
25 batteries) and heat exchangers.

An exemplary construction, or a repeating unit 1 of a fuel cell stack, including said bipolar plate, is shown in Figure 1, which shows the following components:

- 2 bipolar plate with channels
- 30 3 anode
- 4 cathode
- 5 electrolyte

A typical plate of this type can have a size of, for example 150 x 150 x 3 mm.

Further, the present invention concerns a method for manufacturing such a composite structure, e.g. in the form of a plate, by compounding the above described carbon composite material and injection moulding it into the desired shape.

5

The compounding is carried out in order to efficiently mix the various substances that are to form the composite. In this step a conventional mixer can be used. The compounding step generally lasts for less than 10 minutes, the time, however, depending on the efficiency of the mixing (generally between 200 and 1200 rpm). Typically, the residence  
10 time in compounding step is 3 to 5 min. The polymer is optionally melted prior to or during compounding.

According to a preferred embodiment of the invention, the compounding step is carried out using an extruder, such as a twin-screw extruder, to provide a good distribution of the  
15 carbonaceous fillers and the flow modifier(s) in the polymer, as well as to cause the preferred melting of the polymer.

In case of using an extruder, the present composites can suitably be compounded for example at temperatures varying in the range of 300–360°C, preferably 300–330°C and  
20 more preferably 315–320°C, and using a screw speed of about 150 rpm – 300rpm. Further, an elevated pressure can be used, such as a pressure of 50–800bar.

The injection moulding is carried out by injecting the compounded composite material into a mould cavity, generally after heating the material to an elevated temperature. The  
25 temperature profile of injection moulding machine is typically 115 °C – 335 °C – 340 °C – 340 °C – 345 °C. Temperature profile can be changed depending on the filler loading and the combination of carbon fillers, but the temperature is preferably maintained within the range 100–350°. Preferably the mould is separately heated, for example using water to a temperature of at least 80°C (i.e. from 80 to almost 100°C), or using other means, such as  
30 oil, to an even higher temperature (e.g. a temperature of 140°C to 180 °C).

The injection is generally carried out using high pressures, such as a pressure of 100–800bar, depending on the viscosity of the composite material, while the clamping pressure during the moulding step generally is lower, while being higher than atmospheric pressure.

With the given injection pressure range, suitable holding pressures can be, for example 50–500bar.

5 According to another preferred embodiment of the invention, a grinding step is carried out after the moulding step, for example using sanding or abrasive blasting, to remove the lower-quality surface layer (containing less graphite) that often is formed on the composite structures, and to provide even lower resistivities.

10 The composites of the present invention can be applied to, among others, fuel cells, batteries, electrolytic processes, and heat exchangers, preferably fuel cells, redox flow batteries or industrial heat exchangers, with a particularly preferred application being in the field of polymer fuel cells, most suitably high temperature polymer fuel cells using e.g. phosphoric acid doped polybenzimidazole (PBI) as the electrolyte.

15 Fuel cells generally include cell plates that in turn include a complex network of channels that guide liquid and gas flow. Among others due to said channels, precision is essential in the manufacture of these plates. Therefore, injection moulding is a more advantageous procedure in this manufacture than, e.g., the conventional compression moulding.

20 Said fuel cell plates (or bipolar plates) must also be resistant to cracking, chemical reactions and corrosion at a wide range of temperatures, whereby not only the resistivity guides the choice of materials.

25 Other applications include redox flow batteries, electrolytic processes and industrial heat exchangers. The invention also provides the possibility to operate in advantageous conditions in phosphoric acid fuel cells.

The following non-limiting examples are intended merely to illustrate the advantages obtained with the embodiments of the present invention.

## EXAMPLES

In the following examples, unless something different is stated, the compounding was carried out using DSM Micro 15cc twin screw compounder with a temperature profile of 300-310-330°C and a screw speed of 200rpm, while the moulding was carried out using an injection moulding apparatus Haake minijet with an injection temperature of 330°C, an injection pressure of 100–800bar, and a mould temperature of 140°C.

### Example 1 – Effect of the type of carbon component and titanate flow modifier

10

Polyphenylene sulphide (PPS, Ryton PR11 (Chevron Philips), powder) was used as the single polymer substance. This PPS was compounded with different carbon substances, and injection moulded into plates of the size 100 x 100 x 3 mm. The resistivities of these composites were tested.

15

The sample PPS-012 was processed by mixing with a batch mixer Brabender Plasticorder) and compression moulded. The other samples were mixed with a Berstorff twin screw compounder and injection moulded (Demag Ergotech 100/420-120 EL-EXIS S).

20 The lowest resistivities achieved with different filler types are presented in Table 1.

Table 1. Resistivities of PPS-carbon composites

Code	Filler	Flow modifier	Flow modifier w-%	Filler loading, w-%	Resistivity, Ωcm	Resistivity after grinding, Ωcm
PPS-012	Carbon nanotube	No	-	6.0	39.0	not measured
PPS-1016	Graphite	No	-	70.0	1.80	1.10
PPS-1039	Graphite	KR238 <sup>1)</sup>	0.75	74.4	0.50	0.32
PPS-1035	Modified graphite	Lica38 <sup>2)</sup>	0.75	64.5	1.33	not measured
PPS-1059	Graphite + carbon fibre	No	-	77.3	0.59	0.39

PPS-1048	Graphite + carbon fibre	KR238	0.75	77.3	0.16	0.1
PPS-1054	Graphite + carbon fibre	KR238	1.5	77.3	0.23	0.18

<sup>1</sup>)KR238, Titanate(2-),bis[P,P-dioctyl diphosphato(2-)-O',O'''] [1,2-ethanediolato(2-)-O,O']-, dihydrogen, branched and linear . .CAS# 68585-63-7.....90%  
 Titanium IV tetrakis {2,2-bis(2-propenyloxy)methyl-1-butanolato} adduct  
 5 2 moles (ditridecyl phosphito-O), dihydrogen . .CAS# 64157-14-8.....10%

<sup>2</sup>)Lica38, Titanium IV 2,2(bis 2-propenolatomethyl)butanolato, tris(dioctyl)pyrophosphato-O

Graphite-carbon fiber ratio was 75 to 25 (w-%) in recipes PPS-1016 to PPS1054.  
 10

The used graphite was of the type: KS-5 75TT TIMREX (Spherical). The modified graphite means a special graphite grade with “conductive bridges” (Cond20/96, Graphit Kropfmuehl AG).

The used carbon nanotubes were of the type: Nanocyl NC7000.

15 The used carbon fibers were of the type: Grafil PU6-1

In the overall results, a small amount (2 wt-%) of CNT (in the graphite – CNT mixture) lowered the contact resistance between graphite particles in the composites, compared to  
 20 the results obtained with a simple PPS–graphite composite.

As can be seen particularly from the results of Table 1, the use of a flow modifier lowers the resistivity of the produced composites, whereby the electrical conductivity is improved. Further, only small amounts of flow modifier are required (such as 0.75w-%). The  
 25 resistivity of the graphite – carbon fibre mixture (in the PPS composite) was clearly lower (1.7 Ωcm) than that of the reference graphite-PPS composite (3.7 Ωcm) when the total filler loading was 65 wt-%. The lowest resistivity of all PPS composites was achieved with the loading of 77.25 wt-% of synthetic graphite – carbon fibre mixture. The resistivity of the moulded sample of this mixture (code PPS-1048) was 0.16 Ωcm. The qualities of these  
 30 mouldings were also good.

The resistivity of compression moulded composites with the loading of 78.25 w-% of graphite – carbon fibre – carbon black mixture was 0.031  $\Omega\text{cm}$ . After grinding of the skin of the sample of synthetic graphite – carbon fibre mixture, its resistivity was 0.1  $\Omega\text{cm}$ . Similarly, after grinding of the skin of the sample of graphite – carbon fibre – carbon black mixture, its resistivity was 0.030  $\Omega\text{cm}$ . Thus, grinding could be used to decrease the resistivities of the composites even further.

**Example 2** – Effect of addition of CNT and titanate flow modifier

To determine the effect of the addition of a flow modifier on the resistivity of a conductive carbon material, a titanate flow modifier (KR-TTS (Kenrich Petrochemicals), Titanium IV 2-propanolato, tris isooctadecanoato-O) was compounded with carbon nanotubes (CNTs; Nanocyl NC7000, length=1.5 $\mu\text{m}$ , diameter=9.5nm, 3% and 7%) and polyphenylene sulphide (PPS, Ryton V-1 (Chevron Philips), powder), using the above described compounding and moulding conditions, as well as a holding pressure of 50–500bar.

The CNTs were first dissolved in 350 ml isopropanol by ultrasonication. Titanate flow modifier was added (20w-%, calculated based on the CNTs) to the solution and solvent was evaporated by Rotavapor machine. The product was finally dried in a vacuum oven before mixing with the PPS, compounding, injection moulding into a bipolar plate and measuring the resistivity (shown in Figure 2).

In the compounding step, a force of 685N was applied to the 7% CNT with titanate and 1200N to the 7% CNT without titanate.

These results show, among others that the carbon material is essential particularly in providing the sufficiently low through-plane resistivity, while the titanate improves the results even further.

The same experiment and measurement was carried out using two different types of graphite (a spherical KS-5 75TT TIMREX,  $d_{90}$ = 70  $\mu\text{m}$ , and a mixture of this spherical type with a flake-type SGA 20M Kropfmuehl,  $d_{90}$ =  $\leq$ 50  $\mu\text{m}$ ) and the above mentioned titanate (0.75% and 3%). The results are shown in Figure 3.

From these results it can be seen that, while a mixture of graphites is more advantageous when used alone, a spherical type of graphite provides an even smaller resistivity when used with titanate, in a sufficient amount, although even minor amounts of titanate will provide significant improvements.

5

The additional effect of using both graphite (52.5%, 55%, 57.5%, 60%, 67.5% and 70%) and carbon nanotubes (7.5%, 5%, 2.5% and 0%), with 3% titanate, is shown in Figure 4.

Similar results are shown in Figure 5, with carbon filler, either as pure graphite (60w-%) or as a mixture of graphite and CNT (57.5w-% graphite and 2.5w-% CNT), as well as either 1.5w-% or 3w-% titanate.

10

These results demonstrate that a mixture of graphite and CNTs is the most advantageous.

### 15 **Example 3** – Compounding trials

Trials were carried out to test the effect of the titanate flow modifier on the compounding of composite materials.

20 The materials and contents shown in the following Table 2 were used in the composites.

Table 2. Composite materials produced by Berstorff ZE 25 x 48D twin screw extruder

Sample	Total, g	PPS, %	Graphite, %	CNT, %	Titanate, %
CNT-1	3000	27.5	72.5	0	0
CNT-2	3000	27.5	71.25	1.25	0
CNT-3	3000	27.5	70	2.5	0
CNT-4	3000	24.5	72.5	0	3
CNT-5	3000	24.5	71.25	1.25	3
CNT-6	4000	24.5	70	2.5	3

The results are shown in Figure 6. These results demonstrate, among others, that the addition of titanate to the composites will result in a lower requirement for energy input.

25



The materials of Table 2 gave composites, which displayed the electrical conductivities (and resistivities) of the following Table 3.

Table 3. Resistivities and conductivities of composite materials

Samples	Through-Plane		In-Plane	
	Resistivity, $\Omega$ .cm	Standard deviation	Conductivity, $\Omega$ .cm	Standard deviation
CNT-1	0.702	0.070	6.430	0.823
CNT-2	0.278	0.017	16.965	2.368
CNT-3	0.160	0.013	27.201	1.126
CNT-4	0.240	0.014	18.917	5.868
CNT-5	0.094	0.012	31.666	2.540
CNT-6 <sup>a</sup>	0.050	0.007	57.272	10.451
CNT-6 <sup>b</sup>	0.038	0.007	54.237	10.150
Compression Molded CNT-6	0.033	0.012	68.036	5.355

5 <sup>a</sup> prepared using a normal injection speed: 600mm/s

<sup>b</sup> prepared using a higher injection speed: 700mm/s

#### Example 4 – Fuel Cell test

10 Single cell testing:

The in-house developed compression moulded PPS composite 1056 was tested in a single cell hardware in a Fuel Cell technologies test station, University Model. The recipe of PPS-1056 is shown in Table 4, below. This compound was used to prove the performance of carbon filled PPS compound modified with titanate flow modifier. PPS-1056 compound  
15 was grinded and compression moulded in to the sheet form. The required flow field was CNC milled onto the plate.

Table 4. Composite material PPS-1056

Code	Filler	Flow modifier	Flow modifier, w-%	Filler loading, w-%	Resistivity, $\Omega\text{cm}$	Resistivity after grinding, $\Omega\text{cm}$
PPS-1056	Graphite + carbon fibre+ carbon black	KR238	0.75	77.3	0.031	0.021

\* carbon black (Ketjenblack EC-600 JD)

In order to accelerate the testing, the cell temperature was 200 °C (40 °C above the recommended operating temperature of the BASF P1000 Membrane electrode assembly (MEA)). Before the testing the material was cleaned by repeated boiling for 30 minutes in MQ water and rinsing with iso-propanol. In-situ steady-state testing was made 200 °C, a current density of 0.2 A cm<sup>-2</sup>, stoichiometries 2 at air cathode, 1.2 at hydrogen anode and ambient pressure.

10

The results from the accelerated testing of the in-house compression moulded composite material 1056 may be seen in Figure 7. The performance of the same setup with standard BASF isostatic graphite flow field plates is given for reference. The performance follows the same trend that has been observed for a large number of P1000 MEAs with the BASF graphite plates at this temperature. After an initial increase due to the activation of the MEA, the cell voltage reaches a plateau and then decreases with time. The voltage decay is attributed to the MEA degradation, not to the flow plates. The cell voltage with the composite plates is about 10 mV lower than the cell voltages that may be obtained with the BASF test plates, but this can be assigned to the lower conductivity of the composite plates. No degradation was visible in the test plates after the testing.

20

This example shows that the composite plates are as stable as or even more stable than the original graphite plates.

**Claims**

1. A carbon-polymer composite material containing at least one thermoplastic polymer,  
**characterized** in that it contains at least two carbon fillers, at least one being selected from  
5 graphites, and at least one additive selected from titanate flow modifiers.
2. The carbon composite material of Claim 1, **characterized** in that at least one carbon  
filler is in the form of graphite powder, preferably spherical graphite.
- 10 3. The carbon composite material of Claim 2, **characterized** in that >50w-%, preferably  
60–85w-%, of the carbon filler is graphite.
4. The carbon composite material of any preceding claim, **characterized** in that the  
further carbon component(s) is/are selected from carbon black, carbon fibers, graphene and  
15 carbon nanotubes.
5. The carbon composite material of any preceding claims, **characterized** in that at least  
one thermoplastic polymer is polyarylene sulphide, preferably polyphenylene sulphide,  
most suitably used as the only organic polymer.
- 20 6. The carbon composite material of any preceding claim, **characterized** in that its  
content of thermoplastic polymer is 10–45w-%, preferably 10–35w-%, most suitably 15–  
30w-%.
- 25 7. The carbon composite material of any preceding claims, **characterized** in that the  
titanate flow modifier is selected from organic Ti(IV) titanates, whereby at least one ligand  
attached to the titanium atom is an organic C<sub>1-18</sub>-ligand, the titanate most suitably being 2-  
propanolato-(tris-isooctadecanoato-O)-titanium(IV).
- 30 8. The carbon composite material of any preceding claim, **characterized** in that the  
titanate flow modifier is selected from titanates, which are present in a content of 0.5–10w-  
% of the entire composite material.
9. The carbon composite material of any preceding claim, **characterized** in that it  
35 contains >50w-% of carbon fillers, preferably 50–85w-%, most suitably 60–70w-%, the  
remaining substances being thermoplastic polymer and additives.

10. A moulded composite structure, **characterized** in that it has been moulded from the composite material of any of claims 1 to 9.
- 5 11. The composite structure of claim 10, **characterized** in that it is in the form of a plate.
12. The composite structure of claim 10 or 11, **characterized** in that it has a resistivity of  $<2\Omega\text{cm}$ , preferably  $<0.2\Omega\text{cm}$ .
- 10 13. A method for manufacturing the composite structure of any of claims 10 to 12, **characterized** by carrying out a compounding step to form the carbon-polymer composite material of any of claims 1 to 9, and an injection moulding step to mould the material into the desired shape.
- 15 14. The method of claim 13, characterized by carrying out the compounding step with the material to be compounded at an elevated temperature, such as a temperature of  $\geq 200^\circ\text{C}$ , and optionally at an elevated pressure, such as a pressure of 50–800bar.
15. The method of claim 13 or 14, characterized by carrying out the injection moulding by  
20 injecting the compounded composite material into a mould cavity and by subsequently allowing the material to solidify, the injection preferably taking place at an elevated temperature, more preferably a temperature of  $200\text{--}350^\circ\text{C}$ , even more preferably a temperature of  $250\text{--}350^\circ\text{C}$ , most suitably a temperature of  $300\text{--}350^\circ\text{C}$ , and using pressure for the injection, such as a pressure of 100–800bar.
- 25 16. Use of the carbon composite material of any of claims 1 to 9, or of the composite structure of any of claims 10 to 12 in electrochemical applications.
17. The use of claim 16, where the electrochemical applications are selected from fuel  
30 cells, batteries, electrolysis processes or heat exchangers, preferably fuel cells, redox flow batteries or industrial heat exchangers, more preferably polymer fuel cells, most suitably high temperature polymer fuel cells using e.g. phosphoric acid doped polybenzimidazole (PBI) as the electrolyte.

Fig. 1

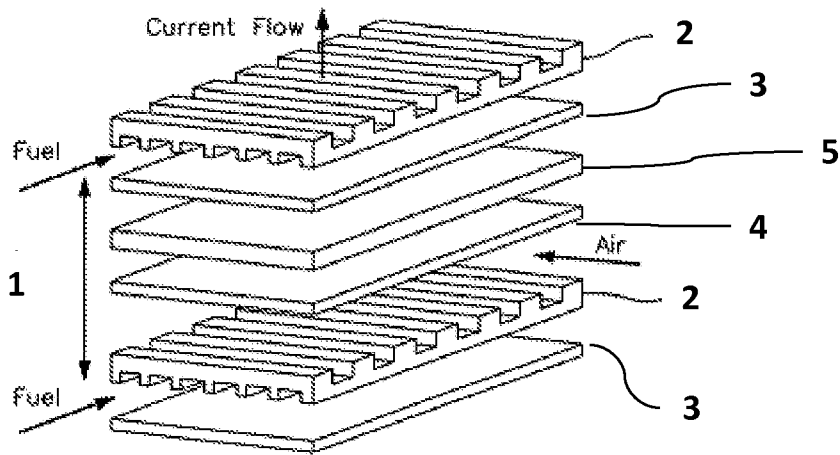


Fig. 2

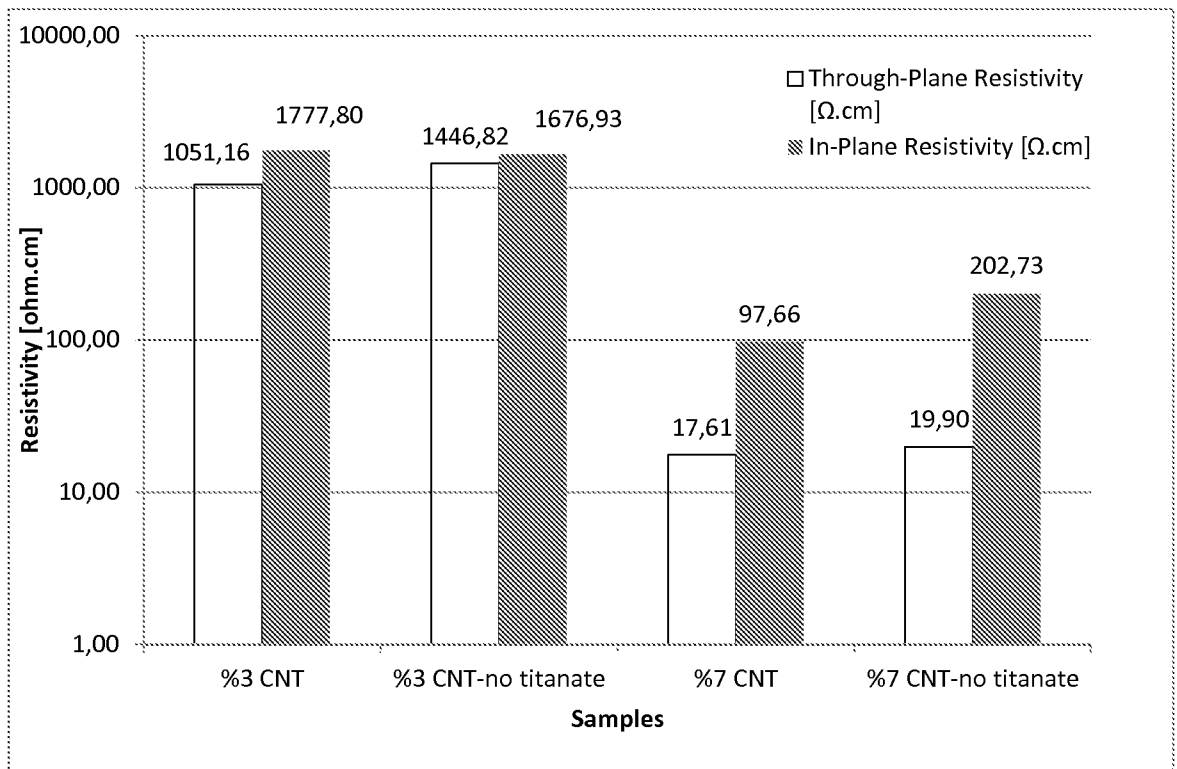


Fig. 3

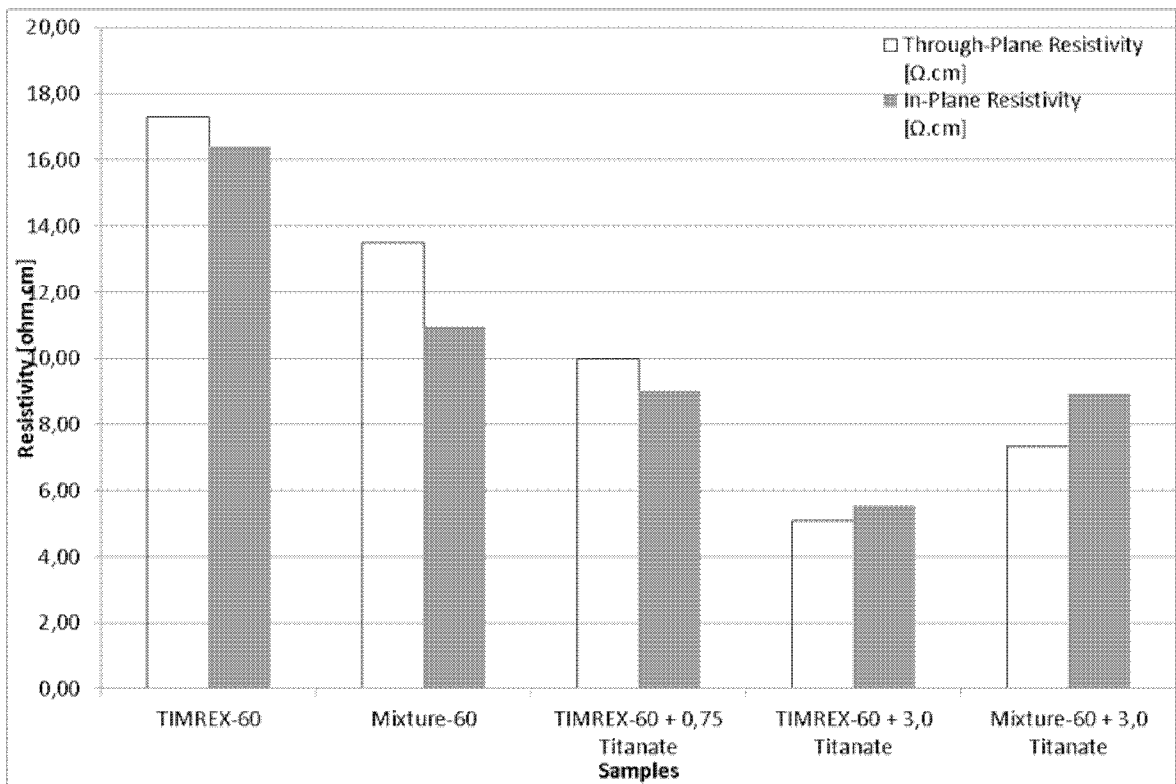


Fig. 4

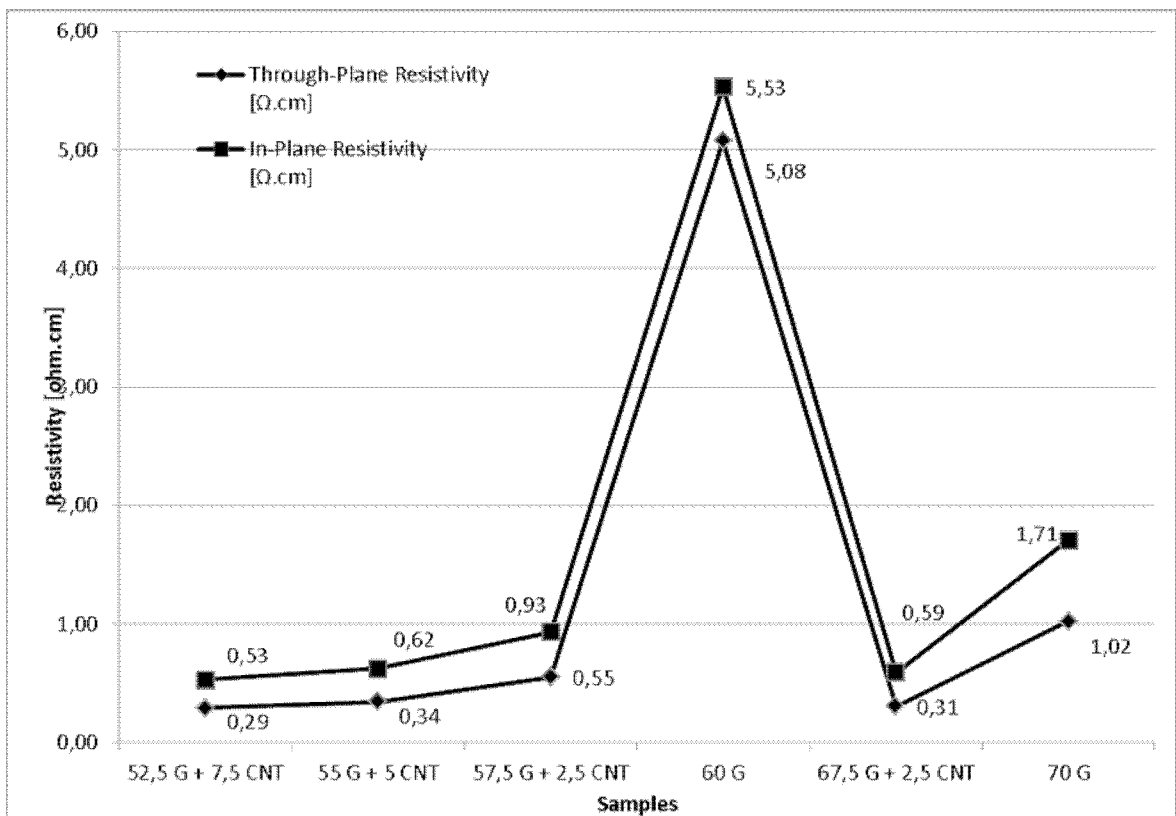


Fig. 5

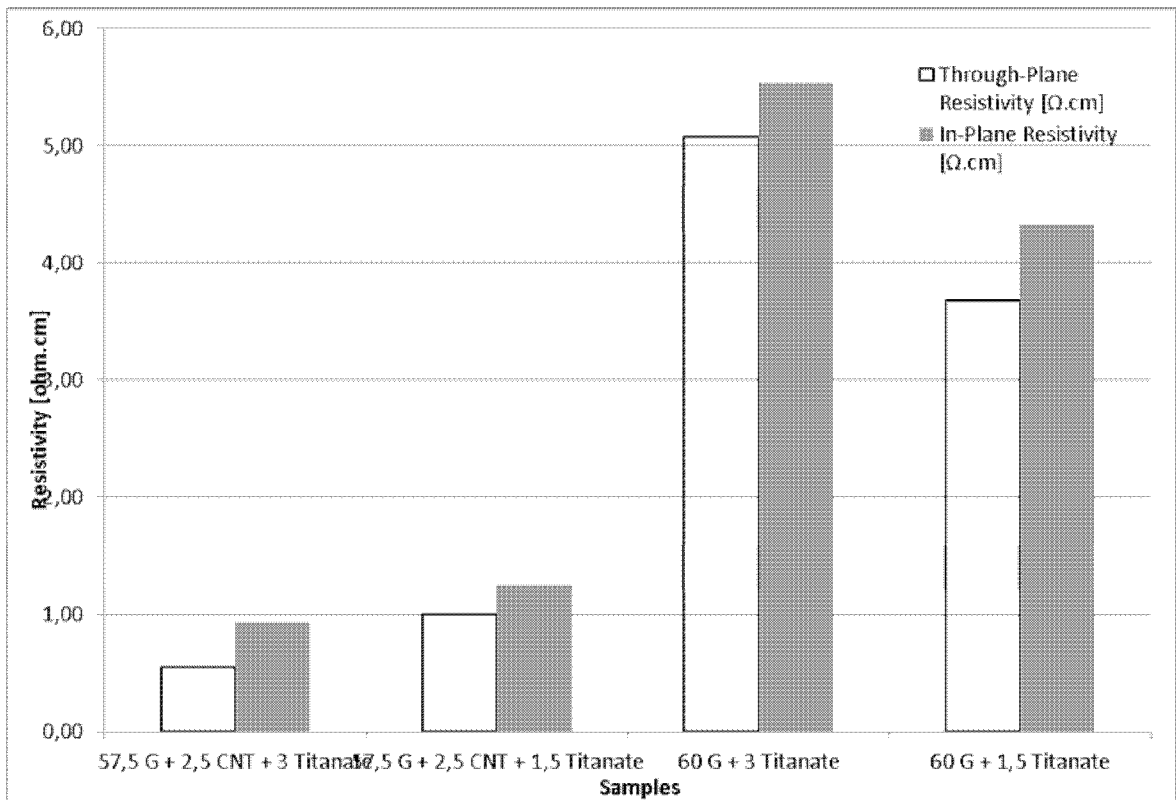


Fig. 6

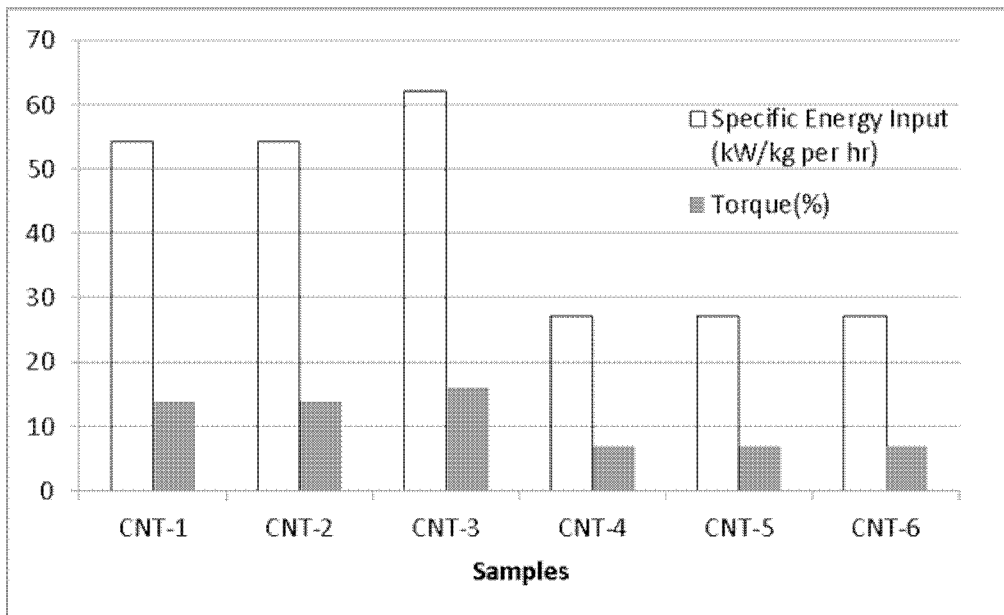
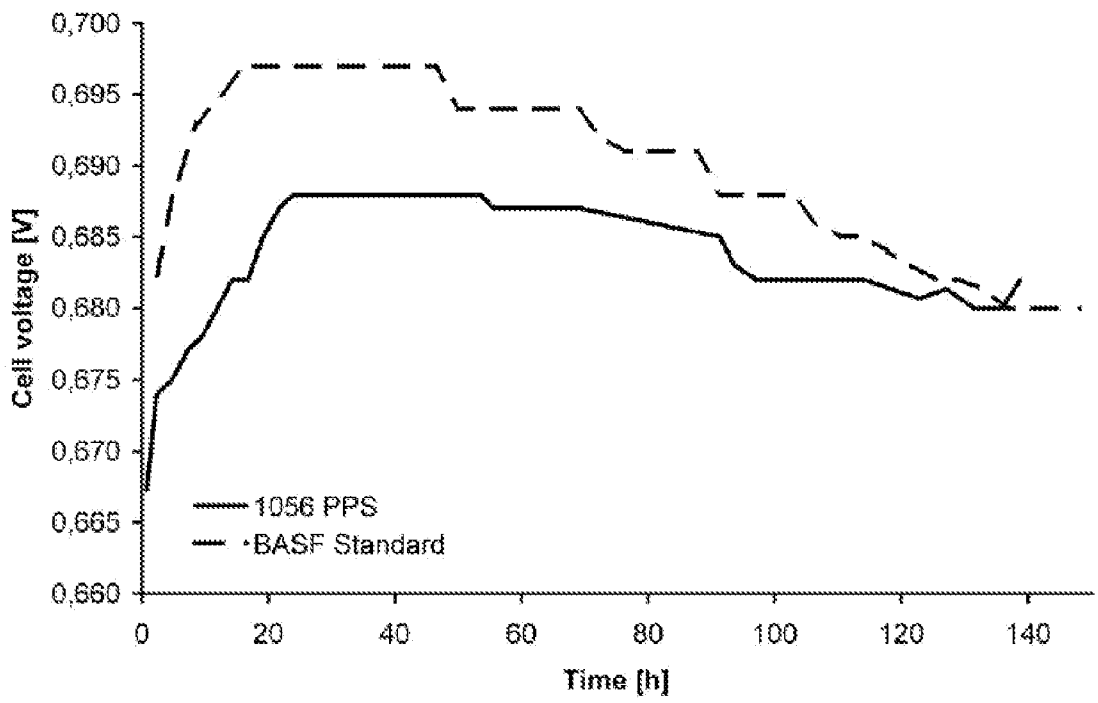


Fig. 7





## INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI2014/050711

**A. CLASSIFICATION OF SUBJECT MATTER**

See extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC: C08K, C08L, H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

FI, SE, NO, DK

Electronic data base consulted during the international search (name of data base, and, where practicable, search terms used)

EPO-Internal, WPI, CA

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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 Further documents are listed in the continuation of Box C.
  See patent family annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

20 January 2015 (20.01.2015)

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International application No.

PCT/FI2014/050711

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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CLASSIFICATION OF SUBJECT MATTER

IPC  
**C08K 3/04** (2006.01)  
**C08L 81/04** (2006.01)  
**H01M 8/02** (2006.01)  
**C08K 5/098** (2006.01)